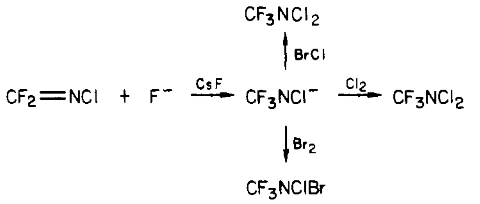
Caution! While we have experienced no explosions during the handling of small quantities of these materials, many structurally similar *N*-halo compounds are known to be powerful explosives. Due caution must be exercised while conducting experiments such as those described here. In a typical reaction, $CF_2{=}NCl$, Br_2, and CsF were allowed to react in a 100-mL glass reactor containing a Teflon-coated magnetic stirring bar at 22 °C in the absence of light. The mixture was stirred for an appropriate time, and the products were then separated by pumpng through a series of cold traps. Essentially pure CF_3NClBr and CF_3NBr_2 were then obtained by brief treatment with excess C_2H_4 at 22 °C to remove unreacted Br_2, followed by reseparation. The reactions are summarized in Table I.

The formation of CF_3NBrCl can be explained by oxidation of the intermediate anion CF_3NCl^- by Br_2, in the same way that CF_3NCl_2 is formed from Cl_2 and $CF_2{=}NCl$ (eq 1) and CF_3NBrF from Br_2 and $CF_2{=}NF$ (eq 2).[5] In the above examples, there is no reaction in the absence of CsF.



$$\begin{tikzcd} & \mathrm{CF_3NCl_2} & \\ \mathrm{CF_2{=}NCl} + \mathrm{F^-} \arrow[r, "\mathrm{CsF}"] & \mathrm{CF_3NCl^-} \arrow[u, "\mathrm{BrCl}"'] \arrow[r, "\mathrm{Cl_2}"] \arrow[d, "\mathrm{Br_2}"] & \mathrm{CF_3NCl_2} \\ & \mathrm{CF_3NClBr} & \end{tikzcd}$$

(1)

$$\mathrm{CF_2{=}NF} + \mathrm{F^-} \xrightarrow{\mathrm{CsF}} \mathrm{CF_3NF^-} \xrightarrow{\mathrm{Br_2}} \mathrm{CF_3NFBr} \qquad (2)$$

The formation of CF_3NBr_2 in the reaction of CF_3NCl^- with Br_2 requires a substitution of Cl by Br in CF_3NBrCl. We have found that this substitution can be readily accomplished in both CF_3NBrCl and CF_3NCl_2 by reaction with Br_2 in the presence of CsF.

$$\mathrm{CF_3NCl_2} \xrightarrow{\mathrm{CsF/Br_2}} \mathrm{CF_3NBrCl} \xrightarrow{\mathrm{CsF/Br_2}} \mathrm{CF_3NBr_2}$$

There is no reaction under the same conditions in the absence of CsF, and CsF alone is also unreactive. Similarly, BrCl does not form a significant amount of either CF_3NBrCl or CF_3NBr_2 in the presence of CsF, and it converts CF_3NBrCl back to CF_3NCl_2.[9] The active species in these reactions may be $CsF{\cdot}Br_2$, which may contain a significant concentration of the anion FBr_2^-.[10] Very active CsF readily absorbs bromine to form a bright yellow-orange solid with only a small equilibrium pressure of Br_2 at 22 °C.[11] The Br_2 is removed very slowly by pumping on the solid under dynamic vacuum at 22 °C, and even heating at 100 °C will not readily remove all the Br_2. Active KF also absorbs Br_2 but to a lesser degree.[11] Potassium fluoride with Br_2 is only effective in converting CF_3NCl_2 to CF_3NBrCl and not to CF_3NBr_2.

We expected that NaF and LiF would be ineffective in promoting the reaction of CF_3NCl_2 with Br_2. However, both result in reasonable yields of CF_3NClBr (see Table I). To ascertain whether the formation of CF_3NClBr was a surface reaction only and not due to the metal fluoride itself, we tried CaF_2 under the same conditions and it was unreactive. This result, combined with the fact that the formation of CF_3NBr_2 is only observed with CsF, would suggest that these reactions are fluoride promoted. However, additional studies with other fluorides and non-fluoride-containing solids will be required to establish this with certainty.

The novel compounds CF_3NBrCl and CF_3NBr_2 are pale yellow solids melting at –62.5 to –61.5 °C and –56.4 to –55.5 °C, respectively. They are thermally stable in the dark at 22 °C, but they readily decompose under the influence of Pyrex-filtered sunlight.

$$2\mathrm{CF_3NBrX} \xrightarrow{h\nu} \mathrm{CF_3N{=}NCF_3} + 2\mathrm{BrX} \quad (\mathrm{X} = \mathrm{Cl, Br})$$

The compounds are readily identified by their MH^+ and M^+ molecular ions with the expected isotope ratios in the CI and EI mass spectra, by their ^{19}F NMR (internal $CFCl_3$) $\delta(CF_3NBrCl) = -72.3$ (s) and $\delta(CF_3NBr_2) = -70.5$ (s), $\delta(CF_3NCl_2) = -78$, and by their characteristic IR spectra. The latter are very similar to those of CF_3NCl_2 except in the 850–650-cm^{-1} region where each show two characteristic strong absorptions (cm^{-1}): CF_3NCl_2, 812 and 708; CF_3NBrCl, 787 and 688; CF_3NBr_2, 758 and 675.

Acknowledgment. Financial support of this research by the National Science Foundation (Grant CHE-8217217) and the U.S. Army Research Office (Grant DAAG29-82-K-0188) is gratefully acknowledged.

Registry No. $CF_2{=}NCl$, 28245-33-2; CF_3NClBr, 88453-17-2; CF_3NCl_2, 13880-73-4; CsF, 13400-13-0; KF, 7789-23-3; NaF, 7681-49-4; LiF, 7789-24-4; CF_3NBr_2, 88453-18-3; $CF_3N{=}NCF_3$, 372-63-4.

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Copper(I)–Dioxygen Reactivity. 2. Reaction of a Three-Coordinate Copper(I) Complex with O_2, with Evidence for a Binuclear Oxo–Copper(II) Species: Structural Characterization of a Parallel-Planar Dihydroxo-Bridged Dimer

Sir:

Investigations of the nature of the reactions of dioxygen with complexes of Cu(I) are relevant both in the bioinorganic chemistry of copper[1] and in oxidation and oxygenation catalysis by copper.[2] In enzymatic systems, hemocyanins are arthropodal and molluscan oxygen carriers containing copper ion active sites, where Cu(I) reacts reversibly with dioxygen.[1] The copper monooxygenases tyrosinase and dopamine β-hydroxylase mediate hydroxylation reactions of organic substrates utilizing O_2 as the oxygen source,[3] whereas the multicopper "blue" oxidases reduce dioxygen to water at copper centers. In synthetic systems, copper(II) complexes are known to carry out efficient oxidation reactions, facilitated by the rapid reoxidation of Cu(I) to Cu(II) in the catalytic cycle.[2a,4]

As part of our studies of new copper(I) coordination chemistry and dioxygen reactivity, we recently observed that

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(9) BrCl is a very powerful chlorination reagent (more reactive than Cl_2) in the CsF-catalyzed reactions of R_fCN and $R_fCF{=}NR_f$: Zheng, Y.; DesMarteau, D. D., to be submitted for publication.

(10) This polyhalogen anion does not appear to be known, and this may indicate that Br_2F^- is not the active species in the reactions with $-NClBr$ and $-NCl_2$. However, Br_2Cl^- is well characterized: Ault, B. S.; Andrews, L. *J. Chem. Phys.* **1976**, *64*, 4853.

(11) Cesium fluoride (99.9%) was activated by fusing it in a Pt dish, followed by grinding in a ball mill to a very fine powder under very anhydrous conditions. Potassium fluoride was similarly activated.

(1) (a) Solomon, E. I. *Met. Ions. Biol.* **1981**, *3*, 41–108. (b) Karlin, K. D., Zubieta, J., Eds. "Copper Coordination Chemistry: Biochemical & Inorganic Perspectives"; Adenine Press: Guilderland, NY, 1983. (c) Zuberbuhler, A. D. In ref 1b, pp 237–258.

(2) (a) Gampp, H.; Zuberbuhler, A. D. *Met. Ions Biol. Syst.* **1981**, *12*, 133–190. (b) Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981.

(3) Lerch, K. *Met. Ions Biol. Syst.* **1981**, *13*, 143–186.

(4) Dedert, P. L.; Sorrell, T.; Marks, T. J.; Ibers, J. A. *Inorg. Chem.* **1982**, *21*, 3506–3517 and references therein.

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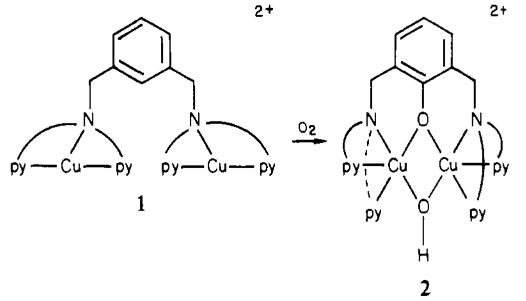
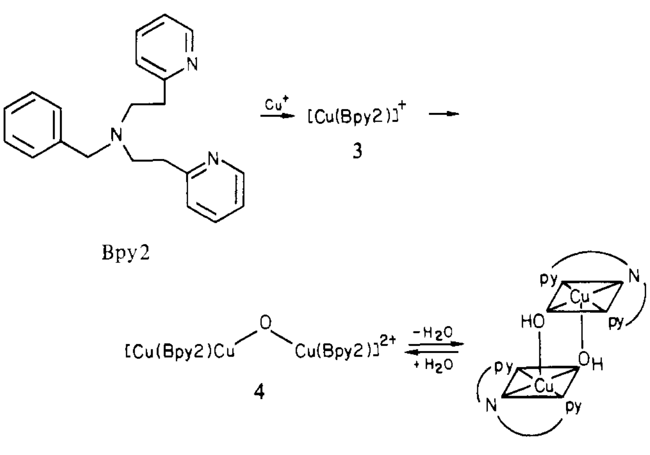
a three-coordinate binuclear Cu(I) complex (**1**) reacts with O_2 with hydroxylation of the xylyl binucleating ligand resulting in the formation of a phenoxo-bridged binuclear Cu(II) compound, **2** (eq 1). Dioxygen incorporation has been demonstrated, making this reaction a mimic to the action of the copper monooxygenases in the coordination chemistry of the binuclear complexes and in the stoichiometry of the transformations.[5]



(1)

In order to help identify the nature of intermediates and course of activation of O_2 in this reaction, studies on a number of synthetic modifications and variations are being pursued.[6] Here, we report the results of the reaction with O_2 of the Cu(I) complex $Cu(Bpy2)^+$ (**3**). This compound possesses the same tridentate chelating group as is found in **1** and is thus expected to be a three-coordinate Cu(I) species. It also contains the aromatic substrate (xylyl group that is found in **1**), which is in the same proximity to the copper ion. However, only a single copper ion per xylyl group is present in **3**. Unlike the reaction of **1** with O_2, we find that hydroxylation of the phenyl group does not occur; instead, a compound formulated as a binuclear oxo-bridged Cu(II) complex, **4**, forms. This reacts further with water to give the dihydroxo-bridged binuclear Cu(II) complex **5**, which we have characterized crystallographically.



Compound **3** was synthesized by reaction of $Cu(CH_3CN)_4PF_6$[7] with the ligand Bpy2 in THF under argon and recrystallized from CH_2Cl_2–Et_2O. Elemental analysis, ^1H NMR, and IR confirm the formula as $Cu(Bpy2)PF_6$.[8] A solution of **3** in CH_2Cl_2 reacts rapidly with O_2 in the mole ratio $Cu:O_2 = 4:1$ to give the green complex **4**, which is isolated by precipitation with Et_2O.[9] In the presence of small amounts of water, **4** is transformed into the blue crystalline complex **5**, $[Cu(Bpy2)(OH)]_2(PF_6)_2 \cdot 2H_2O$.[10]

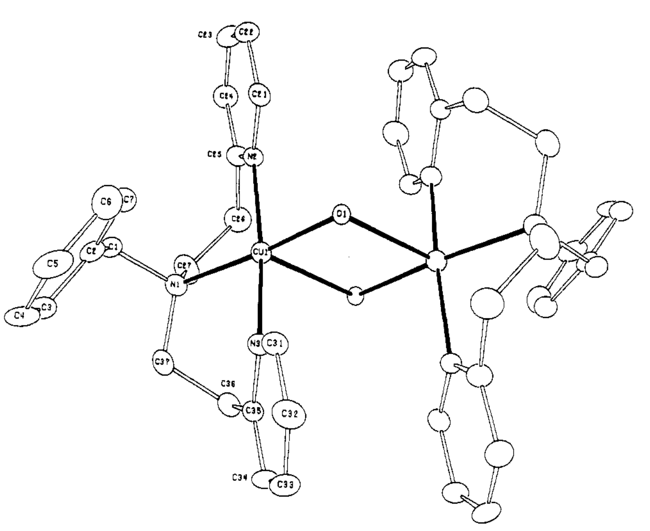


Figure 1. ORTEP diagram of the $[Cu(Bpy2)(OH)]_2^{2+}$ cation, showing the atom-labeling scheme. Relevant bond lengths (Å) and angles (deg) are as follows: Cu···Cu, 3.271; Cu–O1, 1.931 (3); Cu–O1a, 2.298 (4); Cu–N1, 2.063 (5); Cu–N2, 2.021 (7); Cu–N3, 2.000 (7); N1–Cu–N2, 89.6 (2); N1–Cu–N3, 92.3 (2); N2–Cu–N3, 168.0 (2); N1–Cu–O1, 174.4 (2); N1–Cu–O1a, 106.5 (2); N2–Cu–O1, 88.7 (2); N2–Cu–O1a, 100.9 (2); N3–Cu–O1, 88.3 (2); N3–Cu–O1a, 89.9 (2); O1–Cu–O1a, 79.0 (2); Cu–O1–Cu, 101.0 (2).

Crystal data: Complex **5** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.426$ (4) Å, $b = 11.415$ (2) Å, $c = 11.586$ (3) Å, $\alpha = 74.78$ (2)°, $\beta = 88.72$ (2)°, $\gamma = 74.14$ (2)°, $V = 1155.5$ (6) Å^3, and $Z = 1$. A total of 2270 reflections were refined to the current residual values of $R = 0.0588$ and $R_w = 0.0627$ (Mo Kα, $\lambda = 0.71069$ Å).

Complex **5** (Figure 1) is a centrosymmetric dimer possessing a parallel-planar structure. This consists of square-based pyramidal Cu(II) coordination spheres, which are joined by axial- and basal-edged (equatorial) hydroxy groups. This mode of bridging is known for a dimeric Cu(II) complex with two bridging phenoxo ligands,[11] but this is the first example of a dihydroxo-bridged binuclear Cu(II) complex containing other than basal-edged (equatorial–equatorial) bridging groups.[12] Basal coordination to Cu(II) in **5** occurs from the two pyridyl nitrogens (N2 and N3) and the tertiary amino nitrogen atom (N1) of Bpy2 along with the equatorial hydroxy group ($Cu-O_{eq} = 1.931$ (3) Å). The axial distance is $Cu-O_{ax} = 2.298$ (4) Å and Cu···Cu = 3.271 Å.

Support for the formulation of **4** as an oxo-bridged complex comes from several lines of evidence. (1) The stoichiometry of oxygen uptake is consistent with the four-electron reduction of O_2, as is found in other oxo-bridged Cu(II) complexes.[13,14]

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(5) (a) Karlin, K. D.; Dahlstrom, P. L.; Cozzette, S. N.; Scensny, P. M.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1981**, 881–882. (b) Karlin, K. D.; Gultneh, Y.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1982**, *104*, 5240–5242. (c) Karlin, K. D.; Hayes, J. C.; Gultneh, Y.; Cruse, R. W.; McKown, J. W.; Hutchinson, J. P.; Zubieta, J. *Ibid.*, in press.

(6) Karlin, K. D.; Shi, J.; Hayes, J. C.; McKown, J. W.; Hutchinson, J. P.; Zubieta, J. *Inorg. Chim. Acta* **1983**, *91*, L3–L7.

(7) Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90.

(8) Anal. Calcd for $CuC_{21}H_{23}N_{23}N_3PF_6$ (**3**): C, 47.95; H, 4.58; N, 7.99. Found: C, 47.93; H, 4.94; N, 8.29.

(9) Anal. Calcd for $Cu_2C_{42}H_{46}N_6O(PF_6)_2$ (**4**): C, 47.23; H, 4.31; N, 7.87. Found: C, 46.65; H, 4.48; N, 7.83. Visible spectrum (λ_{max} in CH_2Cl_2): 660 nm (ϵ = 760 M^{-1} cm^{-1}).

(10) Anal. Calcd for $[CuC_{21}H_{23}N_3(OH)]_2(PF_6)_2 \cdot 2H_2O$ (**5**): C, 44.96; H, 4.64; N, 7.49. Found: C, 44.82; H, 4.21; N, 7.38. Visible spectrum (λ_{max} in CH_2Cl_2): 685 nm (ϵ = 330 M^{-1} cm^{-1}). IR: Coordinated hydroxide, ν(OH) = 3620 cm^{-1}; lattice H_2O, ν(OH) = 3435 br cm^{-1}.

(11) Calderazzo, F.; Marchetti, F.; Dell'Amico, G.; Pelizzi, G.; Colligiani, A. *J. Chem. Soc., Dalton Trans.* **1980**, 1419–1424.

(12) (a) Drew, M. G. B.; Nelson, J.; Esho, F.; McKee, V.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1837–1843. (b) Axial–equatorial-bridged structures are well-known for Cu(II) dimers with halide bridging: Hatfield, W. E. *Inorg. Chem.* **1983**, *22*, 833–837 and references therein.

(13) (a) Davies, G.; El-Sayed, M. A. *Inorg. Chem.* **1983**, *22*, 1257–1266. (b) Davies, G.; El-Sayed, M. A. In ref 1b, pp 281–310.

(14) Lapinte, C.; Riviere, H.; Roselli, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1109–1110.

Reaction of 2 equiv of **3** with 1 equiv of iodosylbenzene also gives complex **4** (i.e. $2Cu^I + O \rightarrow Cu^{II}\text{–}O\text{–}Cu^{II}$ with PhOI as the source of oxygen). (2) Complexes **4** and **5** are related by a water molecule. When **5**, which exhibits a sharp ν(OH) IR band at 3620 cm^{-1}, is heated under vacuum, this band completely disappears, and the green complex **4** (as identified and compared to authentic **4** by elemental analysis, UV-vis, and IR) is generated.[15] (3) In a polar solvent like methanol, both **4** and **5** dissolve to give identical normal tetragonal EPR spectra ($g_{\parallel} = 2.32$, $A_{\parallel} = 169 \times 10^{-4}$ cm^{-1}, $g_{\perp} = 2.16$), suggesting that weak bridging interactions (e.g., in **5**) are broken to give monomers. In CH_2Cl_2, however, dimeric structures for **4** and **5** are retained as suggested by the similarity of features in the EPR spectra to those observed in related Cu(II) bridged dimers.[11,14,16] (4) Both complexes have room-temperature magnetic moments ($\mu_{eff} = 1.8$ and 1.9 μ_B for **4** and **5**, respectively) that compare favorably with those of compounds having a binuclear structure with bridging interactions.[11,17] (5) Reaction of **4** with triphenylphosphine in CH_2Cl_2 results in the stoichiometric production of triphenylphosphine oxide[18] and regeneration of Cu(I). Other oxo-bridged copper[14] and iron[19] reagents are known to also effect this reaction.

The observation that oxygenation of **3** does not result in hydroxylation of the aromatic group in Bpy2 is consistent with the notion that a second Cu(I) ion (and/or electron) is required for dioxygen activation and insertion into an organic substrate in the two-electron transformation **1** → **2**. Other possibilities exist, but the present results demonstrate the likelihood of reduction of dioxygen beyond the peroxy stage in the presence of "excess" copper(I) (e.g. complex **3**),[13] which may detract from a pathway where oxygenation of a substrate may occur. We are investigating further the nature of Cu(I)–O_2 interactions in this and related systems, as well as examining the potential usefulness of species such as **4** for oxygenation of organic substrates.

Acknowledgment. The authors gratefully acknowledge the National Institutes of Health (K.D.K., Grant GM 28962; J.Z., Grants GM 22566 and GM 27459) for support of this research.

Note Added in Proof. The structure of $[Cu(Bpy2)]PF_6$ has now been determined crystallographically, showing three-coordinate Cu(I), as expected.

Registry No. **3**, 88326-42-5; **4**, 88343-61-7; **5**, 88326-45-8; $Cu(CH_3CN)_4PF_6$, 64443-05-6.

Supplementary Material Available: Listings of atom coordinates and temperature factors (Table 1), bond lengths (Table 2), bond angles (Table 3), anisotropic temperature factors (Table 4), and hydrogen coordinates and temperature factors (Table 5) (8 pages). Ordering information is given on any current masthead page.

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[15] Monitoring water loss by IR spectroscopy indicates that the lattice H_2O ($\nu(OH) = 3435$ cm^{-1}) is lost first, followed by the H_2O from the dihydroxo bridge.

[16] **4** and **5** are characterized by weak $M_s = 2$ transitions in the $g = 4$ region, both as polycrystalline solids and in dichloromethane solutions, indicating dimeric structures in both cases.

[17] Barnes, J. A.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1972**, *11*, 144-148.

[18] (a) Addition of excess triphenylphosphine (4 mol/Cu dimer) to a green solution of **4** in dichloromethane (under Ar) gave a colorless solution in the first 5-10 min. Adding ether precipitated a colorless solid, which showed a strong IR absorption at 1165 cm^{-1} due to the ν(P═O) stretch of coordinated O═PPh_3.[18b] Extraction with toluene of the solid obtained by ether precipitation after the reaction was allowed to stir overnight gave free triphenylphosphine oxide, identified by IR ($\nu(P{=}O) = 1195$ cm^{-1}) and its ^1H NMR spectrum ($CDCl_3$, δ 7.20 mult). (b) Moyer, B. A.; Sipe, B. K.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 1475-1480 and references therein.

[19] (a) Ercolani, C.; Gardini, M.; Pennesi, G.; Rossi, G. *J. Chem. Soc., Chem. Commun.* **1983**, 549-550. (b) Ito, S.; Inoue, K.; Matsumoto, M. *J. Am. Chem. Soc.* **1982**, *104*, 6450-6452.

Observation of Distinct Cadmium-113 NMR Signals for Complexes of N-Donor Chelate Ligands in Solution at Ambient Temperature

Sir:

Cadmium(II) amine complexes are typically in fast exchange, confounding the assignment of ^{113}Cd NMR chemical shifts and the assessment of the expected range (in ppm) of the shifts of complexes with N-donor ligands.[1-3] An assignment of shifts would be valuable not only in the study of the chemistry of this toxic heavy-metal environmental contaminant but also in enhancing the utility of the ^{113}Cd nuclide as an NMR metallobioprobe.[4,5]

We now report that N-donor chelate ligands such as ethylenediamine (en) and 2,2′-bipyridine (bpy), which have been utilized in the past,[5,6] unfortunately form complexes having the most difficult to observe or interpret ^{113}Cd NMR signals. We find that the vast majority of N-donor chelate ligands give complexes with distinct, readily interpretable ^{113}Cd NMR signals in solution at ambient temperature. Furthermore, we have found some specific conditions under which the shifts can be calculated with an expression that incorporates both the number and type of ligating N donors. To our knowledge, such a well-defined correlation has not been observed previously for any metal nuclide.

Cadmium-113 NMR spectra of solutions of $CdSO_4$ and en (pH <6) appeared consistent with fast ligand exchange with a small downfield shift of the one observable ^{113}Cd signal.[6] Similarly, the complex $Cd^{II}(bpy)_2(NO_3)_2 \cdot xH_2O$ in DMF/CH_3OH gave one signal.[5] We find that solutions of $Cd(NO_3)_2$ in D_2O *at high pH* (12-13) give distinct NMR signals for chelated and unchelated Cd(II) complexes. For solutions 1.0 M in $Cd(NO_3)_2$ and 0.5 M in L, the shift values (in ppm, relative to 1 M $Cd(NO_3)_2$ in D_2O; see also Figure 1 caption and Table I footnote) for uncomplexed and complexed species, respectively, for representative ligands were as follows: *N,N,N′,N′*-tetramethylethylenediamine (*N,N,N′,N′*-$(CH_3)_4$en), 0, 76; *N,N*-dimethyldiethylenetriamine (*N,N*-$(CH_3)_2$dien), 2, 143; *N,N,N′,N″,N″*-$(CH_3)_5$dien, 3, 105. In D_2O, solutions of en gave no readily observable signals.

Ligand and complex solubility is often a problem in D_2O, and we find that the use of $Me_2SO\text{-}d_6$[7] allows a broader range of studies and in some cases (en) permits the study of complexes that have very broad or no resonances in D_2O.

For example, sequential addition of *N,N′*-dimethylethylenediamine (*N,N′*-$(CH_3)_2$en) to a $Cd(NO_3)_2$ solution in

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[1] Dechter, J. J. *Prog. Inorg. Chem.*, in press.

[2] Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1980**, *10*, 1.

[3] Haberkorn, R. A.; Que, L., Jr.; Gillum, W. O.; Holm, R. H.; Liu, C. S.; Lord, R. C. *Inorg. Chem.* **1976**, *15*, 2408.

[4] Coleman, J. E.; Chlebowski, J. F. *Adv. Inorg. Biochem.* **1979**, *1*, 1.

[5] Turner, R. W.; Rodesiler, P. F.; Amma, E. L. *Inorg. Chim. Acta* **1982**, *66*, L13. (See references therein for a recent list of biological studies.)

[6] Kostelnik, R. J.; Bothner-By, A. A. *J. Magn. Reson.* **1974**, *14*, 141.

[7] The Me_2SO ligand is ambidentate, but ^{113}Cd resonances are upfield in this solvent relative to D_2O solution (both extrapolated to infinite dilution). This is strong evidence for O binding by Me_2SO.

0020-1669/84/1323-0521$01.50/0