Experimental and Theoretical Study of the Coordination of 1,2,4-Triazolato, Tetrazolato, and Pentazolato Ligands to the [K(18-crown-6)]⁺ Fragment

Issam Kobrsi, Wenjun Zheng, John E. Knox, Mary Jane Heeg, H. Bernhard Schlegel, and Charles H. Winter*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received July 6, 2006

Treatment of 3,5-diisopropyltriazole, 3,5-diphenyltriazole, 3,5-di-3-pyridyltriazole, phenyltetrazole, pyrrolidinyltetrazole, or *tert*-butyltetrazole with equimolar quantities of potassium hydride and 18-crown-6 in tetrahydrofuran at ambient temperature led to slow hydrogen evolution and formation of (3,5-diisopropyl-1,2,4-triazolato)(18-crown-6)potassium (88%), (3,5-diphenyl-1,2,4-triazolato)(tetrahydrofuran)(18-crown-6)potassium (87%), (3,5-di-3-pyridyl-1,2,4-triazolato)-(18-crown-6)potassium (81%), (phenyltetrazolato)(18-crown-6)potassium (94%), (pyrrolidinyltetrazolato)(18-crown-6)potassium (90%), and (*tert*-butyltetrazolato)(18-crown-6)potassium (94%) as colorless crystalline solids. (1,2,4-Triazolato)(18-crown-6)potassium was isolated as a hemi-hydrate in 81% yield upon treatment of 1,2,4-triazole with potassium metal in tetrahydrofuran. The X-ray crystal structures of these new complexes were determined, and the solid-state structures consist of the nitrogen heterocycles bonded to the (18-crown-6)potassium cationic fragments with η^2-bonding interactions. In addition, (3,5-diphenyl-1,2,4-triazolato)(tetrahydrofuran)(18-crown-6)-potassium has one coordinated tetrahydrofuran ligand on the same face as the 3,5-diphenyl-1,2,4-triazolato ligand, while (3,5-di-3-pyridyl-1,2,4-triazolato)(18-crown-6)potassium forms a polymeric solid through coordination of the distal 3-pyridyl nitrogen atoms to the potassium ion on the face opposite the 1,2,4-triazolato ligand. The solid-state structures of the new complexes show variable asymmetry in the potassium–nitrogen distances within the η^2-interactions and also show variable bending of the heterocyclic C_2N_3 and CN_4 cores toward the best plane of the 18-crown-6 ligand oxygen atoms. Molecular orbital and natural bond order calculations were carried out at the B3LYP/6-311G(d,p) level of theory on the model complex, (phenyltetrazolato)(18-crown-6)potassium, and demonstrate that the asymmetric potassium–nitrogen distances and bending of the CN_4 core toward the 18-crown-6 ligand are due to hydrogen bond-like interactions between filled nitrogen-based orbitals and carbon–hydrogen σ^* orbitals on the 18-crown-6 ligands. Calculations carried out on the model pentazolato complex (pentazolato)(18-crown-6)-potassium predict a structure in which the pentazolato ligand N_5 core is bent by 45° toward the best plane of the 18-crown-6 oxygen atoms. Such bending is induced by the formation of intramolecular nitrogen–hydrogen–carbon hydrogen bonds. Examination of the solid-state structures of the new complexes reveals many intramolecular and intermolecular nitrogen–hydrogen distances of ≤3.0 Å which support the presence of nitrogen–hydrogen–carbon hydrogen bonds.

Introduction

The coordination chemistry of anionic five-membered nitrogen heterocyclic ligands has generated considerable recent interest from several different perspectives. Complexes containing pyrazolato ligands have been extensively explored for metals across the periodic table,[1] and many new and unexpected coordination modes have been documented for this seemingly simple donor ligand.[1−5] Among the surprising developments in this area, terminal η^2-pyrazolato ligand

* To whom correspondence should be addressed. E-mail: chw@chem.wayne.edu.

(1) For reviews of pyrazolato complexes, see: (a) Nief, F. *Eur. J. Inorg. Chem.* **2001**, 891. (b) Cosgriff, J. E.; Deacon, G. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 286. (c) La Monica, G.; Ardizzoia, G. A. *Progr. Inorg. Chem.* **1997**, *46*, 151. (d) Sadimenko, A. P.; Basson, S. S. *Coord. Chem. Rev.* **1996**, *147*, 247. (e) Trofimenko, S. *Progr. Inorg. Chem.* **1986**, *34*, 115. (f) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497.

coordination was initially very rare compared to other bonding modes,[2] apparently due to the divergent nitrogen lone pairs imparted by the five-membered ring structure. However, work in the past 10 years has provided many examples across the periodic table.[3−5] In contrast to the now extensive examples of terminal η^2-pyrazolato ligands, there are few structurally characterized complexes containing terminal η^2-1,2,4-triazolato and η^2-tetrazolato ligands. Due to the presence of many nitrogen atoms in 1,2,4-triazolato and tetrazolato ligands, complexes containing these ligands have a strong tendency to form oligomeric and polymeric compounds through bridging ligand coordination modes.[6,7] Furthermore, η^1-coordination is the most commonly observed binding mode in monomeric complexes containing 1,2,4-

triazolato and tetrazolato ligands.[8] To date, there are only four examples of crystallographically characterized metal complexes containing terminal η^2-1,2,4-triazolato ligands. We have described the synthesis and structure of Ti(3,5-tBu$_2$pz)$_3$(3,5-Me$_2$trz) (tBu$_2$pz = 3,5-di-*tert*-butylpyrazolato, Me$_2$trz = 3,5-dimethyl-1,2,4-triazolato),[9] as well as (3,5-diisopropyl-1,2,4-triazolato)(18-crown-6)potassium,[10] and found terminal η^2-coordination of the 1,2,4-triazolato ligands in these complexes. Molecular orbital calculations of model d^0 titanium(IV) complexes demonstrated that terminal η^2-coordination of 1,2,4-triazolato and tetrazolato ligands is more stable than the η^1-coordination mode in the absence of steric effects.[9] Mösch-Zanetti has reported the synthesis and structure of Ti(^{i}Pr$_2$trz)$_4$ and Ti(C$_5$Me$_4$CH$_2$Ph)(^{i}Pr$_2$trz)-Cl$_2$ (^{i}Pr$_2$trz = 3,5-diisopropyl-1,2,4-triazolato), both of which contain terminal η^2-1,2,4-triazolato ligands.[11] Crystallographically characterized complexes that contain terminal η^2-tetrazolato ligands are limited to our preliminary communications describing (phenyltetrazolato)(18-crown-6)potassium[10] and the barium complexes Ba(Rtetz)$_2$(18-crown-6) (Rtetz = 5-dimethylaminotetrazolato, 5-diisopropylaminotetrazolato).[12] η^2-Bonding interactions of 1,2,4-triazolato and tetrazolato ligands within more complex bridging coordination modes are rare and are restricted to [(C$_5$H$_4$(CH$_3$))$_2$Ln(μ:η^2(N,N''),η^1-(N'')-Phtetz)]$_2$ (Ln = Yb, Gd, Dy, Er; Phtetz = phenyltetrazolato)[13] and 5-cyanotetrazolatocesium.[14]

Theoretical predictions regarding the high stability of the pentazolate (N$_5^-$) ion suggest that metal complexes containing this ligand might be stable enough to allow isolation.[15] Recent tantalizing results in this area include the first experimental detection of the N$_5^-$ ion (in the gas phase),[16] as well as a claim for the synthesis of pentazolic acid[17]

(2) Early examples of η^2-pyrazolato ligand coordination: (a) Eigenbrot, C. W., Jr.; Raymond, K. N. *Inorg.* Chem. **1982**, *21*, 2653. (b) Schumann, H.; Lee, P. R.; Loebel, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1033. (c) Deacon, G. B.; Gatehouse, B. M.; Nickel, S.; Platts, S. N. *Aust. J. Chem.* **1991**, *44*, 613. (d) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M.; Hemling, H.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 874. (e) Cosgriff, J. E.; Deacon, G. B.; Gatehouse, B. M. *Aust. J. Chem.* **1993**, *46*, 1881. (f) Röttger, D.; Erker, G.; Grehl, M.; Frölich, R. *Organometallics* **1994**, *13*, 3897.

(3) Selected examples of η^2-pyrazolato ligand coordination in main group and lanthanide complexes: (a) Pfeiffer, D.; Heeg, M. J.; Winter, C. H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2517. (b) Deacon, G. B.; Delbridge, E. E.; Forsyth, C. M.; Junk, P. C.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1999**, *52*, 733. (c) Deacon, G. B.; Delbridge, E. E.; Skelton, B. W.; White, A. H. *Eur. J. Inorg. Chem.* **1999**, 751. (d) Deacon, G. B.; Gitlits, A.; Roesky, P. W.; Bürgstein, M. R.; Lim, K. C.; Skelton, B. W.; White, A. H. *Chem. Eur. J.* **2001**, *7*, 127. (e) Pfeiffer, D.; Heeg, M. J.; Winter, C. H. *Inorg.* Chem. **2000**, *39*, 2377. (f) Zheng, W.; Mösch-Zanetti, N. C.; Blunck, T.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 3299. (g) Kunrath, F. A.; Casagrande, O. L., Jr.; Toupet, L.; Carpentier, J.-F. *Polyhedron* **2004**, *23*, 2437. (h) Hitzbleck, J.; Deacon, G. B.; Ruhlandt-Senge, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5218.

(4) Selected examples of η^2-pyrazolato ligand coordination in d^0 transition metal complexes: (a) Guzei, I. A.; Baboul, A. G.; Yap, G. P. A.; Rheingold, A. L.; Schlegel, H. B.; Winter, C. H. *J. Am. Chem. Soc.* **1997**, *119*, 3387. (b) Guzei, I. A.; Yap, G. P. A.; Winter, C. H. *Inorg. Chem.* **1997**, *36*, 1738. (c) Yélamos, C.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **1999**, *38*, 1871. (d) Yélamos, C.; Heeg, M. J.; Winter, C. H. *Organometallics* **1999**, *18*, 1168. (e) Gust, K. R.; Heeg, M. J.; Winter, C. H. *Polyhedron* **2001**, *20*, 805. (f) Dezelah, C. L., IV; El-Kadri, O. M.; Heeg, M. J.; Winter, C. H. *J. Mater. Chem.* **2004**, *14*, 3167. (g) Sebe, E.; Guzei, I. A.; Heeg, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Winter, C. H. *Eur. J. Inorg. Chem.* **2005**, 3955. (h) Most, K.; Hossbach, J.; Vidović, D.; Magull, J.; Mösch-Zanetti, N. C. *Adv. Synth. Catal.* **2005**, *347*, 463. (i) Mösch-Zanetti, N. C.; Sachse, A.; Pfoh, R.; Vidović, D.; Magull, J. *Dalton Trans.* **2005**, 2124.

(5) For examples of η^2-pyrazolato ligands in transition metal complexes with partially filled d-orbitals: (a) Mösch-Zanetti, N. C.; Kratzner, R.; Lehmann, C.; Schneider, T. R.; Uson, I. *Eur. J. Inorg. Chem.* **2000**, 13. (b) Gust, K. R.; Knox, J. E.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 1591. (c) Gust, K. R.; Knox, J. E.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *Eur. J. Inorg. Chem.* **2002**, 2327. (d) Mösch-Zanetti, N. C.; Vidović, D.; Magull, J. *Organometallics* **2003**, *22*, 5485. (e) Zhu, G.; Tanski, J. M.; Parkin, G. *Polyhedron* **2003**, *22*, 199. (f) Vela, J.; Vaddadi, S.; Kingsley, S.; Flaschenriem, C. J.; Lachicotte, R. J.; Cundari, T. R.; Holland, P. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 1607.

(6) For a review of 1,2,4-triazolato ligand coordination chemistry, see: Haasnoot, G. *Coord. Chem. Rev.* **2000**, *200−202*, 131.

(7) For recent leading references to complexes with bridging tetrazolato ligands, see: (a) Zhang, X.-M.; Zhao, Y.-F.; Wu, H.-S.; Batten, S. R.; Ng, S. W. *Dalton Trans.* **2006**, 3170. (b) Dinca, M.; Yu, A. F.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 8904. (c) Luo, T.-T.; Tsai, H.-L.; Yang, S.-L.; Liu, Y.-H.; Yadav, R. D.; Su, C.-C.; Ueng, C.-H.; Lin, L.-G.; Lu, K.-L. *Angew. Chem., Int. Ed.* **2005**, *44*, 6063. (d) Wang, X.-S.; Tang, Y.-Z.; Huang, X.-F.; Qu, Z.-R.; Che, C.-M.; Chan, P. W. H.; Xiong, R.-G. *Inorg. Chem.* **2005**, *44*, 5278. (e) Tao, J.; Ma, Z.-J.; Huang, R.-B.; Zheng, L.-S. *Inorg. Chem.* **2004**, *43*, 6133. (f) Shao, Z. H.; Lu, J.; Cai, R.-F.; Zhou, X.-G.; Weng, L.-H.; Chen, Z.-X. *Acta Crystallogr., Sect. E: Struct. Rep.* **2004**, *60*, m225.

(8) For recent leading references to metal complexes containing η^1-tetrazolato ligands, see: (a) Jiang, C.; Yu, Z.; Wang, S.; Jiao, C.; Li, J.; Wang, Z.; Cui, Y. *Eur. J. Inorg. Chem.* **2004**, 3662. (b) Hunyh, M. H. V.; Meyer, T. J.; Labouriau, A.; White, P. S.; Morris, D. E. *J. Am. Chem. Soc.* **2003**, *125*, 2828. (c) Chang, C.-W.; Lee, G.-H. *Organometallics* **2003**, *22*, 3107. (d) Palazzi, A.; Stagni, S.; Bordoni, S.; Monari, M.; Selva, S. *Organometallics* **2002**, *21*, 3774. (e) Xue, X.; Wang, X.-S.; Wang, L.-Z.; Xiong, R.-G.; Abrahams, B. F.; You, X.-Z.; Xue, Z.-L.; Che, C.-M. *Inorg.* Chem. **2002**, *41*, 6544. (f) Hammerl, A.; Holl, G.; Klapötke, T. M.; Mayer, P.; Noth, H.; Piotrowski, H.; Warchold, M. *Eur. J. Inorg. Chem.* **2002**, 834.

(9) Yélamos, C.; Gust, K. R.; Baboul, A. G.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *Inorg. Chem.* **2001**, *40*, 6451.

(10) Zheng, W.; Heeg, M. J.; Winter, C. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 2761.

(11) Mösch-Zanetti, N. C.; Hewitt, M.; Schneider, T. R.; Magull, J. *Eur. J. Inorg. Chem.* **2002**, 1181.

(12) Kobrsi, I.; Knox, J. E.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *Inorg. Chem.* **2005**, *44*, 4894.

(13) Zhou, X.-G.; Huang, Z.-E.; Cai, R.-F.; Zhang, L.-X.; Hou, X.-F.; Feng, X.-J.; Huang, X.-Y. *J. Organomet. Chem.* **1998**, *563*, 101.

(14) Arp, H. P. H.; Decken, A.; Passmore, J.; Wood, D. J. *Inorg. Chem.* **2000**, *39*, 1840.

(15) Selected recent papers describing theoretical studies of N$_5^-$ and metal complexes thereof: (a) Frunzke, J.; Lein, M.; Frenking, G. *Organometallics* **2002**, *21*, 3351. (b) Lein, M.; Frunzke, J.; Timoshkin, A.; Frenking, G. *Chem. Eur. J.* **2001**, *7*, 4155. (c) Burke, L. A.; Butler, R. N.; Stephens, J. C. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1679. (d) Fau, S.; Wilson, K. J.; Bartlett, R. J. *J. Phys. Chem. A* **2002**, *106*, 4639. (e) Gagliardi, L.; Orlandi, G.; Evangelisti, S.; Roos, B. O. *J. Chem. Phys.* **2001**, *114*, 10733. (f) Wang, X.; Hu, H.-R.; Tian, A.; Wong, N. B.; Chien, S.-H.; Li, W.-K. *Chem. Phys. Lett.* **2000**, *329*, 483. (g) Perera, S. A.; Bartlett, R. J. *Chem. Phys. Lett.* **1999**, *314*, 381. (h) Glukhovtsev, M. N.; Schleyer, P. v. R.; Maerker, C. *J. Phys. Chem.* **1993**, *97*, 8200.

(which was later challenged[18]). In addition, there is ongoing development of metal complexes containing the isoelectronic P_5^- ligand.[19] As experimental work moves toward ligands with higher nitrogen content, a considerable barrier to development remains the formation of insoluble oligomeric or polymeric complexes in which the nitrogen atoms of the heterocyclic ligands bridge between metal ions.[6,7] Since complexes containing N_5^- ligands may be at the edge of isolability due to facile loss of dinitrogen, it is important to develop a knowledge base that allows the synthesis of soluble, tractable 1,2,4-triazolato and tetrazolato complexes. Presumably, the basic coordination chemistry of pentazolato ligands will share similarities with that of tetrazolato ligands.

Several years ago, we communicated the synthesis and X-ray crystal structures of (3,5-diisopropyl-1,2,4-triazolato)-(18-crown-6)potassium and (phenyltetrazolato)(18-crown-6)-potassium, which constituted a rare example of a complex containing a terminal η^2-1,2,4-triazolato ligand and the first complex with a terminal η^2-tetrazolato ligand.[10] These complexes contained several puzzling structural distortions, including asymmetric η^2-bonding between the potassium ions and the heterocyclic ligands ($\Delta_{K-N} = 0.35-0.60$ Å), as well as a pronounced bending of the tetrazolato ligand CN_4 core toward the best plane of the 18-crown-6 ligand oxygen atoms. Subsequently, we reported the synthesis, structure, and molecular orbital calculations of a series of barium complexes of the formula $Ba(Rtetz)_2(18\text{-crown-6})$, as well as calculations of $Ba(N_5)_2(18\text{-crown-6})$.[12] These complexes also contained highly distorted tetrazolato and pentazolato ligand bonding. Molecular orbital calculations of $Ba(Rtetz)_2(18\text{-crown-6})$ suggested that these bonding distortions arose from intramolecular nitrogen−hydrogen−carbon hydrogen bond interactions between the heterocyclic ligand nitrogen atoms and the 18-crown-6 hydrogen atoms, which led to asymmetric barium−nitrogen distances and bending of the heterocyclic five-membered cores toward the 18-crown-6 ligands. Such insight caused us to take a more detailed look at our potassium complexes. Herein, we report the synthesis, structure, and molecular orbital calculations of a series of complexes containing 1,2,4-triazolato and tetrazolato ligands coordinated to the (18-crown-6)potassium fragment.

(16) (a) Vij, A.; Pavlovich, J. G.; Wilson, W. W.; Vij, V.; Christe, K. O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3051. (b) Ostmark, H.; Wallin, S.; Brinck, T.; Carlqvist, P.; Claridge, R.; Hedlund, E.; Yudina, L. *Chem. Phys. Lett.* **2003**, *379*, 539.

(17) Butler, R. N.; Stephens, J. C.; Burke, L. A. *Chem. Commun.* **2003**, 1016.

(18) Schroer, T.; Haiges, R.; Schneider, S.; Christe, K. O. *Chem. Commun.* **2005**, 1607.

(19) For selected leading references to P_5^- complexes, see: (a) Urzenius, E.; Brennessel, W. W.; Cramer, C. J.; Ellis, J. E.; Schleyer, P. v. R. *Science* **2002**, *295*, 832. (b) Sekar, P.; Scheer, M.; Voigt, A.; Kirmse, R. *Organometallics* **1999**, *18*, 2833. (c) Scherer, O. J.; Hilt, T.; Wolmershäuser, G. *Organometallics* **1998**, *17*, 4110. (d) Detzel, M.; Friedrich, G.; Scherer, O. J.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1321. (e) Hughes, A. K.; Murphy, V. J.; O'Hare, D. *J. Chem. Soc., Chem. Commun.* **1994**, 163. (f) Rink, B.; Scherer, O. J.; Wolmershäuser, G. *Chem. Ber.* **1995**, *128*, 71. (g) Rink, B.; Scherer, O. J.; Heckmann, G.; Wolmershäuser, G. *Chem. Ber.* **1992**, *125*, 1011.

Results

Synthesis of New Complexes. Treatment of 3,5-diisopropyltriazole, 3,5-diphenyltriazole, 3,5-di-3-pyridyltriazole, phenyltetrazole, pyrrolidinyltetrazole, or *tert*-butyltetrazole with equimolar quantities of potassium hydride and 18-crown-6 in tetrahydrofuran at ambient temperature led to slow hydrogen evolution and formation of (3,5-diisopropyl-1,2,4-triazolato)(18-crown-6)potassium (**1**, 88%), (3,5-diphenyl-1,2,4-triazolato)(tetrahydrofuran)(18-crown-6)potassium (**2**, 87%), (3,5-di-3-pyridyl-1,2,4-triazolato)(18-crown-6)potassium (**3**, 81%), (phenyltetrazolato)(18-crown-6)potassium (**4**, 94%), (pyrrolidinyltetrazolato)(18-crown-6)potassium (**5**, 90%), and (*tert*-butyltetrazolato)(18-crown-6)-potassium (**6**, 94%) as colorless crystalline solids (eq 1).

1, 88%, n = 0
E = CCH(CH$_3$)$_2$,
R = CH(CH$_3$)$_2$
2, 87%, n = 1
E = CC$_6$H$_5$
R = C$_6$H$_5$
3, 81%, n = 0
E = C(3-C$_5$H$_4$N)
R = 3-C$_5$H$_4$N
4, 94%, n = 0
E = N
R = C$_6$H$_5$
5, 90%, n = 0
E = N
R = N(CH$_2$)$_4$
6, 82%, n = 0
E = N
R = C(CH$_3$)$_3$
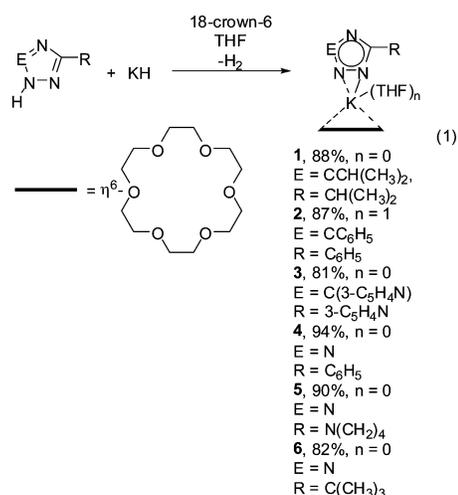
Complexes **1**−**6** can be alternatively prepared by a two-step sequence in which the potassium salts are formed first and are then treated with 18-crown-6. Complexes **1**−**6** are very soluble in alcohols and hot tetrahydrofuran and are easily crystallized from the latter. The microanalytical data are consistent with the proposed formulations, and the ^{1}H and ^{13}C-$\{^1$H$\}$ NMR data show the expected resonances for the nitrogen heterocycles and 18-crown-6 ligands. The sharp single resonances in the ^{1}H NMR spectra of the 18-crown-6 ligands in **1**−**6** suggest that the ligands are involved in dynamic exchange processes in solution at room temperature that rapidly interconvert the two faces of the 18-crown-6 ligand.

Triazolato(18-crown-6)potassium·$(H_2O)_{0.5}$ (**7**·$(H_2O)_{0.5}$) was prepared in 81% yield by an alternate synthetic strategy entailing treatment of potassium metal with triazole in the presence of 18-crown-6 (eq 2). Upon crystallization, **7**·
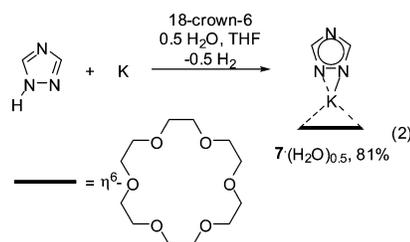
$(H_2O)_{0.5}$ was isolated as the hemi-hydrate. X-ray crystallography, as described below, demonstrated that the water

Coordination of Ligands to the [K(18-crown-6)]+ Fragment

Table 1. Crystal Data and Data Collection Parameters for **2**, **3**, **5**, **6**, and **7**·(H₂O)₀.₅

	2	**3**	**5**	**6**	**7**·(H₂O)₀.₅
empirical formula	$C_{30}H_{42}KN_3O_7$	$C_{24}H_{32}KN_5O_6$	$C_{17}H_{32}KN_5O_6$	$C_{17}H_{33}KN_4O_6$	$C_{14}H_{27}KN_3O_{6.5}$
fw	595.77	525.65	441.58	428.57	380.49
space group	$P2_12_12_1$	$Pna2_1$	$P2_12_12_1$	$Pnma$	$P2_1/n$
a (Å)	9.0914(8)	23.039(4)	8.5472(11)	15.8892(5)	11.6226(11)
b (Å)	16.2210(17)	14.659(3)	15.941(2)	13.9002(3)	8.2450(7)
c (Å)	21.612(2)	7.9911(11)	16.426(3)	10.0422(3)	20.6727(19)
β (°)					98.944(2)
V (Å³)	3187.2(5)	2698.9(8)	2238.1(6)	2217.95(11)	1956.9(3)
Z	4	4	4	4	4
cryst size (mm³)	0.50 × 0.40 × 0.30	0.80 × 0.18 × 0.18	0.40 × 0.10 × 0.10	0.18 × 0.18 × 0.06	0.60 × 0.15 × 0.10
frames collected	2450	1850	2450	1783	1850
total/independent reflns	22 492/7489	14 061/3855	15 941/5167	18 218/3616	10 107/4399
T (K)	295(2)	193(2)	295(2)	100(2)	207(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
γ calcd (g cm⁻³)	1.242	1.294	1.310	1.283	1.291
μ (mm⁻¹)	0.214	0.243	0.279	0.278	0.306
$R(F)^a$ (%)	5.71	3.96	6.01	3.64	3.41
$R_w(F)^b$ (%)	14.92	9.22	14.70	7.39	8.42

$^a R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w(F)^2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**, **3**, **5**, **6**, and **7**·(H₂O)₀.₅

	2	**3**	**5**	**6**	**7**·(H₂O)₀.₅
K−N(1)	2.783(3)	2.822(3)	2.757(4)	2.704(2)	2.827(2)
K−N(2)	2.937(3)	2.819(3)	2.906(5)	2.881(1)	2.725(1)
K−N(5)′		2.855(3)			
K−O(1)	2.910(4)	2.899(3)	2.793(4)	2.877(1)	2.848(1)
K−O(2)	3.050(4)	2.801(3)	2.762(4)	2.963(1)	2.963(1)
K−O(3)	2.863(5)	2.854(3)	2.851(4)	2.914(1)	2.808(1)
K−O(4)	3.051(4)	2.832(3)	2.904(4)	2.800(1)	2.882(1)
K−O(5)	2.917(4)	2.880(3)	2.896(4)		2.809(1)
K−O(6)	2.941(4)	2.789(3)	2.952(4)		2.922(1)
K−O(7)	2.940(4)				
N(1)−K−N(2)	27.29(9)	28.17(9)	27.59(13)	27.88(4)	28.41(4)
N(1)−K−O(7)	72.37(10)				
N(2)−K−O(7)	71.63(10)				

Table 3. Comparison of Metrical Parameters for **1**−**6** and **7**·(H₂O)₀.₅

	Δ_{K-N} (Å)	$KN_2/core^a$ (deg)	$O_6/core^a$ (deg)
1	0.595	2.1	85.9
2	0.154	5.7	68.5
3	0.003	32.7	45.7
4	0.358	19.5	61.5
5	0.149	3.6	82.2
6	0.177	0^b	90^b
7·(H₂O)₀.₅	0.102	2.0	77.8

^{a} Core refers to the 1,2,4-triazolato C_2N_3 or tetrazolato CN_4 planes. Values listed are dihedral angles. ^{b} By symmetry

molecule in **7**·(H₂O)₀.₅ is not coordinated to the potassium ion and instead resides in holes between the molecules. The microanalytical data are consistent with the proposed formulation, and the ¹H and ¹³C{¹H} NMR data show the expected resonances for the 1,2,4-triazolato and 18-crown-6 ligands. The infrared spectrum exhibits an absorption at 3383 cm⁻¹ that corresponds to the oxygen−hydrogen stretch of the water molecule.

Crystal Structures. To establish the solid-state geometries, the X-ray crystal structures of **2**, **3**, **5**, **6**, and **7**·(H₂O)₀.₅ were determined. The X-ray crystal structures of **1** and **4** were described in our preliminary communication.[10] Crystallographic data for **2**, **3**, **5**, **6**, and **7**·(H₂O)₀.₅ are summarized in Table 1. Selected bond lengths and angles are provided in Tables 2 and 3, and perspective views of **2**, **3**, **5**, **6**, and **7**·(H₂O)₀.₅ are presented in Figures 1−5.
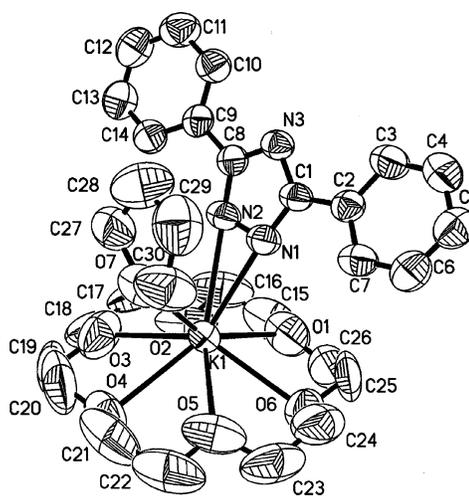
Figure 1. Perspective view of **2** with thermal ellipsoids at the 50% probability level.
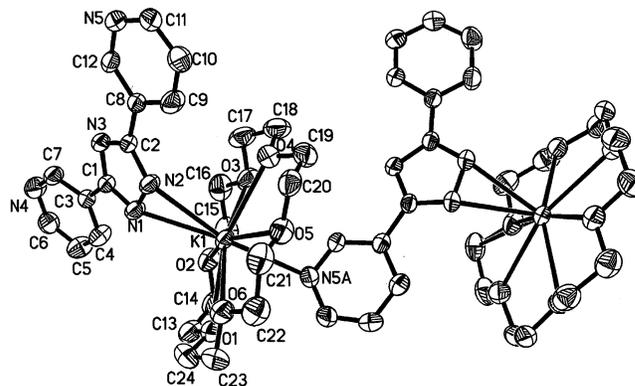
Figure 2. Perspective view of **3** with thermal ellipsoids at the 50% probability level.

Complexes **2**, **3**, **5**, **6**, and **7**·(H₂O)₀.₅ share a common [K(18-crown-6)]⁺ moiety, to which a 1,2,4-triazolato or tetrazolato ligand is bonded with η^2-coordination to the potassium ion. The heterocylic ligand bonding ranges from an ideal η^2-interaction to highly asymmetric. In the case of **2**, a tetrahydrofuran ligand is present, in addition to the η^2-3,5-diphenyl-1,2,4-triazolato ligand. Complexes **2**, **5**, **6**, and
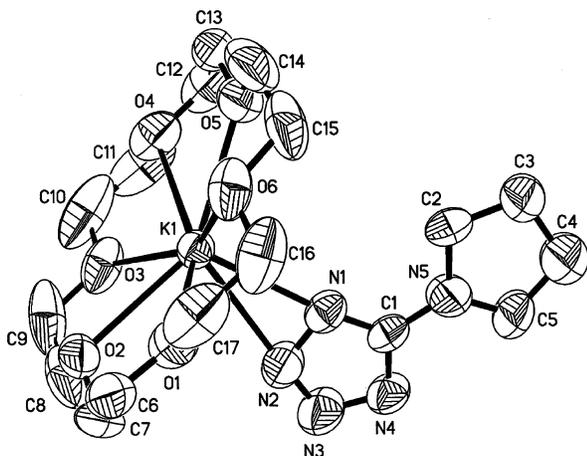
Figure 3. Perspective view of **5** with thermal ellipsoids at the 50% probability level.
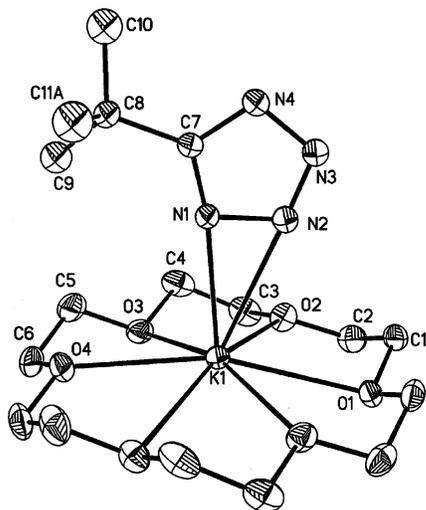
Figure 4. Perspective view of **6** with thermal ellipsoids at the 50% probability level.
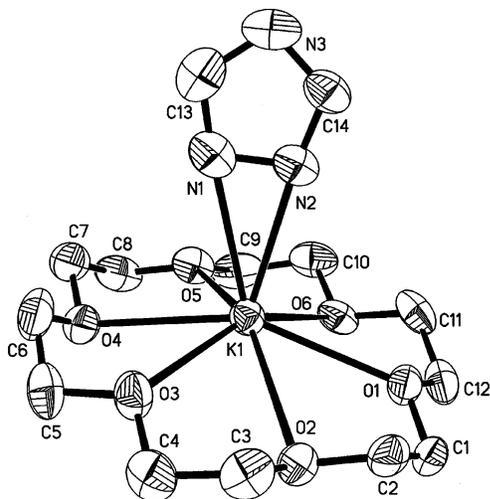
Figure 5. Perspective view of $7 \cdot (H_2O)_{0.5}$ with thermal ellipsoids at the 50% probability level.

$7 \cdot (H_2O)_{0.5}$ are monomeric in the solid state, while **3** is a polymer through coordination of a 3-pyridyl nitrogen atom to an adjacent potassium ion. The potassium−oxygen bond distances for **3, 5, 6,** and $7 \cdot (H_2O)_{0.5}$ average between 2.84

and 2.88 Å, with short distances in each molecule between 2.79 and 2.81 Å and long distances in each molecule between 2.90 and 2.96 Å. The average potassium−oxygen distance for the 18-crown-6 ligand in **2** is 2.955 Å, with short and long distances of 2.863(5) and 3.051(4) Å, respectively. The potassium−oxygen bond length for the tetrahydrofuran ligand is 2.940(4) Å. The longer potassium−oxygen bond distances in **2**, relative to the other complexes, can be ascribed to the higher coordination number in **2** (9 versus 8). The bonding of the heterocyclic ligands to the potassium ions in **2, 3, 5, 6,** and $7 \cdot (H_2O)_{0.5}$ is generically described as η^2. The shorter potassium−nitrogen distances range from 2.70 to 2.82 Å, while the longer distances range from 2.82 to 2.94 Å. Complex **3** exists as a polymer in the solid state through coordination of one 3-pyridyl nitrogen atom to an adjacent potassium ion on the face opposite the 1,2,4-triazolato ligand. The potassium−nitrogen bond length for this interaction is 2.855(3) Å, which is similar within experimental error to the potassium−nitrogen bond lengths associated with the 1,2,4-triazolato ligand (2.819(3), 2.833-(3) Å).

Table 3 lists some selected metrical parameters that highlight the bonding distortions that are present in **1−6** and $7 \cdot (H_2O)_{0.5}$. A striking difference among these complexes is the variation in the potassium−nitrogen bond distances. In **1** and **4**, the heterocyclic ligand bonding is highly asymmetric ($\Delta_{K-N} = 0.595, 0.358$ Å, respectively), while the asymmetry in **4−6** and $7 \cdot (H_2O)_{0.5}$ is still present but is smaller ($\Delta_{K-N} = 0.102-0.177$ Å). Complex **3** exhibits ideal η^2-1,2,4-triazolato ligand bonding ($\Delta_{K-N} = 0.003$ Å). There is no obvious relationship between asymmetry in the heterocyclic ligand bonding with the steric bulk of the heterocyclic carbon atom substituents. For example, **3** has ideal η^2-bonding of the 1,2,4-triazolato ligand, whereas **2** shows distinct asymmetry. Both contain six-membered aromatic substituents on the 1,2,4-triazolato ligands. Another distortion that occurs in **1−6** and $7 \cdot (H_2O)_{0.5}$ is variable bending of the heterocyclic ligands toward the 18-crown-6 ligand. From a repulsion viewpoint, the five-membered ring core of the heterocyclic ligands should be approximately perpendicular to the best plane of the 18-crown-6 ligand oxygen atoms. The angles between the KN_2/heterocyclic core and 18-crown-6 O_6 best plane/heterocyclic core have been used to quantify these distortions. There are no regular trends in these angles across the series **1−6** and $7 \cdot (H_2O)_{0.5}$. By virtue of symmetry, **6** has KN_2/core and O_6/core angles of 0° and 90°, respectively. Complex **3**, which is nine-coordinate, has KN_2/core and O_6/core angles of 32.7° and 45.7°, respectively. Of the remaining complexes, only the KN_2/core angle in **4** (19.5°) exceeds 6°. In **1, 5, 6,** and $7 \cdot (H_2O)_{0.5}$, the O_6/core angles range from 78° to 90°, which are close to perpendicular orientations between the heterocyclic cores and the best planes of the 18-crown-6 oxygen atoms. However, the KN_2/core angles in **2** (68.5°) and **4** (61.5°) are consistent with significant bending of the heterocyclic ligands toward the 18-crown-6 ligands.

Molecular Orbital Calculations. In view of the irregular structural trends summarized in Table 3, we sought to carry

out molecular orbital calculations to gain a deeper understanding of the structural distortions in **1**−**6** and **7**·(H₂O)₀.₅. As a model, we chose **4** since it possesses the largest solid-state distortions. In addition, the model complex pentazolato-(18-crown-6)potassium (**8**) was also studied to afford insight
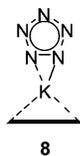
into the relationship between **1**−**6** and **7**·(H₂O)₀.₅ and so far unknown complexes containing the pentazolato ligand. Calculations on **4** and **8** were carried out with the Gaussian 03 suite of programs.[20] The B3LYP hybrid density functional[21] was used along with the 6-311G(d,p) basis set[22] on all atoms. The optimized structures of **4** and **8** are shown in Figures 6 and 7, along with selected predicted bond lengths and angles.

The optimized gas-phase structure for **4** possesses potassium−nitrogen distances of 2.693 and 2.750 Å, potassium−oxygen distances between 2.77 and 3.02 Å, and a KN_2/CN_4 angle of 2.8°. For comparison, the related values in the X-ray crystal structure determination of **4** are 2.744(2) and 3.102-(3) Å, 2.777−2.926 Å, and 19.5°. The most striking differences between the calculated and X-ray crystal structure results is that the degree of potassium−nitrogen bond length asymmetry and bending of the phenyltetrazolato ligand CN_4 core in the gas-phase structure are much smaller than those of the solid-state structure. The Mulliken charges on the 1- and 2-nitrogen atoms in the calculated structure of **4** are −0.38 and −0.20, respectively. Thus, the 1-nitrogen atom is more basic than the 2-nitrogen atom, which follows the expected trend for a nitrogen atom bonded to one carbon atom and one nitrogen atom versus a nitrogen atom bonded to two nitrogen atoms. The potassium−nitrogen bond length asymmetry can thus be partially rationalized by the difference in basicity between the 1- and 2-nitrogen atoms. To assess the energies associated with distorting the bonding of the phenyltetrazolato ligand, complex **4** was recalculated with
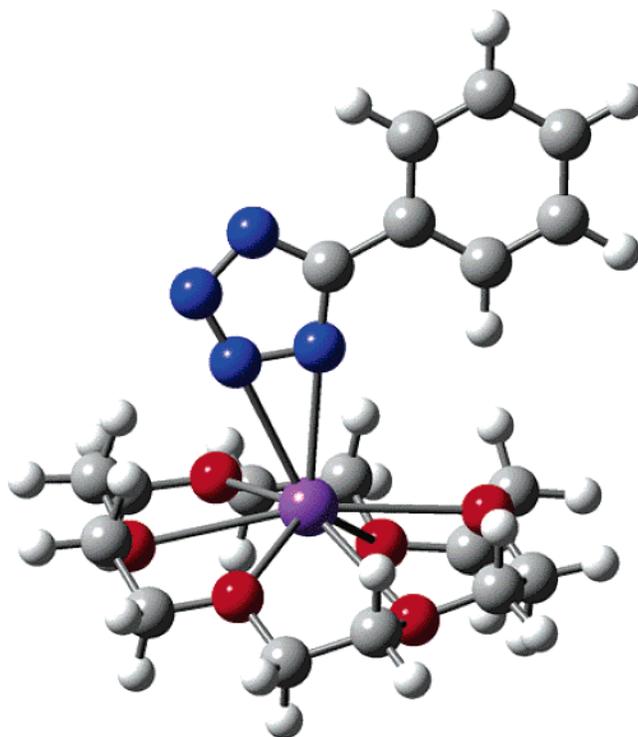
Figure 6. Optimized structure of **4** at the B3LYP/6-311G(d,p) level of theory. Selected bond lengths (Å) and angles (deg): K−N, 2.690, 2.750; K−O 2.77−3.02; KN_2/N_4C 2.8.
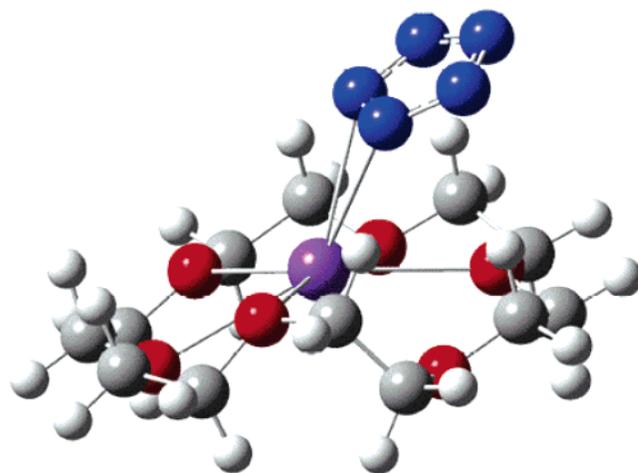
Figure 7. Optimized structure of **8** at the B3LYP/6-311G(d,p) level of theory. Selected bond lengths (Å) and angles (deg): K−N, 2.753, 2.873; K−O 2.72−2.98; KN_2/N_5 45.3.

the shorter potassium−nitrogen distance set to the value in the optimized complex (2.693 Å) and the longer potassium−nitrogen distance set to the sum of the shorter potassium−nitrogen distance and the difference between the two potassium−nitrogen bond lengths in **4** (3.051 Å). Optimization with these bond length constraints afforded a structure that was only 0.8 kcal/mol higher in energy than the unconstrained structure. Thus, relatively large distortions in the potassium−phenyltetrazolate bonding are low energy, consistent with the ionic bonding interactions present in **4**. The optimized gas-phase structure for **8** possesses predicted potassium−nitrogen distances of 2.753 and 2.873 Å, potassium−oxygen distances between 2.72 and 2.98 Å, and a $KN_2/$

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision A.01; Gaussian, Inc.: Wallingford, CT, 2004.
(21) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Lee, C.; Yang, W.; Parr, R. D. *Phys. Rev. B* **1988**, *37*, 785.
(22) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

Figure 8. NBO fragment orbitals showing the stabilization in **4** between occupied tetrazolato ligand orbitals: (a) nitrogen−nitrogen π and a carbon−hydrogen σ^* orbital and (b) nitrogen-based lone pair and a carbon−hydrogen σ^* orbital.

N_5 angle of 45.3°. The potassium−nitrogen bond distances for **8** are longer than those of **4**, which is consistent with the expected lower basicity of pentazolato versus tetrazolato ligands. In addition, the pentazolato ligand is bent significantly toward the 18-crown-6 ligand.

Natural bond order (NBO) analyses[23] were performed on **4** and **8** to gain a deeper insight into the interactions that lead to the structural distortions. For the NBO analyses, the complexes were divided into three fragments: the potassium ion, the 18-crown-6 ligand, and the phenyltetrazolato or pentazolato ligand. Stabilization energies were then calculated for interactions between the occupied and unoccupied orbitals localized on the three fragments. Because the B3LYP density functional does not include the effects of dispersion and the basis set does not include diffuse functions, the estimates of the stabilization energies are only semiquantitative. Orbital interactions in **4** between the nitrogen atoms in the tetrazolato ligand and the crown ether carbon−hydrogen bonds accounted for nearly 3 kcal/mol of stabilization. The majority of this stabilization energy involved two types of orbital interactions (Figure 8). An occupied out-of-plane nitrogen−nitrogen π orbital interaction with the two unoccupied carbon−hydrogen σ^* orbitals on the adjacent atoms of the crown ether had a stabilization of around 0.5 kcal/mol (Figure 8a). More significant stabilization came from the interaction of the in plane nitrogen-based lone pairs and the same carbon−hydrogen σ^* orbitals (Figure 8b). The interaction between these orbitals accounted for 2.1 kcal/mol of the calculated stabilization energy. Stabilization of **8** through orbital interactions amounted to 4.4 kcal/mol. The three largest contributions to this energy are shown in Figure 9. The first interaction is with an out-of-plane nitrogen-based orbital and carbon−hydrogen σ^* orbital, which accounts for about 0.75 kcal/mol per side, or 1.5 kcal/mol (Figure 9a). The interaction between the nitrogen−nitrogen out-of-plane π orbitals and the carbon−hydrogen σ^* orbital was 0.4 kcal/mol for each side, adding 0.8 kcal/mol to the overall stabilization (Figure 9b). The final major contribution to the orbital interaction stabilization came from the interaction of the symmetric nitrogen−nitrogen σ orbital interaction with a higher lying hydrogen atom Rydberg state. This interaction also had about 0.4 kcal/mol of stabilization per side (Figure 9c). The remaining orbital interactions were small, but all arose from the same occupied orbitals on the pentazolato
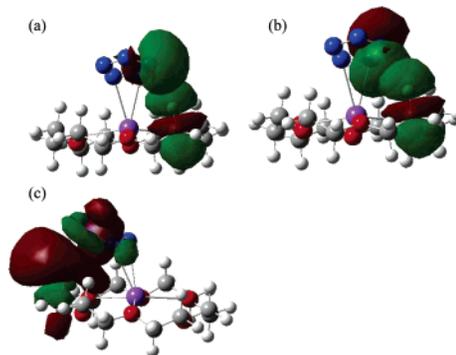
Figure 9. NBO fragment orbitals showing the stabilization in **8** between occupied pentazolato ligand orbitals: (a) a nitrogen-based lone pair and a carbon−hydrogen σ^* orbital, (b) an out of plane nitrogen−nitrogen π orbital and carbon−hydrogen σ^* orbital, and (c) a symmetric nitrogen−nitrogen σ orbital and hydrogen atom Rydberg state.

ligands interacting to a lesser degree with unoccupied crown ether carbon−hydrogen orbitals.

Intramolecular and Intermolecular Nitrogen−Hydrogen−Carbon Interactions in the Solid-State Structures of 1−6 and 7·(H₂O)₀.₅. The results of the molecular orbital calculations on **4** and **8** predict that there are intramolecular hydrogen bonds between some of the nitrogen atoms and the carbon−hydrogen bonds of the 18-crown-6 ligand that are on the same face as the azolato ligand. To probe for such interactions in the solid state, the crystal structures of **1−6** and **7**·$(H_2O)_{0.5}$ were reexamined to look for the presence of short nitrogen−hydrogen contacts. Table 4 lists nitrogen−hydrogen contacts that are <3 Å. The sum of the van der Waals radii for nitrogen and hydrogen atoms is about 2.7−3.0 Å,[24] so distances of >3 Å do not represent significant interactions. For brevity, the following section highlights only selected interactions, but complete contacts are listed in Table 4. Complex **1** contains highly asymmetric potassium−nitrogen distances (Δ_{K-N} = 0.595 Å), and the nitrogen atom involved in the longer potassium−nitrogen bond (N(2)) has two intramolecular close contacts (2.734, 2.786 Å) with two hydrogen atoms on the same face of the 18-crown-6 ligand as the 1,2,4-triazolato ligand. Complex **2**, which also contains a tetrahydrofuran ligand coordinated to the same face as the 1,2,4-triazolato ligand, does not contain any short intramolecular interactions between the 1,2,4-triazolato and 18-crown-6 ligands. However, there are intermolecular contacts between the nitrogen atoms and the hydrogen atoms of adjacent 18-crown-6 ligands (2.79−2.90 Å). Complex **3** likewise does not show any short intramolecular interactions between the 1,2,4-triazolato and hydrogen atoms of the 18-crown-6 ligand. Complex **4** also contains highly asymmetric potassium−nitrogen distances (Δ_{K-N} = 0.358 Å), and the nitrogen atom involved in the longer potassium−nitrogen bond (N(2)) has two intramolecular close contacts (2.76, 2.95 Å) with two hydrogen atoms on the same face of the 18-crown-6 ligand as the tetrazolato ligand. Complex **5** has slightly asymmetric potassium−nitrogen distances (Δ_{K-N} = 0.149 Å). The nitrogen atom associated with the shorter potas-

(23) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(24) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Allinger, N. L.; Hirsch, J. A.; Miller, M. A.; Tyminski, I. J.; Van-Catledge, F. A. *J. Am. Chem. Soc.* **1968**, *90*, 1199.

Table 4. Short Intramolecular and Intermolecular Nitrogen−Hydrogen Distances Associated with the Heterocyclic Core Nitrogen Atoms in **1**−**6** and **7**·($H_2O)_{0.5}$

complex	contacts to N(1) (Å)[a,b]	contacts to N(2) (Å)[a,b]	contacts to N(3) (Å)[a,b]	contacts to N(4) (Å)[a,b]
1	2.892 (H4C)	2.734 (H10B)	2.474 (H3)	
	2.986 (H4B)	2.786 (H11A)	2.757 (H5B)	
		2.720 (H7B)	2.556 (H6)	
		2.924 (H7A)	2.580 (H8B)	
		2.821 (H(14A)′)	2.683 ((H16A′)	
			2.683 (H17A′)	
2	2.591 (H7)	2.603 (H14)	2.683 (H3)	
	2.835 (H21A′)	2.786 (H21A′)	2.536 (H10)	
			2.897 (H(21B′)	
3	2.594 (H4)	2.627 (H9)	2.588 (H7)	
	2.808 (H6′)	2.701 (H16A′)	2.580 (H12)	
4	2.580 (H15)	2.763 (H8B)	2.752 (H3A′)	2.599 (H19)
		2.951 (H9B)	2.833 (H12A′)	2.921 (H3B′)
		2.852 (H(1B)′)		
5	2.699 (H2B)	2.878 (H13A′)	2.867 (H13A′)	2.824 (H5B)
	2.980 (H2A)		2.890 (H13B′)	2.903 (H5A)
	2.739 (H11B′)			2.722 (H8A′)
6	2.833 (H3A′)	2.698 (H3A′)	2.754 (H3A′)	2.922 (H3A′)
		2.968 (H1A)	2.991 (H4B′)	2.731 (H1B′)
			2.987 (H6A′)	
7·($H_2O)_{0.5}$	2.768 (H5A′)	2.794 (H5A′)		
	2.950 (H9B′)	2.987 (H7B′)		
		2.862 (H9B′)		

[a] Contact is to the hydrogen atom in parentheses. Hn, HnA, HnB, and HnC indicate hydrogen atoms bound to Cn. [b] Primed hydrogen atoms refer to intermolecular contacts.

sium−nitrogen bond (N(1)) has intramolecular close contacts to two hydrogen atoms in the 2-position of the pyrrolidinyl group (2.70, 2.98 Å), as well as an intermolecular contact with a hydrogen atom of an adjacent 18-crown-6 ligand (2.74 Å). The nitrogen atom associated with the longer potassium−nitrogen bond (N(2)) has an intermolecular contact with a hydrogen atom of an adjacent 18-crown-6 ligand (2.88 Å). Complex **6** has slightly asymmetric potassium−nitrogen distances (Δ_{K-N} = 0.177 Å). Unlike the other complexes, there is an intermolecular hydrogen bond between the π-cloud of the tetrazolato ligand and an adjacent hydrogen atom of an 18-crown-6 ligand. This interaction is characterized by hydrogen−nitrogen distances of 2.70−2.92 Å. In addition, the nitrogen atom associated with the longer potassium−nitrogen bond (N(2)) has an intramolecular close contact of 2.97 Å to a hydrogen atom of the 18-crown-6 ligand. Complex **7** possesses only intermolecular contacts with hydrogen atoms of adjacent 18-crown-6 ligands (2.77−2.99 Å).

Discussion

A significant outcome in the present work is demonstration of terminal η^2-1,2,4-triazolato and η^2-tetrazolato ligand coordination in the solid-state structures of **1**−**6** and **7**·($H_2O)_{0.5}$. The molecular orbital calculations show no evidence for covalent bonding between the potassium ion and the ligands in **4** and **8**, so it is likely that the observed η^2-bonding in **1**−**6** and **7**·($H_2O)_{0.5}$ arises from maximization of charge contact between the potassium ion and the nitrogen atoms. Terminal η^2-pyrazolato ligand coordination is rare in group 1 elements and is limited to K(Ph₂pz)(18-crown-6),[25] K(Me₂-

pz)(18-crown-6)(H_2O),[25] and Na(tBu₂pz)(18-crown-6).[26] Structurally characterized pyrazolato complexes that contain η^2-interactions within more complex coordination modes include [K(tBu₂pz)(THF)]₆,[27] Na[Ln(tBu₂pz)₄],[28] and a series of lithium, sodium, and potassium complexes containing Me₂-pz and tBu₂pz ligands.[26] η^2-Pentazolato ligand coordination has been predicted to be the most stable in theoretical studies of MN₅ (M = Li, Na, K, Rb) and M($N_2)_5$ (M = Mg, Ca).[15c,29] However, in these studies, the lowest energy structures were predicted to be ones in which the metal atoms lie in the plane of the N₅ ring.

In addition to the intramolecular nitrogen−hydrogen−carbon hydrogen bonds documented in **1**−**6** and **7**·($H_2O)_{0.5}$, there is an approximately equal number of intermolecular nitrogen−hydrogen−carbon hydrogen bonds present in the solid-state structures. This doubles the stabilization energy of **4** if one assumes that the energies of the intermolecular hydrogen bonds are approximately equal to the intramolecular interactions. Thus, the heterocyclic ligands gain considerable stabilization by formation of these hydrogen bonds, and these hydrogen bonds appear to be the origin of the heterocyclic ligand bonding distortions across the series. Even though each nitrogen−hydrogen−carbon interaction is weak, the sum of these interactions is much larger than the energy required to distort the potassium−nitrogen bonding. Thus, the overall energies of **1**−**6** and **7**·($H_2O)_{0.5}$ are lowered by ligand bonding distortions and attendant hydrogen bond formation. The NBO analyses predict a higher sum of bond energies for the hydrogen bonding in **8** than in **4**. This trend

(25) Zheng, W.; Heeg, M. J.; Winter, C. H. *Eur. J. Inorg. Chem.* **2004**, 2652.

(26) Cortés-Llama, S.-A.; Hernéndez-Lamoneda, R.; Velázquez-Carmona, M.-A.; Muòoz-Hernández, M.-A.; Toscano, R. A. *Inorg. Chem.* **2006**, *45*, 286.

(27) Yélamos, C.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **1998**, *37*, 3892.

(28) Deacon, G. B.; Delbridge, E. E.; Evans, D. J.; Harika, R.; Junk, P. C.; Skelton, B. W.; White, A. H. *Chem. Eur. J.* **2004**, *10*, 1193.

(29) Zhao, J. F.; Li, N.; Li, Q. S. *Theor. Chem. Acc.* **2003**, *110*, 10.

can be ascribed to the higher effective electronegativity of the nitrogen atoms involved in each hydrogen bond in **8**, compared to **4**, due to the presence of five electronegative nitrogen atoms in **8** and only four such atoms in **4**. This situation implies that bonding distortions arising from nitrogen−hydrogen−carbon hydrogen bonding are likely to be stronger and more significant in complexes containing more nitrogen-rich heterocyclic ligands, compared to nitrogen heterocyclic ligands containing fewer nitrogen atoms. The gas-phase structure of **4** that is predicted by molecular orbital calculations does not match the X-ray crystal structure of **4** in several key aspects, including the asymmetry in the potassium−nitrogen bond lengths and the bending of the tetrazolato CN_4 core toward the best plane of the 18-crown-6 oxygen atoms. The difficulty in reproducing the solid-state structure suggests that the intermolecular hydrogen bonds play an important role in determining the exact coordination modes of the heterocyclic ligands. Finally, the results provide insight into the weak interactions that are collectively described as crystal packing forces.[30]

Weak element−hydrogen−carbon (element = N, O) hydrogen bonding interactions are well-known in organic molecules and affect structures in many systems.[31] The effects of similar interactions on the structures of metal complexes are much less documented. Our recent report describing the synthesis, structure, and molecular orbital calculations of $Ba(Rtetz)_2(18\text{-crown-}6)$ and molecular orbital calculations of $Ba(N_5)_2(18\text{-crown-}6)$ demonstrates that intramolecular and intermolecular nitrogen−hydrogen−carbon hydrogen bonding produces structural distortions that are very similar to those documented herein.[12] A search of the Cambridge Crystallographic Database listed 720 structures that contain the $[M(18\text{-crown-}6)]^{n+}$ (M = group 1, 2 metal, n = 1, 2) fragment, in addition to various anionic species and neutral donor ligands. Many of these complexes contain electronegative donor atoms such as oxygen and nitrogen or contain organic π-systems, and it is therefore possible that element−hydrogen−carbon hydrogen bonding interactions can lead to ligand structural distortions in at least some of these species. Intramolecular carbon−hydrogen−oxygen hydrogen bonding is observed between a perchlorate oxygen atom and a carbon−hydrogen bond of the 18-crown-6 ligand in $Na(ClO_4)(18\text{-crown-}6)(H_2O)$,[32] and a similar interaction is present between the nitrato ligand and the carbon−hydrogen bond of the 18-crown-6 ligand in $Na(NO_3)(18\text{-crown-}6)(H_2O)$.[32] Accommodation of these intramolecular hydrogen bonds causes slight distortions in the bonding between the sodium ion and the anionic ligands. In other group 1 and 2 complexes, the presence and effects of weak

hydrogen bonding on metal−ligand bonding are less well established. The complex $Na(tBu_2pz)(18\text{-crown-}6)$ has sodium−nitrogen distances of 2.3175(15) and 2.5767(15) Å,[26] and it is possible that this asymmetry originates from the formation of intramolecular and intermolecular nitrogen−hydrogen−carbon hydrogen bonds. The acetylide ligands in $M(CCR)_2(18\text{-crown-}6)$ (M = Ca, Sr, Ba) are bent significantly toward the 18-crown-6 ligands.[33] The bending may be due to attractive $C-H\cdots C_\pi$ interactions between the acetylide π-system and adjacent 18-crown-6 carbon−hydrogen bonds, although other explanations are possible. In the group 12 complex $Hg(NO_3)_2(18\text{-crown-}6)$, intramolecular carbon−hydrogen−oxygen interactions were proposed between the nitrato and 18-crown-6 ligands to account for the observed nitrato ligand bonding distortions.[34]

To date, there have been no reports of an isolable complex containing a pentazolato ligand.[15,29] In the present work, **1**−**6** and $\mathbf{7}\cdot(H_2O)_{0.5}$ are thermally stable; all except for **5** melt without decomposition at temperatures as high as 182 °C, and none shows evidence for cycloreversion reactions. Accordingly, the pentazolato complex $K(N_5)(18\text{-crown-}6)$ (**8**) may possess sufficient thermal stability to allow isolation, if a synthetic approach can be established. The nitrogen−hydrogen−carbon hydrogen bonding described herein for **8** should provide additional thermodynamic stabilization in the solid state, which should assist with isolation efforts.

Experimental Section

General Considerations. All new complexes were air stable in the absence of moisture but slowly formed oily solids upon extended exposure to ambient atmosphere presumably by absorption of water vapor. Hence, all reactions were performed under an inert atmosphere of argon using either glovebox or Schlenk line techniques. Potassium hydride, 18-crown-6, and phenyltetrazole were purchased from Aldrich Chemical Co. and were used as received. 3,5-Diisopropyltriazole,[35] 3,5-diphenyltriazole,[36] 3,5-di-3-pyridyltriazole,[37] pyrrolidinyltetrazole,[38] and *tert*-butyltetrazole[39] were prepared by literature procedures. ^1H and $^{13}C\{^1H\}$ NMR were obtained at 300 or 75 MHz in CD_3OD or $CDCl_3$ as indicated. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected. X-ray structure searches were conducted using version 5.27 (November 2005) of the Cambridge Crystallographic Database.

General Procedure for the Preparation of 1−6. A Schlenk flask was charged with the appropriate heterocycle (2.5 mmol), potassium hydride (0.100 g, 2.5 mmol), and 18-crown-6 (0.660 g, 2.5 mmol). Tetrahydrofuran (30 mL) was added, and the mixture was stirred for 18 h at room temperature. The solvent was then

(30) For an overview, see: Martin, A.; Orpen, A. G. *J. Am. Chem. Soc.* **1996**, *118*, 1464.
(31) Selected recent examples: (a) Quinn, J. R.; Zimmerman, S. C. *Org. Lett.* **2004**, *6*, 1649. (b) Cappelli, A.; Giorgi, G.; Anzini, M.; Vomero, S.; Ristori, S.; Rossi, C.; Donati, A. *Chem. Eur. J.* **2004**, *10*, 3177. (c) Freisinger, E.; Rother, I. B.; Luth, M. S.; Lippert, B. *PNAS* **2003**, *100*, 3748. (d) Baures, P. W.; Beatty, A. M.; Dhanasekaran, M.; Helfrich, B. A.; Pérez-Segarra, W.; Desper, J. *J. Am. Chem. Soc.* **2002**, *124*, 11315. (e) Jiang, L.; Lai, L. *J. Biol. Chem.* **2002**, *277*, 37732. (f) May, E.; Destro, R.; Gatti, C. *J. Am. Chem. Soc.* **2001**, *123*, 12248. (g) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441.
(32) Steed, J. W.; Junk, P. C. *J. Chem. Soc., Dalton Trans.* **1999**, 2141.

(33) Green, D. C.; Englich, U.; Ruhlandt-Senge, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 354.
(34) Calleja, M.; Steed, J. W. *J. Chem. Crystallogr.* **2003**, *33*, 609.
(35) Grüner, R.; Benes, Z.; Schuber, E.; Arman, M. *Monatsh. Chem.* **1927**, *48*, 37.
(36) Francis, J. E.; Gorczyca, L. A.; Mazzenga, G. C.; Meckler, H. *Tetrahedron Lett.* **1987**, *28*, 5133.
(37) Browne, E. *Aust. J. Chem.* **1975**, *28*, 2543.
(38) Garbrecht, W. L.; Herbst, R. M. *J. Org. Chem.* **1953**, *18*, 1003.
(39) Amantini, D.; Beleggia, R.; Fringuelli, F.; Pizzo, F.; Vaccaro, L. *J. Org. Chem.* **2004**, *69*, 2896.

removed under reduced pressure to afford a white residue. The white solid was washed with hexane to remove any unreacted heterocycle and was then dissolved in tetrahydrofuran (20 mL). The solution was filtered through a 2-cm pad of Celite on a coarse glass frit. Hexane (10 mL) was added to the filtered solution, and the flask was then placed in a −20 °C freezer for 24 h. The products were isolated by removal of the solvent with cannula, followed by vacuum-drying. In the case of **3**, the product was insoluble in tetrahydrofuran at room temperature. Therefore, **3** was refluxed until it dissolved and the product was isolated as colorless needles by allowing the reaction mixture to cool to room-temperature undisturbed. The synthesis of **7·(H$_2$O)$_{0.5}$** required a different procedure, which is described below.

(3,5-Diisopropyl-1,2,4-triazolato)(18-crown-6)potassium (1). This product was isolated in 88% yield: mp 167 °C; ^{1}H NMR (CD$_3$-OD, 23 °C, ppm) 3.61 (s, 24 H, 18-crown-6 C*H*), 3.01 (septet, *J* = 7.2 Hz, 2 H, C*H*), 1.27 (d, *J* = 7.2 Hz, 12 H, C*H$_3$*); ^{13}C{^{1}H} NMR (CD$_3$OD, 23 °C, ppm) 168.23 (s, N-*C*-CH), 71.33 (s, 18-crown-6 C*H*), 29.15 (s, *C*H−CH$_3$), 22.59 (s, *C*H$_3$); MS (EI) *m/z* (%): 303 ([K(18-crown-6)]$^+$), 100%). Anal. Calcd for C$_{20}$H$_{38}$KN$_3$O$_6$: C, 52.72; H, 8.41; N, 9.22. Found: C, 52.59; H, 8.34; N, 9.24.

(3,5-Diphenyl-1,2,4-triazolato)(tetrahydrofuran)(18-crown-6)-potassium (2). This product was isolated in 87% yield: mp 86 °C; IR (Nujol, cm^{-1}) 3044 (s), 2902 (s), 1977 (w), 1895 (w), 1828 (w), 1768 (w), 1602 (m), 1503 (m), 1462 (m), 1410 (m), 1352 (m), 1265 (s), 1110 (s), 962 (m), 840 (m), 731 (s); ^{1}H NMR (CDCl$_3$, 22 °C, ppm) 8.23 (m, 4 H, *ortho*-C*H*), 7.28 (m, 4 H, *meta*-C*H*), 7.14 (m, 2 H, *para*-C*H*), 3.70 (m, 4 H, O(C*H$_2$*CH$_2$)$_2$), 3.43 (s, 24 H, 18-crown-6 C*H*), 1.81 (m, 4 H, O(CH$_2$C*H$_2$*)$_2$); ^{13}C{^{1}H} NMR (CDCl$_3$, 22 °C, ppm) 162.88 (s, triazolato ring *C*), 135.16 (s, *ipso*-*C*), 127.68 (s, *ortho*-*C*H), 126.00 (s, *meta*-*C*H), 123.49 (s, *para*-*C*H), 69.80 (s, 18-crown-6 *C*H), 67.88 (s, O(*C*H$_2$CH$_2$)$_2$), 25.52 (s, O(CH$_2$*C*H$_2$)$_2$). Anal. Calcd for C$_{30}$H$_{42}$KN$_3$O$_7$: C, 60.48; H, 7.11; N, 7.05. Found: C, 60.21; H, 7.15; N, 7.09.

(3,5-Di-3-pyridyl-1,2,4-triazolato)(18-crown-6)potassium (3). This product was isolated in 81% yield: mp 109−110 °C; IR (neat, cm^{-1}) 3050 (m), 2898 (s), 1590 (w), 1572 (w), 1452 (m), 1352 (s), 1250 (m), 1109 (s), 993 (m), 962 (s), 834 (w), 714 (w); ^{1}H NMR (CDCl$_3$, 22 °C, ppm) 9.48 (m, 2 H, 2-C*H*), 8.47 (m, 2 H, 4-C*H*), 8.42 (m, 2 H, 6-C*H*), 7.26 (m, 2 H, 5-C*H*), 3.55 (s, 24 H, 18-crown-6 C*H*); ^{13}C{^{1}H} NMR (CDCl$_3$, 22 °C, ppm) 161.27 (s, triazolato ring *C*), 147.89 (s, 2-*C*H or 6-*C*H), 147.45 (s, 2-*C*H or 6-*C*H), 133.14 (s, 5-*C*H), 131.20 (s, 3-*C*H), 123.37 (s, 4-*C*H), 70.22 (s, 18-crown-6 *C*H). Anal. Calcd for C$_{24}$H$_{32}$KN$_5$O$_6$: C, 54.84; H, 6.14; N, 13.32. Found: C, 55.15; H, 6.20; N, 13.08.

(Phenyltetrazolato)(18-crown-6)potassium (4). This product was isolated in 94% yield: mp 157 °C; ^{1}H NMR (CD$_3$OD, 23 °C, ppm) 7.28 (m, 5 H, aromatic C*H*), 3.41 (s, 24 H, 18-crown-6 C*H*); ^{13}C{^{1}H} NMR (CD$_3$OD, 23 °C, ppm) 162.93 (s, tetrazolato ring core *C*), 131.42 (s, Ph ring, para-*C*H), 129.71 (s, Ph ring, overlapping *meta*-*C*H and *ipso*-*C*), 127.73 (s, Ph- ring *ortho*-*C*H), 71.31 (s, 18-crown-6 *C*H); MS (EI) *m/z* (%): 303 ([K(18-crown-6)]$^+$, 100%). Anal. Calcd for C$_{19}$H$_{29}$KN$_4$O$_6$: C, 50.88; H, 6.52; N, 12.49. Found: C, 50.32; H, 6.46; N, 12.55.

(5-N-Pyrrolidinyltetrazolato)(18-crown-6)potassium (5). This product was isolated in 90% yield: mp 185 °C dec; IR (neat, cm^{-1}) 2900 (m), 1530 (m), 1470 (m), 1352 (m), 1105 (s), 962 (s), 836 (m); ^{1}H NMR (CDCl$_3$, 22 °C, ppm) 3.62 (s, 24 H, 18-crown-6 C*H*), 3.49 (m, 4 H, N(C*H$_2$*CH$_2$)$_2$), 1.90 (m, 4H, N(CH$_2$C*H$_2$*)$_2$); ^{13}C{^{1}H} NMR (CDCl$_3$, 22 °C, ppm) 164.52 (s, tetrazolato ring *C*), 70.03 (s, 18-crown-6 *C*H), 49.21 (s, N(*C*H$_2$CH$_2$)$_2$), 25.42 (s, N(CH$_2$*C*H$_2$)$_2$). Anal. Calcd for C$_{17}$H$_{32}$KN$_5$O$_6$: C, 46.24; H, 7.30; N, 15.86. Found: C, 46.01; H, 7.15; N, 15.92.

(*Tert*-butyltetrazolato)(18-crown-6)potassium (6). This product was isolated in 82% yield: mp 172 °C dec; IR (Nujol, cm^{-1}) 1555 (w), 1283 (s), 1104 (s), 962 (s), 839 (s); ^{1}H NMR (CDCl$_3$, 22 °C, ppm) 3.62 (s, 24 H, 18-crown-6 C*H*), 1.43 (s, 9 H, C(C*H$_3$*)$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, 22 °C, ppm) 163.57 (s, tetrazolato ring *C*), 70.82 (s, 18-crown-6 *C*H), 30.94 (s, *C*(CH$_3$)$_3$), 29.53 (s, C(*C*H$_3$)$_3$). Anal. Calcd for C$_{17}$H$_{33}$KN$_4$O$_6$: C, 47.64; H, 7.76; N, 13.07. Found: C, 47.44; H, 7.55; N, 13.21.

Preparation of (1,2,4-Triazolato)(18-crown-6)potassium·(H$_2$O)$_{0.5}$ (7·(H$_2$O)$_{0.5}$). A mixture of 1,2,4-triazole (0.69 g, 10.0 mmol), potassium metal (0.78 g, 20 mmol), and 18-crown-6 (2.77 g, 10.5 mmol) in tetrahydrofuran (100 mL) was refluxed for 5 h, after which time hydrogen evolution was complete and a white precipitate had formed. The hot suspension was filtered through a 2-cm pad of Celite on a coarse glass frit. The frit was washed with an additional portion of hot tetrahydrofuran (100 mL). After cooling to ambient temperature, the solvent was removed with a cannula and the resultant solid was dried under reduced pressure to afford a crude solid (3.0 g, 81%). Crystallization of this solid from tetrahydrofuran always afforded crystals of **7·(H$_2$O)$_{0.5}$**, but in variable yields. To address this problem, a suspension of the crude product (0.37 g, 1.0 mmol) in tetrahydrofuran (10 mL) was treated with water (36 μL, 2.0 mmol). The flask containing this mixture was warmed with a heating mantle until all of the solids had dissolved. While still hot, the clear solution was then concentrated to a volume of about 5 mL under reduced pressure. Colorless crystals formed upon cooling to room temperature and were isolated by removal of the supernatant solution with a cannula and then vacuum-drying to afford colorless crystals of **7·(H$_2$O)$_{0.5}$** (0.31 g): mp 182 °C; IR (Nujol, cm^{-1}) 3383 (ν_{OH}, m), 3068 (m), 1377 (s), 1350 (s), 1103 (s), 961 (s), 838 (s), 682 (s); ^{1}H NMR (CD$_3$OD, 23 °C, ppm) 7.76 (s, 1 H, C*H*), 3.48 (s, 24 H, 18-crown-6 C*H*); ^{13}C{^{1}H} NMR (CD$_3$OD, 23 °C, ppm) 150.02 (s, *C*H), 71.33 (s, 18-crown-6 C*H*); MS(EI) *m/z* (%): 303 ([K(18-crown-6)]$^+$, 100). Anal. Calcd for C$_{14}$H$_{26}$KN$_3$O$_6$·(H$_2$O)$_{0.5}$: C, 44.19; H, 6.89; N, 11.04. Found: C, 44.22; H, 6.94; N, 11.21.

X-ray Crystallographic Structure Determinations. Diffraction data for **2**, **3**, **5**, and **7·(H$_2$O)$_{0.5}$** were measured on a Bruker P4/CCD diffractometer equipped with Mo radiation and a graphite monochromator. The samples were mounted in thin-walled glass capillaries under a dry nitrogen atmosphere. A sphere of data was measured at 10 s/frame and with 0.2° between frames for each complex. The frame data were indexed and integrated with the manufacturer's SMART software.[39] All structures were refined using Sheldrick's SHELX-97 software.[40]

Complex **2** crystallized as colorless rods. Hydrogen atom positions were calculated or observed. The asymmetric unit contains one neutral complex including one tetrahydrofuran ligand. Complex **3** crystallized as colorless rods. Hydrogen atom positions were observed or calculated. The asymmetric unit contains one di-3-pyridyl-1,2,4-triazolato ligand, one 18-crown-6 ligand, and one potassium ion. A polymeric structure is formed by the association of the potassium ions with an adjacent di-3-pyridyl-1,2,4-triazolato ligand nitrogen atom through the crystallographic *n*-glide. Complex **5** crystallized as colorless needles. The crystal did not diffract well, and only 2502 of the 5167 independent reflections were observed (*I* > 2σ(*I*)). The frame data also showed wide and smeared diffraction, indicating a disordered mosaic character. Hydrogen atoms were placed in calculated positions. The final model showed large thermal ellipsoids in the 18-crown-6 ligand, confirming the

(40) *SMART*, *SAINT*, *SADABS*, and *APEX-II* collection and processing programs are distributed by the manufacturer. Bruker AXS Inc., Madison WI.

poor crystallinity of the sample. Complex **7** crystallized as colorless rods. Hydrogen atoms were placed in observed and calculated positions. The asymmetric unit contains one neutral complex and 0.5 equiv of water. The water electrons were placed by use of Spek's SQUEEZE portion of the PLATON software.[41]

Diffraction data for **6** were measured on a Bruker X8 APEX-II kappa geometry diffractometer with Mo radiation and a graphite monochromator. Frames were collected as a series of sweeps with the detector at 40 mm and 0.2° between each frame. Frames were recorded for 20 s. APEX-II[39] and SHELX-97[40] software were used in the collection and refinement of the models. The crystals were colorless needles. The asymmetric unit consists of one-half neutral complex. There is a disordered *tert*-butyl group that occupies a crystallographic mirror plane. The methyl groups therein were assigned partial occupancies and kept isotropic. This disorder persisted even when the symmetry was lowered to exclude the mirror in the molecule (acentric space group $Pna2_1$).

Supporting Information Available: Tables of coordinates for the molecular orbital calculations on **4** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC061256U

(41) Sheldrick, G. *SHELX-97*; University of Göttingen: Göttingen, Germany, 2003 and 1997.
(42) (a) Spek, A. L. *PLATON*; Utrecht University: Utrecht, The Netherlands, 2003. (b) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.