Reaction of 2 equiv of **3** with 1 equiv of iodosylbenzene also gives complex **4** (i.e. $2Cu^{I} + O \rightarrow Cu^{II}–O–Cu^{II}$ 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 (ν(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.

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[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 (ν(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.

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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-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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[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.

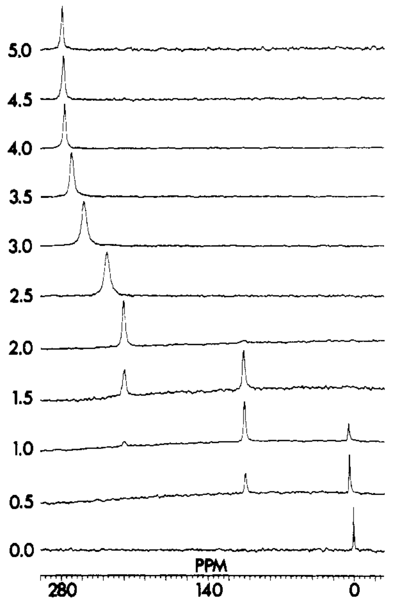

Figure 1. ^{113}Cd NMR spectra of 1.0 M $Cd(NO_3)_2$ in Me_2SO-d_6 with N,N'-$(CH_3)_2$en at L/Cd ratios indicated at the left of each trace. Relevant information follows: 44.39 MHz; IBM WP200SY; 10-mm tubes; 30° pulses; typically 1000 scans; no relaxation delay; 50-μs preacquisition delay; 30-kHz spectral window; quadrature-phase detection; 16K data points, ^2H solvent lock.

Table I. ^{113}Cd NMR Chemical Shifts for $Cd(NO_3)_2$ Complexes of N-Donor Chelating Ligands in Me_2SO-d_6[a]

ligand	obsd shifts, ppm mono	bis	tris
1,10-phenanthroline	61		
N,N,N',N'-$(CH_3)_4$en	66		
2,2',2''-terpyridine	88		
N,N,N',N'',N''-$(CH_3)_5$dien	92		
N,N'-$(CH_3)_2$en	103	219	278
N,N-$(CH_3)_2$en	106	226	
2-(aminomethyl)pyridine	114		
N-(CH_3)en	126	262	359
en	149	290	403
N,N-$(CH_3)_2$dien	155	308	
dipropylenetriamine	200		
dien	207	386	
3,2,3-tetramine[b]	256		
trien[c]	262		
N,N-$(CH_3)_2$dien + N,N-$(CH_3)_2$en	272		

[a] $[Cd(NO_3)_2]$ = 1.0 M. Externally referenced to 1.0 M $Cd(NO_3)_2$ in Me_2SO-d_6 (δ 0). For comparison, $\delta(Cd(ClO_4)_2)$(0.1 M, D_2O) = 50 and $\delta(Cd(NO_3)_2)$(1.0 M, D_2O) = 30 with use of 1.0 M $Cd(NO_3)_2$ in Me_2SO-d_6 in a capillary as a reference.
[b] $NH_2CH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2NH_2$.
[c] Triethylenetetramine.

Me_2SO-d_6 (Figure 1) leads to solutions with well-defined ^{113}Cd NMR spectra. At low N,N'-$(CH_3)_2$en/Cd ratios, the amine-free species, the mono species, and the bis species are in slow, almost stopped, exchange and give distinct resonances. Comparative studies with $Cd(ClO_4)_2$ indicate that under these conditions nitrate is also coordinated. The stability constants are such that the conversion to amine complex is almost quantitative. As the concentration of N,N'-$(CH_3)_2N$ is increased so that L/Cd exceeds 2, a less favored equilibrium species is observed that is probably a tris species. The shift of this species is independent of counterion (NO_3^-, ClO_4^-, $CH_3CO_2^-$, Br^-, I^-), as expected. The equilibrium between bis and tris species is fast on the NMR time scale.

Shifts for N,N'-$(CH_3)_2$en complexes and complexes with other ligands are given in Table I. In contrast to D_2O solutions, en gives somewhat broad but nevertheless identifiable mono, bis, and tris signals. The bis and tris signals are observed at lower L/Cd ratios and are shifted further downfield than is the case for N,N-$(CH_3)_2$en. These factors, in addition to more rapid ligand exchange, may contribute to the broadening. In this vein, N,N,N',N'-$(CH_3)_4$en gives only a mono complex at achievable concentrations of ligand. Tri- and tetradentate N-donor ligands gave similar results. Mixed-ligand complexes can also be observed.

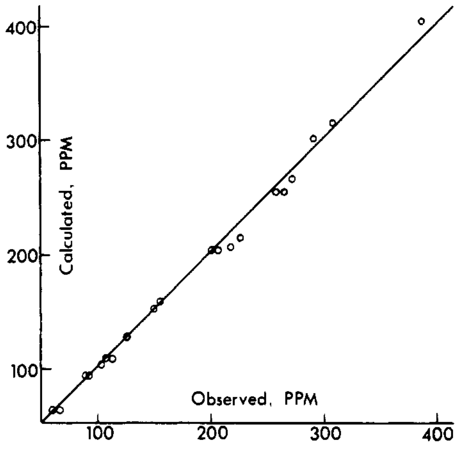

Figure 2. Plot of calculated vs. observed chemical shift (ppm) for complexes with the following ligand or ligands in the coordination sphere (progression from left to right): 1,10-phenanthroline, N,N,N',N'-$(CH_3)_4$en, 2,2',2''-terpyridine, N,N,N',N'',N''-dien, N,N-$(CH_3)_2$en, N,N-$(CH_3)_2$en, 2-(aminomethyl)pyridine, N-(CH_3)en, en, N,N-$(CH_3)_2$dien, dipropylenetriamine, dien, $(N,N'$-$(CH_3)_2$en$)_2$, $(N,N$-$(CH_3)_2$en$)_2$, 3,2,3-tetramine, trien, $(N$-(CH_3)en$)_2$, N,N-$(CH_3)_2$dien + N,N-$(CH_3)_2$en, $(en)_2$, $(N,N$-$(CH_3)_2$dien$)_2$, $(dien)_2$. The line has a slope of 1 and does not represent a least-squares fit of the data.

In Figure 2, we demonstrate that these shifts can be calculated, usually to within 5%, by using the relationship, shift = $75A + 51B + 31C$, where A, B, and C are the number of primary, secondary, and tertiary amine donors, respectively. The relationship holds well for all species observed except those in fast exchange.

It should be noted that the counterion employed can have a significant influence. The counterion that gives results closest to NO_3^- is ClO_4^-, another weakly coordinating oxyanion. On the other hand, acetate precludes the observation of distinct resonances, although the ^{113}Cd signal is readily observed. No signal can be seen with halide salts (Cl, Br, I) unless all the coordination sites appear occupied by amines, as in tris bidentate species. Also, addition of Br^- (as LiBr) to $Cd(NO_3)_2$ (1.0 M) solution broadens the ^{113}Cd signal with a small downfield shift. Similarly, at low concentrations, bidentate ligands that can form only six-membered chelate rings (1,3-propylenediamine, N,N,N',N'-tetramethyl-1,3-propylenediamine) give a broad resonance consistent with rapid exchange. This problem does not occur for dipropylenetriamine at low concentrations. However, the equilibrium between the mono and bis complexes is fast on the NMR time scale, in contrast to the tridentate ligand dien and its derivatives, which form five-membered chelate rings.

The complexes observed range in shift from ~60 to 400 ppm. This range is much larger than the 220 ppm range previously suggested.[1-3] Earlier estimates were made with cautionary statements regarding the limited data and the problems associated with lability.

The N-donor atoms in the ligands employed here may occupy nearly regular coordination positions. However, the ligating atoms in proteins may present a distorted environment to the metal, and we have not been able to find a close relationship between shift and the number and type of ligating atoms in cadmium metalloproteins. The problems and po-

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tential of ^{113}Cd NMR spectroscopy in biological systems have been recently reviewed.[8]

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Registry No. $\mathrm{CdB(NO_3)_2}$ (B = 1,10-phenanthroline), 88425-75-6; $\mathrm{Cd(}\mathit{N,N,N',N'}\mathrm{\text{-}(CH_3)_4en)(NO_3)_2}$, 88425-76-7; $\mathrm{CdB(NO_3)_2}$ (B = 2,2′,2″-terpyridine), 88425-78-9; $\mathrm{Cd(}\mathit{N,N,N',N'',N''}\mathrm{\text{-}(CH_3)_5dien)(NO_3)_2}$, 88425-80-3; $\mathrm{Cd(}\mathit{N,N'}\mathrm{\text{-}(CH_3)_2en)(NO_3)_2}$, 88425-81-4; $\mathrm{Cd(}\mathit{N,N'}\mathrm{\text{-}(CH_3)_2en)_2(NO_3)_2}$, 88425-82-5; $\mathrm{Cd(}\mathit{N,N'}\mathrm{\text{-}(CH_3)_2en)_3(NO_3)_2}$, 88425-84-7; $\mathrm{Cd(}\mathit{N,N}\mathrm{\text{-}(CH_3)_2en)(NO_3)_2}$, 88425-85-8; $\mathrm{Cd(}\mathit{N,N}\mathrm{\text{-}(CH_3)_2en)_2(NO_3)_2}$, 88425-86-9; $\mathrm{CdB(NO_3)_2}$ (B = 2-(aminomethyl)pyridine), 88425-87-0; $\mathrm{Cd(}\mathit{N}\mathrm{\text{-}(CH_3)en)(NO_3)_2}$, 88425-88-1; $\mathrm{Cd(}\mathit{N}\mathrm{\text{-}(CH_3)en)_2(NO_3)_2}$, 88425-89-2; $\mathrm{Cd(}\mathit{N}\mathrm{\text{-}(CH_3)en)_3(NO_3)_2}$, 88425-91-6; $\mathrm{Cd(en)(NO_3)_2}$, 88425-92-7; $\mathrm{Cd(en)_2(NO_3)_2}$, 88425-93-8; $\mathrm{Cd(en)_3(NO_3)_2}$, 56123-55-8; $\mathrm{Cd(}\mathit{N,N}\mathrm{\text{-}(CH_3)_2dien)(NO_3)_2}$, 88425-95-0; $\mathrm{Cd(}\mathit{N,N}\mathrm{\text{-}(CH_3)_2dien)_2(NO_3)_2}$, 88425-97-2; $\mathrm{CdB(NO_3)_2}$ (B = dipropylenetriamine), 88425-99-4; $\mathrm{Cd(dien)(NO_3)_2}$, 88426-01-1; $\mathrm{Cd(dien)_2(NO_3)_2}$, 88426-02-2; $\mathrm{CdB(NO_3)_2}$ (B = 3,2,3-tetramine), 88426-04-4; $\mathrm{Cd(trien)(NO_3)_2}$, 88426-05-5; $\mathrm{Cd(}\mathit{N,N}\mathrm{\text{-}(CH_3)_2dien)(}\mathit{N,N}\mathrm{\text{-}(CH_3)_2en)(NO_3)_2}$, 88426-07-7; ^{113}Cd, 14336-66-4; $\mathrm{Me_2SO}\text{-}d_6$, 2206-27-1.

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Articles

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Mechanism of Heterolytic Iron–Iron Bond Cleavage in (μ-Dimethylarsenido)(tetracarbonyliron)dicarbonylnitrosyliron(*Fe*–*Fe*)

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Reactions of the title complex with a series of P-, As-, or Sb-donor ligands lead to heterolytic cleavage of the Fe→Fe bond and addition of the ligands at the $\mathrm{Fe(CO)_2(NO)}$ moiety. The rate equations for the reactions in Decalin or cyclohexane are dominated by a term first order in the entering ligand. The dependence of the rate parameters on the nature of the nucleophile suggests that most of the reactions occur by an associative or $\mathrm{I_a}$ attack at the Fe atom but that the weak nucleophiles $\mathrm{P(OPh)_3}$, $\mathrm{AsPh_3}$, and $\mathrm{SbPh_3}$ probably react by an $\mathrm{I_d}$ mechanism. Spectroscopic and kinetic evidence suggests that equilibrium mixtures of reactant and product complexes are formed in reactions with $\mathrm{P(OPh)_3}$ and $\mathrm{SbPh_3}$. The data suggest that the Fe→Fe bond strength is probably ≳ca. 100 kJ $\mathrm{mol^{-1}}$. These results are compared with those for similar reactions of $\mathrm{(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3}$.

Introduction

Synthetic and structural studies of metal carbonyl clusters have proceeded on an increasingly massive scale over the last decade,[1] and this has been in large part due to the hope that useful catalysts may be discovered among them.[2] One of the features necessary for catalysis to be uniquely assignable to a cluster is the absence of fragmentation into active mononuclear species. In this context, the chemistry of polynuclear carbonyls in which the metal atoms are strongly bound together by bridging groups has become of considerable interest.[2,3] Fission of a metal–metal bond to give geminal reactive metal centers is seen as a potentially important modus operandi of catalytically active clusters.[3] Clusters containing more than one type of metal are also believed to be particularly promising.[3] Heteronuclear arsenido- and phosphido-bridged complexes form a class of this type, and $\mathrm{(OC)_4\overline{Fe(\mu\text{-}AsMe_2)M}}$ (M = $\mathrm{Co(CO)_3}$ and $\mathrm{Fe(CO)_2(NO)}$) have been shown to catalyze the dimerization of norbornadiene.[4]

Kinetic studies of such complexes are important in defining the energetics of their reactions and in suggesting the types of reactive intermediates that might be involved. Thus, an early study concerned the "ring-opening" reaction shown in eq 1.[5] The forward reaction was first order in [L] even when

$$\mathrm{(OC)_3\overline{Co(\mu\text{-}CO)(\mu\text{-}GePh_2)Co}(CO)_3 + L \rightarrow (OC)_4Co(\mu\text{-}GePh_2)Co(CO)_3L} \quad (1)$$

L was the very weak nucleophile CO, and the small dependence of the values of k_2 on the nature of L was taken to indicate reaction via an initial, highly reversible, ring opening to form $\mathrm{(OC)_4Co(\mu\text{-}GePh_2)Co(CO)_3}$, which was then attacked at the vacant coordination site by the incoming nucleophile. More recently, ring-opening reactions of $\mathrm{(\eta^5\text{-}C_5H_5)Mn\overline{Fe_2(CO)_7}(\mu\text{-}PPh)}$[6] and $\mathrm{(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3}$[7] have also been shown to be first order in incoming nucleophile.

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