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Versatile Host for Metallo Anions and Cations

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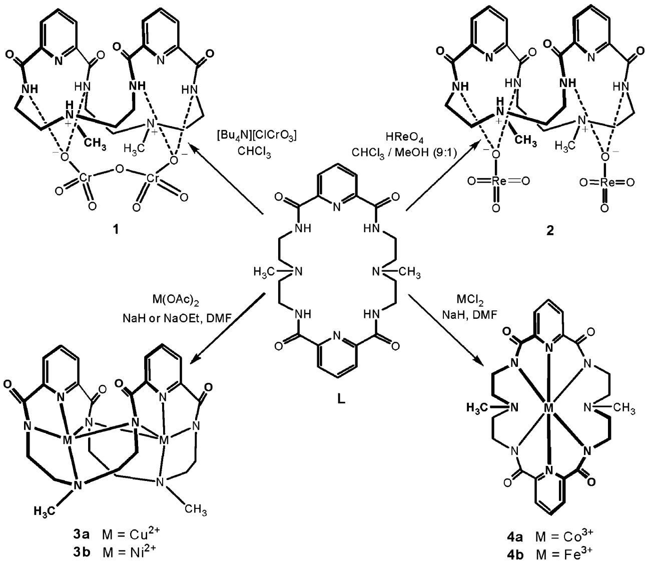
The crystal structures of two metallo oxides, perrhenate and dichromate, are reported with a diprotonated tetraamido/diamino-based macrocycle, **L**, in which the floppy ligand assumes a folded conformation. When the four amides are deprotonated, this same ligand binds transition-metal ions in its tetraanionic form, H_{-4}**L**. For the divalent metal ions Cu^{2+} and Ni^{2+}, H_{-4}**L** again folds and dinuclear complexes are formed. With trivalent metal ions Co^{3+} and Fe^{3+}, the ligand wraps about the metal ions, resulting in mononuclear complexes.

The number of striking structural similarities between hydrogen-bond coordination of anions to host ligands and coordinate covalent bonds from ligands to transition-metal ions is increasing with the expanding stockpile of crystallographic data on anion complexes.[1−4] Even ligands that have traditionally been used for transition-metal binding such as aza macrocycles and cryptands display a binding duality, binding transition metals when neutral and anions when protonated. Recently, we have chosen to study a mixed tetraamido/diamino macrocycle **L** (Scheme 1),[5] with a framework that mimics early aza macrocycle anion/transition-metal ion hosts.[3] A number of researchers in anion host/guest chemistry have focused on amides because of their prevalence in biological systems.[1,6,7] After studying a variety of anion complexes with these new ligands, we decided to explore whether a similar anion/transition-metal ion binding duality was possible for these hosts. Herein are reported the crystal structures of two oxometalate anion complexes of H_2**L**$^{2+}$ as well as transition-metal ion complexes of H_{-4}**L**, illustrating once again the duality of these ligands.

Scheme 1



In its diprotonated form, H_2**L**$^{2+}$ folds to bind a single $Cr_2O_7^{2-}$ (Scheme 1, **1**) or two ReO_4^- ions (Scheme 1, **2**).

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Upon deprotonation, $H_{-4}\mathbf{L}^{4-}$ forms either dinuclear (Scheme 1, **3**) or mononuclear complexes (Scheme 1, **4**). Interestingly, the ligand conformations for the ditopic M^{2+} complexes are distinctly similar to that observed for the $Cr_2O_7^{2-}$ and ReO_4^- complexes.

The ligand **L** was prepared as previously reported.[5] The orange $Cr_2O_7^{2-}$ complex, **1**, was obtained by reacting **L** with $[Bu_4N][ClCrO_3]$ (1:5 equiv) in $CHCl_3$, while the ReO_4^- complex was prepared by reacting **L** with $HReO_4$ (6 equiv) in $CHCl_3$/MeOH (9:1). Crystals of **1** were obtained from slow evaporation from a H_2O/CH_3CN solution, and **2** was crystallized from water. In both cases, **L** crystallized in the diprotonated form $H_2\mathbf{L}^{2+}$.

The transition-metal complexes were prepared from the reaction of **L** with the acetate or chloride salts of Ni^{2+}, Cu^{2+}, Co^{2+}, or Fe^{2+} (L:M = 1:2 or 1:1) in the presence of either NaH in dry *N*,*N*-dimethylformamide (DMF) or NaOEt in CH_2Cl_2/MeOH. Crystals of the Cu^{2+} and Ni^{2+} complexes (**3a** and **3b**, respectively) were obtained from slow evaporation of a CH_2Cl_2/MeOH solution. For the Ni^{2+} and Cu^{2+} complexes, it is possible to prepare the complexes without a base depending on conditions. Although Co^{2+} and Fe^{2+} were reacted with **L** under Ar, the products that were isolated were the oxidized Fe^{3+} and Co^{3+} complexes (**4a** and **4b**, respectively). Crystals of **4a** and **4b** were obtained from vapor diffusion of diethyl ether in DMF. Detailed syntheses are provided in the Supporting Information.

Our initial goal was to study the binding of metallo oxo anions, such as chromate, with **L**. Because of solubility issues with CrO_4^{2-}, however, $[Bu_4N][ClCrO_3]$ was used for binding studies. NMR titrations to determine binding between **L** and $[Bu_4N][ClCrO_3]$ in dimethyl sulfoxide showed slow exchange and were thus inconclusive. $ClCrO_3^-$ readily undergoes hydrolysis in the presence of water to give $CrO_3(OH)^-$, which is in equilibrium with the orange-red $Cr_2O_7^{2-}$ at pH 2−6.[8] Thus, isolation of the $Cr_2O_7^{2-}$ complex is a reasonable expectation.

In the $Cr_2O_7^{2-}$ complex, **1**, **L** crystallized in the diprotonated form $H_2\mathbf{L}^{2+}\cdot Cr_2O_7^{2+}\cdot 2H_2O$. $H_2\mathbf{L}^{2+}$ is folded with the two pyridine planes almost coplanar and separated by about 3.5 Å (Figure 1A,B). As drawn in the figure, $Cr_2O_7^{2-}$ lies below the macrocycle. The two $Cr_2O_7^{2-}$ O atoms closest to the macrocycle lie at distances ranging from 2.833 to 2.989 Å from macrocyclic amides, and each is hydrogen-bonded to two of the amide H atoms, not to the protonated amine. Rather, the protonated amine H atoms are "flipped up" by internal hydrogen bonds with two of the macrocyclic carbonyl O atoms, allowing for a clean approach of the oxo anion at the underside of the macrocycle. The two $Cr_2O_7^{2-}$ O atoms are separated by 3.764 Å, coinciding with the N4···N28 and N13···N19 separations of 3.761 and 3.666 Å, respectively. Two of the remaining $Cr_2O_7^{2-}$ O atoms are hydrogen-bonded to neighboring water molecules. Bond distances and angles within the $Cr_2O_7^{2-}$ ion agree well with those of other crystal structure reports.[6]

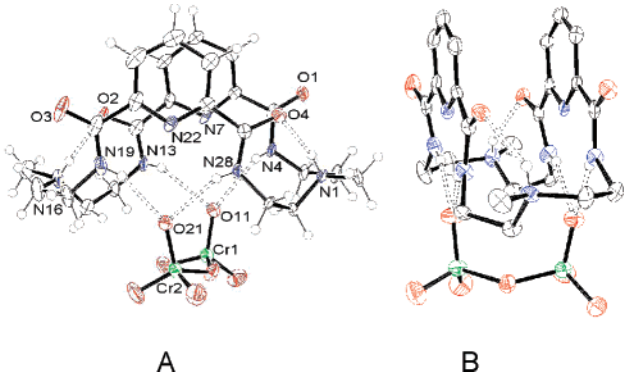

Figure 1. ORTEP views of the crystal structure of the $H_2\mathbf{L}^{2+}\cdot Cr_2O_7^{2-}$ complex: (A) perpendicular to the pyridine rings; (B) almost parallel with the pyridine rings. Solvent molecules are omitted for clarity, and thermal ellipsoids are shown at 50% probability. H atoms are omitted in B for clarity, except for the amide H atoms.

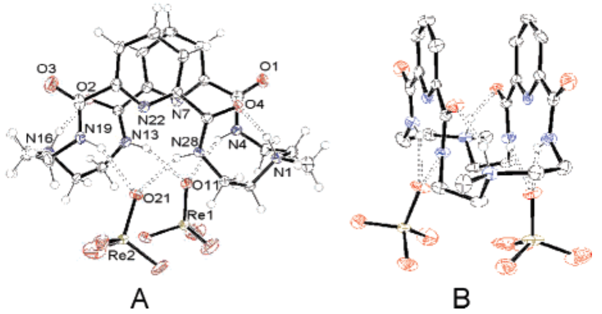

Figure 2. ORTEP drawings for the hydrated $H_2\mathbf{L}^{2+}\cdot 2[ReO_4^-]$ complex: (A) perpendicular to the pyridine rings; (B) almost parallel with the pyridine rings. Solvent molecules are omitted for clarity, and thermal ellipsoids are shown at 50% probability. H atoms are omitted in B for clarity, except for the amide H atoms.

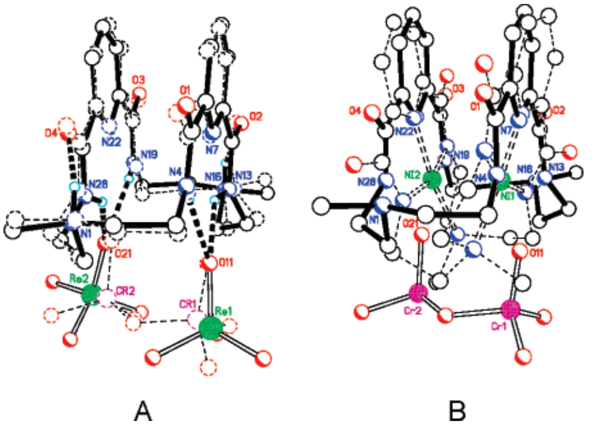

Figure 3. (A) Superposition of the ReO_4^- and $Cr_2O_7^{2-}$ structures. (B) Superposition of the Ni^{2+} and $Cr_2O_7^{2-}$ structures.

The asymmetric unit for crystals of the ReO_4^- complex, **2**, contains two crystallographically independent, yet nearly isodimensional, $H_2\mathbf{L}^{2+}\cdot 2ReO_4^-\cdot 3H_2O$ formula units (Figure 2). Each of these structural units also bears a striking resemblance to the asymmetric unit of the $Cr_2O_7^{2-}$ complex. In fact, the 36 macrocycle non-H atoms and the hydrogen-bonded O atoms of the anions superimpose to within 0.41 Å (Figure 3A). The two Re···Re separations are 4.854 Å (Re1···Re2) and 4.802 Å (Re3···Re4), and the two O···O separations for the hydrogen-bonded ReO_4^- O atoms are 4.149 Å (O11···O21) and 4.111 Å (O31···O41). Once again,

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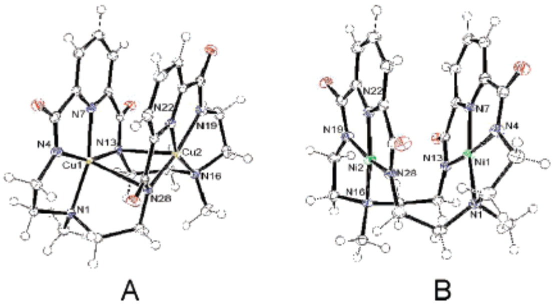

Figure 4. ORTEP views of the crystal structures of $[(Cu^{2+})_2(H_{-4}\mathbf{L})]\cdot 2H_2O$ (left) and $[(Ni^{2+})_2(H_{-4}\mathbf{L})]\cdot 2H_2O$ (right). Solvent molecules are omitted for clarity, and thermal ellipsoids are shown at 50% probability.

the formation of a folded macrocycle in **2** is enhanced by intramolecular hydrogen bonds between the amine H atoms and contiguous carbonyl O atoms.

Both of the Cu^{2+} and Ni^{2+} complexes, **3a** and **3b**, crystallize as neutral isomorphous solvates, with **L** in its tetraanionic form, $H_{-4}\mathbf{L}$ (Figure 4). The two complexes are essentially isomorphous and isostructural. In both structures, **L** folds around the two metal ions, resulting in a "face-to-face" orientation of their coordination polyhedra. Each of the metal ions coordinates to a pyridine, an amine, and two amide N atoms on one side of the macrocycle in a nearly square-planar arrangement. Both of the d^9 Cu^{2+} ions complete a square-pyramidal coordination by forming a long 2.648(1) Å bond to an amide N atom (Cu1−N28 and Cu2−N13) on the opposite face of the ligand. Even though the nickel complex, **3b**, is isomorphous with the copper complex, **3a**, these "apical" Ni···N separations are 0.209 Å longer because the d^8 Ni^{2+} ions prefer to remain four-coordinate and square-planar. Likewise, the Cu···Cu separation is shorter (3.303 Å) than the Ni···Ni distance (3.516 Å). The macrocyclic conformation in the nickel structure is almost like that observed for the $Cr_2O_7^{2-}$ complex, e.g., $N_{py}\cdots N_{py} = 3.518$ and 3.528 Å in the nickel and $Cr_2O_7^{2-}$ complexes, respectively. Presumably, $\pi-\pi$ stacking interactions are a contributing factor for macrocycle folding in all four of these complexes. For comparison, the $Cr_2O_7^{2-}$ Cr···Cr separation is slightly less than either of the two metal distances at 3.222 Å.

The Co^{3+} and Fe^{3+} structures, **4a** and **4b**, are also isostructural, and the two crystalline complexes are isomorphous as the hydrated Et_4N^+ salts (Figure 5). However, unlike the Ni^{2+} and Cu^{2+} cases, **4a** and **4b** are mononuclear, with the tetranionic $H_{-4}\mathbf{L}^{4-}$ wrapping around a single metal ion. The four amide and two pyridine N atoms are used for binding, resulting in an octahedral coordination polyhedron with a slight (∼0.1 Å) tetragonal compression. Once again, the two tertiary amines are not coordinated. This coordination mode allows the diamido pyridine rings and associated amides to form a tridentate chelate. This pincerlike binding is also seen for planar tridentate ligands such as terpyridine, as observed earlier by one of us for the Co^{3+} complex with terpyridine.[9]

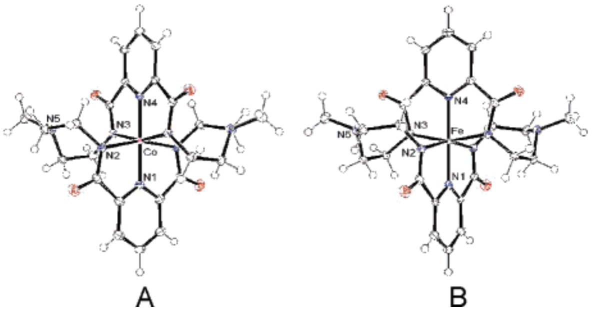

Figure 5. ORTEP views of the crystal structures of $[Co^{3+}(\mathbf{L})]^-$ (left) and $[Fe^{3+}(\mathbf{L})]^-$ (right). The countercations and solvent molecules are omitted for clarity, and thermal ellipsoids are shown at 50% probability.

The "equatorial" $M-N_{am}$ bonds in both complexes are elongated slightly compared to the "axial" $M-N_{py}$ bonds, averaging 1.959(1) and 1.858(2) Å for the Co^{3+} complex (**4a**) and 1.966(2) and 1.879(3) Å for the Fe^{3+} complex (**4b**), respectively. Because **4a** and **4b** are isomorphous, their M−N distances should rigorously reflect differences in their ionic radii. The observed differences in the respective Co−N and Fe−N distances are slightly larger than the negligible difference expected for low-spin Co^{3+} and low-spin Fe^{3+} although smaller than the ∼0.10 Å difference expected for low-spin Co^{3+} and high-spin Fe^{3+}. However, both **4a** and **4b** exhibit racemic twinning, which may influence these bond distances (see the Supporting Information).

The observation of the two types of metal ion coordination can be rationalized on the basis of charge and possibly ligand-field effects. The more electropositive M^{3+} ions exert a larger attractive force on the ligand amide and pyridine N atoms, promoting the wrapping and hexadentate coordination. Also Co^{3+} and Fe^{3+} less frequently form square-planar complexes. Charge neutrality can be attained by ditopic binding of the less electropositive divalent metal ions, so the macrocycle folds. In the $Cr_2O_7^{2-}$ and ReO_4^- structures, **L** has added two protons to achieve charge neutrality. This charge neutrality, and the fit of the folded macrocycle to the single $Cr_2O_7^{2-}$ or double ReO_4^- ions, can be cited as a driving force to produce these species. These findings once again illustrate the similarities to be found in both anion and metal cation coordination, in addition to adding a significant new series of potential ligands for transition metals.

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Supporting Information Available: Detailed synthetic and crystallographic procedures and one crystallographic file for the five structures in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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