

Cofacial Dicobalt Complex of a Binucleating Hexacarboxamide Cryptand Ligand

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A hexacarboxamide cryptand featuring appended polyether moieties is used as a binucleating ligand for two Co^{II} centers, marking the first time cryptands have been used as hexaanionic N donors for metal coordination. A synthesis for the hexacarboxamide cryptand, culminating in a 23% yield high-dilution step and proceeding in 8% overall yield, is reported. The ligand is metalated using cobalt(II) acetate, and a solid-state structure is presented, revealing an intermetallic void over 6.4 Å in length. The reactivity of this new type of cryptate is also probed; treatment of the dicobalt cryptate with potassium cyanide at elevated temperature results in a bridging cyanide complex.

Originally conceived as a three-dimensional extension of the contemporary crown ethers,^{1,2} cryptands have been used in a wide variety of synthetic capacities, although they are more classically known for their alkali cation sequestration abilities.³ Their ability to bind a transition metal is associated with the proclivity of tris(2-aminoethyl)amine (TREN) to envelop metals within its trigonal-pyramidal cleft.⁴ The discovery that the treatment of 3 equiv of an aryl dialdehyde with 2 equiv of TREN to furnish hexaiminocryptands in good yield,⁵ without the need for high-dilution conditions,^{6,7} facilitated the extension to a bimetallic motif: hexaiminocryptands, as well as their reduced octaaza counterparts, are competent binucleating ligands for transition metals⁸ and for the formation of cascade complexes, wherein a small molecule or anion bridges the metal centers.⁹ To date, these ligands have been predominantly utilized as neutral donors.

Notably, whereas cryptands bearing carboxamide functionalities have been used to bind anions,¹⁰ they have not yet been employed as anionic ligands in transition-metal chemistry, despite the well-documented chemistry as trianions of their monometallic TREN-based parentage.⁴ With the foregoing precedent in mind, we sought to develop the coordination chemistry of hexacarboxamido cryptands, with an emphasis on employing them in hexadeprotonated form as binucleating ligands. Herein we report the first such complex, obtained as a cofacial dicobalt(II) species lacking any axial bridging ligand, together with information on cyanide insertion into this system's central cavity.

The target ligand was furnished by following the protocol delineated in Scheme 1. Iodination of dimethyl isophthalate was achieved using iodine and sodium periodate in neat sulfuric acid,¹¹ an economical alternative to the more commonly employed *N*-iodosuccinimide used in the iodination of deactivated arenes.¹² Installation of the dipropoxyphenoxy substituent was achieved through the use of a copper(I) triflate-catalyzed coupling.¹³ Attachment of the polyether moiety to the ligand significantly enhances its solubility. Saponification of the ester residues and subsequent activation with *N*-hydroxysuccinimide and *N*-[3-(dimethylamino)propyl]-*N'*-ethylcarbodiimide hydrochloride (EDAC) yielded disuccinimido ester **1**. Treatment of **1** with 0.67 equiv of TREN under high-dilution conditions resulted in the ligand H₆L (**2**) in 8% overall yield. The final step in this synthesis proceeds in 23% yield, engendering a useful methodology on the laboratory scale; multigram quantities of the ligand can be isolated routinely.

Double cobalt(II) insertion into and hexadeprotonation of the cryptand ligand were accomplished as shown in Scheme 2, reaction a. Treatment of a slurry of **2** and 2 equiv of cobalt(II) acetate with 6.1 equiv of potassium hexamethyldisilazide in *N,N*-dimethylformamide (DMF) resulted in the formation of K₂(DMF)₆Co₂L (**3**) in 60% yield with concomitant precipitation of potassium acetate. The desired product precipitates directly from the crude DMF reaction solution upon the

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(1) Dietrich, B.; Lehn, J.-M.; Sauvage, J. P. *Tetrahedron Lett.* **1969**, *10*, 2885–2888.

(2) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017–7036.

(3) Dietrich, B.; Lehn, J.-M.; Sauvage, J. P. *Tetrahedron Lett.* **1969**, *10*, 2889–2892.

(4) (a) Cummins, C. C.; Lee, J.; Schrock, R. R.; Davis, W. D. *Angew. Chem., Int. Ed.* **1992**, *31*, 1501–1503. (b) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9–16.

(5) MacDowell, D.; Nelson, J. *Tetrahedron Lett.* **1988**, *29*, 385–386.

(6) Dietrich, B. Cryptands. In *Comprehensive Supramolecular Chemistry*; Gokel, G. W., Ed.; Elsevier Science: New York, 1996; Vol. 1, pp 153–211.

(7) Krakowiak, K. E.; Bradshaw, J. S. *Isr. J. Chem.* **1992**, *32*, 3–13.

(8) Drew, M. G. B.; MacDowell, D.; Nelson, J. *Polyhedron* **1988**, *7*, 2229–2232.

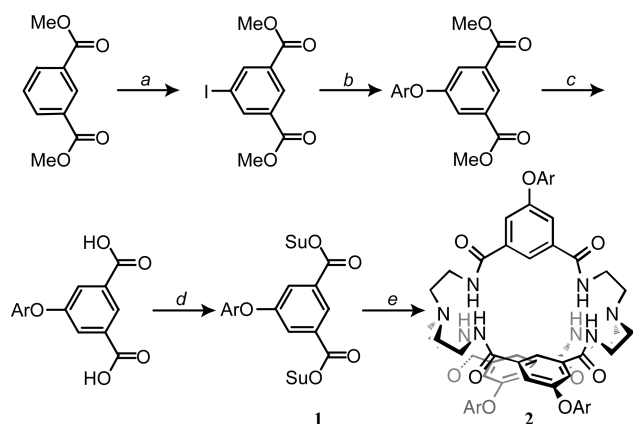
(9) Lehn, J.-M. *Pure Appl. Chem.* **1977**, *6*, 857–870.

(10) Bowman-James, K. *Acc. Chem. Res.* **2005**, *38*, 671–678.

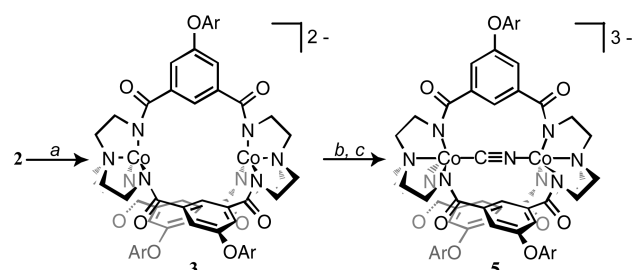
(11) Kraszkiewicz, L.; Sosnowski, M.; Skulski, L. *Synthesis* **2006**, 1195–1199.

(12) Prakash, G. K. S.; Mathew, T.; Hoole, D.; Esteves, P. M.; Wang, Q.; Rasul, G.; Olah, G. A. *J. Am. Chem. Soc.* **2004**, *126*, 15570–15776.

(13) Marcoux, J.-F.; Doye, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 10539–10540.

Scheme 1. Synthesis of Ligand 2^a

^a (a) NaIO_4 , I_2 , H_2SO_4 , 30 °C, 61%. (b) 3,5-Dipropoxyphenol, $(\text{CuOTf})_2 \cdot \text{C}_6\text{H}_6$, CsCO_3 , molecular sieves, THF, 100 °C, 61%. (c) Aqueous NaOH , MeOH, 20 °C, 99%. (d) NHS, EDAC, CH_2Cl_2 , 92% (Su = succinimido). (e) 0.67 equiv of TREN, CH_2Cl_2 , 23%.

Scheme 2. Synthesis of μ -Cyanide Complex 5 from Ligand 2^a

^a (a) 2 equiv of $\text{Co}(\text{OAc})_2$, 6.1 equiv of $\text{KN}(\text{SiMe}_3)_2$, DMF, 2 h, -61 °C to rt, -4 KOAc. (b) 2 equiv of 18-crown-6, THF, rt, 1 h. (c) 18-crown-6, KCN, DMF, 75 °C, 48 h.

addition of ether. ^1H NMR resonances in the spectrum of **3** are paramagnetically broadened and shifted, as expected for a complex incorporating a pair of weakly coupled d^7 metal ions (a solution-phase magnetic susceptibility measurement¹⁴ yielded $\mu_{\text{eff}} = 6.52 \mu_{\text{B}}$). Shifts corresponding to phenylene and propyl protons from the propoxyphenoxy moiety are observed between δ 2.5 and 11.2. Six resonances corresponding to the phenylene spacer aryl and TREN methylene protons are observed between δ -60 and +70. Four resonances are observed for the TREN methylene residues, suggesting that these protons are diastereotopic for the compound in solution, an indication of rigidity of the C_{3h} -symmetric molecular framework on the NMR time scale. NMR studies also reveal the stability of **3** to water: overnight agitation in the presence of 14 equiv of water in a deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$) solution indicated no decomposition; heating of this mixture at 75 °C for 2 days resulted in no change in the NMR spectrum.

Crystals suitable for X-ray diffraction studies were obtained by vapor diffusion of ether into a DMF solution of **3**. Structural analysis of **3** reveals that two crystallographically independent but chemically equivalent units compose the asymmetric unit. The core of one of these units can be seen in Figure 1, with the solubilizing polyether groups omitted for clarity. This view clearly shows the metal centers residing in

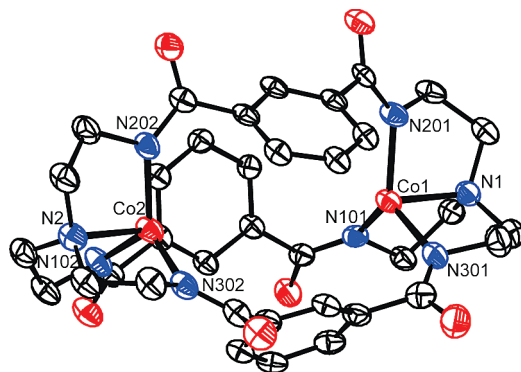


Figure 1. PLATON rendering of **3** with thermal ellipsoids drawn at 50% probability. Solvent molecules of crystallization, K^+ counterions, dipropoxyphenoxy groups, and H atoms are omitted for clarity.

anionic TREN pockets [sum of $N_{\text{eq}}-\text{Co}-N_{\text{eq}}$ (avg) = 358.2°] with trigonal-monopyramidal geometry. No residual electron density was observed in the void between the Co centers, ruling out the presence of a second axial ligand. The distance between the metal centers is 6.4078 Å (avg).

The structure of **3** reveals that K^+ ions bridge the dicobalt cryptate units, resulting in an extended three-dimensional structure. This is in analogy to protonated cryptands, which may form an extended three-dimensional structure by hydrogen bonding to interstitial anions.¹⁵ Perhaps because of this extended structure, **3** is soluble only in highly polar solvents such as DMF and DMSO. Treatment of a slurry of **3** in tetrahydrofuran (THF) with 2 equiv of 18-crown-6, however, results in a homogeneous solution. The K^+ ions in $[\text{K}(\text{18-crown-6})]_2\text{Co}_2\text{L}$ (**4**) are sequestered, thus interrupting the extended structure. Accordingly, compound **4** is soluble in less polar solvents such as THF, methylene chloride, chloroform, and acetonitrile.

While a VOID analysis performed by PLATON¹⁶ suggests that there is not enough space in the intermetallic cleft to accommodate ligands even as small as a water molecule, treatment of **4** with an excess of potassium cyanide and 18-crown-6 in DMF at 75 °C for 2 days elicits a color change from turquoise to vibrant pink, indicative of cyanide binding,¹⁷ as well as the appearance of a weak band at 2129 cm^{-1} in the IR spectrum (see the Supporting Information for UV/vis and IR spectra). The weakness of stretches arising from cyanide ligands bridging metal centers in trigonal-bipyramidal geometries is preceded.¹⁸ ^1H NMR spectra of the new species indicate a smooth conversion to a paramagnetic entity ($\mu_{\text{eff}} = 6.21 \mu_{\text{B}}$)¹⁴ that no longer possesses reflective symmetry through a mirror plane perpendicular to the metal-metal vector, as observed for complexes **3** and **4**. Crystals of cyanide adduct $[\text{K}(\text{18-crown-6})]_3\text{Co}(\mu\text{-CN})\text{CoL}$ (**5**) were grown from a THF solution layered with pentane; the ensuing structure is depicted in Figure 2. It is an affirmative illustration of cryptand internal cavity accessibility that the cyanide anion undergoes a reaction to penetrate the barrier defined by the xylene spacer arms of **4** and to take up residence there as an axial bridging ligand; that water does not bind may speak to

(15) Chin, A.; Edgar, M.; Harding, C. J.; McKee, V.; Nelson, J. *Dalton Trans.* **2009**, 6315–6326.

(16) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

(17) Jones, M. B.; MacBeth, C. E. *Inorg. Chem.* **2007**, *46*, 8117–8119.

(18) (a) Duggan, D. M.; Jungst, R. G.; Mann, K. R.; Stucky, G. D.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1974**, *96*, 3443–3450. (b) Scott, M. J.; Lee, S. C.; Holm, R. H. *Inorg. Chem.* **1994**, *33*, 4651–4662.

(14) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005. (b) Sur, S. K. *J. Magn. Reson.* **1989**, 169–173.

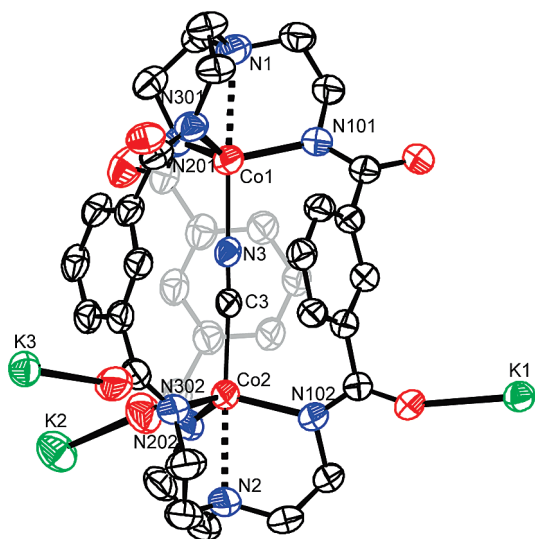


Figure 2. PLATON rendering of **5** with thermal ellipsoids drawn at 50% probability. Crown ethers, solvents of crystallization, dipropoxyphenoxy groups, and H atoms are omitted for clarity. One phenylene spacer has been grayed for ease of viewing.

the ability of the spacers to protect against the coordination of weaker ligands. Cyanide insertion between the Co centers has a profound effect on the geometry of the supporting bimetallic scaffold. The Co metal centers are pulled from their respective TREN binding pockets [**3**, Co1—Co2 = 6.4078 Å (avg); **5**, Co1—Co2 = 5.3263(9) Å] to a sufficient extent that the primary coordination sphere of the metal is best described as tetrahedral [$\sum_{\text{Co1}(\text{eq})} = 340.76(23)^\circ$; $\sum_{\text{Co2}(\text{eq})} = 343.07(24)^\circ$]. The distance between the Co centers and their respective apical N atoms increases from an average of 2.142(5) Å in **3** to 2.494(3) Å (Co1—N1) and 2.425(3) Å (Co2—N2) in **5**. Cyanide coordination also affects the electrochemical properties of the cobalt complex (Figure 3). While **3** exhibits an irreversible oxidation wave at 1090 mV, cyanide complex **5** exhibits a cathodic wave at -1200 mV and an anodic wave at -225 mV (voltages quoted vs Fc/Fc⁺); these features are independent of one another.

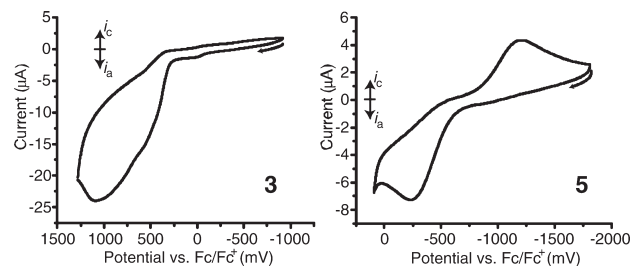


Figure 3. Cyclic voltammograms of **3** (left) and **5** (right). Voltammograms are referenced to ferrocene/ferrocenium.

Modeling the cyanide ligand as positionally disordered in an end-over-end fashion yielded the best crystallographic model. The free variable associated with this aspect of the model refined to a value of 0.63(3), indicating that, in 63% of the crystalline sample, C3 is bound to Co2. The observed albeit moderate preference for C3 binding to Co2 is coincident with the coordination of all three K⁺ counterions to this pole of the cryptand complex.

The present work provides an efficient, reproducible hexa-carboxamide cryptand ligand synthesis that is potentially variable at the xylylene spacer substituent, here chosen as 3,5-dipropoxyphenoxy for solubility purposes. In addition, a convenient protocol has been established for the concomitant hexadeprotonation of and double divalent metal-ion insertion into the new ligand framework. Structural data have been obtained both for the empty dicobalt(II) derivative and for its cyanide inclusion complex, setting the stage for an exploration of the small-molecule chemistry of such systems employing metal ions transiting the 3d series.

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Supporting Information Available: Experimental procedures and characterization data for all new compounds, as well as crystallographic details for compounds **3** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.