Synthesis and Structure of a Trigonal Monopyramidal Fe(II) Complex and Its Paramagnetic Carbon Monoxide Derivative

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We report the isolation and structural characterization of an Fe(II) complex containing a trigonal monopyramidal coordination geometry. Trigonal monopyramidal coordination to a metal ion is rare and, to our knowledge, has not been observed previously for Fe(II) ions. To stabilize this coordination geometry, the triposid ligand, tris-(N-isopropylcarbamoylmethyl)amine (H$_3$iPr), was synthesized consisting of a tertiary amine and three deprotonated amides with appended isopropyl groups. These isopropyl groups are designed to limit access to exogenous ligands to the Fe(II) center. This constrained microenvironment can lead to iron adducts with new structural and physical properties, as is illustrated by the formation of a paramagnetic Fe(II)−carbon monoxide complex.

H$_3$iPr$^-$ was obtained in a one-step synthesis by treating iPr$_2$NH$_2$CH$_2$CO$_2$H$_2$ with K$_2$CO$_3$ and Fe$_2$(OAc)$_3$ (1:2). The crude product was chromatographed on silica gel to obtain Fe(OAc)$_2$ (0.110 g, 0.632 mmol), and the mother liquor was concentrated to dryness under reduced pressure to yield a pale yellow powder (0.24 g, 78%). Pale yellow crystals were obtained by diffusing diethyl ether into a DMF solution of K[Fe$i$Pr$^-$]$^{13}$ ($5.38$ g).

Toxically the Fe$i$Pr$^-$ complex forms a cavity about the Fe(II) ion similar to those found in other Fe$i$Pr$^-$ complexes. The molecular structure of K[Fe$i$Pr$^-$]$^{13}$ also reveals that the isopropyl groups of this complex are oriented in an Fe$i$Pr$^-$ fashion in the molecule.

The "gearing" of isopropyl groups$^{13}$ observed in [Fe$i$Pr$^-$]$^{13}$ produces a flexible cavity that can accommodate exogenous ligands to the Fe(II) center to form five-coordinate complexes. This is demonstrated by the formation of [Fe$i$Pr$^-$](CO)$_2$ whose molecular structure is shown in Figure 1B.$^{13}$ Note that in [Fe$i$Pr$^-$](CO)$_2$ the isopropyl groups have rotated, enlarging the size of the cavity, as can be seen by the $17.4^\circ$ reduction in the angle between the planes formed by $\mathrm{C}_{\text{methylene}}-\mathrm{H}_{\text{methylene}}$. The binding of an exogenous ligand to [Fe$i$Pr$^-$]$^{13}$ contrasts with the results found for TMP complexes of [118-1]-, a ligand similar to [118-1]- except for the appended tert-butyl groups.$^{13}$ In these complexes the conformations of $\mathrm{C}_\text{Bu}^+$ groups prevent binding of exogenous ligands to the metal.

Scheme 1

![Complex Scheme](attachment:complex_scheme.png)

| $^{13}$KFe$i$Pr$^-$ | crystallized with one DMF solvate per molecule in the triclinic space group $P1$ with the following cell constants: $a = 8.6150(7)$ Å, $b = 10.3838(9)$ Å, and $c = 14.2888(11)$ Å; $\alpha = 69.8000(1)$°, $\beta = 83.897(1)$°, and $\gamma = 84.599(1)$°; $V = 1187.70(2)$ Å$^3$, $Z = 2$. Of 4918 reflections collected (1.52 ≤ $\theta$ ≤ 24.12°, 1732 [K]), 3499 were unique data ($F^2 > 2.00\sigma(F^2)$); $R_I = 0.0574$ and $wR_2 = 0.1462$ with $GOF(R^2) = 1.101$.


| $^{10}$The $\mu$-complex structure of a four-coordinate Fe(II) complex with a trigonal ligand has been reported recently; the iron center in this complex has a distorted tetrahedral coordination geometry: Govindaswamy, N.; Quarless, D. A., Jr.; Koch, S. A. J. Am. Chem. Soc. 1995, 117, 8468.

| $^{11}$Similar conformations of isopropyl groups have been observed in the molecular structures of [118-1]- and [118-1]-, unpublished results.

| $^{12}$There are no agostic interactions present in [Fe$i$Pr$^-$]$^{13}$. The "gearing" has been used to describe the arrangement of geminal or vicinal isopropyl groups attached to a planar framework. In these systems, the isopropyl groups are oriented such that the methylene hydrogens of one group are positioned into the space formed by the two methyl groups of an adjacent isopropyl group:Siegel, J.; Gutiérrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. J. Am. Chem. Soc. 1986, 108, 1569. |
The binding of CO causes a reduction in the Fe–N bond distance. As shown in Table 1, the average Fe–N(1) distance is shortened by 0.023 Å to 1.991 Å in [Fe\(^{II}\)\(\text{CO}\)\(^{2+}\)], while the Fe–N(1) distance has been reduced to 1.991 Å. This shortening of bond lengths is suggestive of a reduction in spin state at the Fe(II) center.\(^{15}\) Carbon monoxy binds to Fe(II) normally produces complexes that are diamagnetic,\(^{15,16}\) yet both [Fe\(^{III}\)(CO)]\(^{2+}\) and [Fe\(^{III}\)(CO)]\(^{3+}\) are paramagnetic. At room temperature [Fe\(^{III}\)(CO)]\(^{2+}\) is a high spin with an \(\mu_{eff} = 5.38\ \mu_B\) magnetic moment that is similar to those reported for other \(S = 2\) Fe(II) complexes.\(^{17}\) In contrast, [Fe\(^{III}\)(CO)]\(^{3+}\) has an \(\mu_{eff} = 3.41(2)\ \mu_B\) consistent with an \(S = 1\) spin state.\(^{18}\) The Mössbauer spectra of a powder sample of [Fe\(^{III}\)(CO)]\(^{2+}\) at \(-2\) K shows a single quadrupole doublet with parameters relative to iron metal of \(\delta = 0.26\) and \(\Delta E_Q = 1.07\) mm/s. The spectrum is not affected by a weak applied magnetic field of 45 mT, which is consistent with a non-Kramers spin system for the complex. The powder Mössbauer spectrum of [Fe\(^{III}\)(CO)]\(^{2+}\) at \(-2\) K exhibits a paramagnetic pattern spanning approximately 9 mm/s in a field of 45 mT; this paramagnetic spectrum collapses to a single quadrupole doublet at 77 K with parameters of \(\delta = 1.05\) and \(\Delta E_Q = 3.31\) mm/s. The Mössbauer parameters observed for [Fe\(^{III}\)(CO)]\(^{2+}\) are typical of high-spin Fe(II) centers, while those found for [Fe\(^{III}\)(CO)]\(^{3+}\) are within the range of the few known \(S = 1\) Fe(II) complexes for which Mössbauer data are available.\(^{19,20}\) Powder and frozen solution EPR spectra of [Fe\(^{III}\)(CO)]\(^{2+}\) at 4.2 K exhibit an integer spin resonance near \(g \approx 8\), which is typical of \(S = 2\) Fe(II) complexes and consistent with the observation of a paramagnetic Mössbauer spectrum in a weak applied field.\(^{21}\) Extended Hückel calculations\(^{22}\) indicate that for [Fe\(^{III}\)(CO)]\(^{2+}\) the \(d_2\) (a) and \(d_{2z}\) (b) orbitals have nearly the same energy and lie higher than the \(d_{xy}\) and \(d_{yz}\) orbitals; upon CO binding the \(d_2\) orbital is raised significantly leading to an orbital arrangement that gives rise to the paramagnetism found in [Fe\(^{III}\)(CO)]\(^{2+}\).

The \(S = 1\) spin state observed in [Fe\(^{III}\)(CO)]\(^{2+}\) represents the first example of a paramagnetic Fe(II)–CO complex. The formation of this complex results from the ability of the [\(\text{Fe}^{3+}\)]\(^{2-}\) to control the cavity architecture around Fe(II) to restrict the binding of additional ligands and produce a trigonal bipyramidal coordination geometry. The difference in \(S = 1\) state is readily achieved in [Fe\(^{III}\)(CO)]\(^{2+}\), but not in six-coordinate Fe(II) carbonyl complexes, owing to the inaccessibility of the \(S = 0\) in trigonal symmetry. The binding of CO to [Fe\(^{III}\)(CO)]\(^{2+}\) is unusually weak: [Fe\(^{III}\)(CO)]\(^{2+}\) reversibly binds CO with a \(K_{CO}\) of 0.0091 Torr.\(^{1,23}\) This binding constant is significantly lower than those reported for most Fe(II) complexes, especially for complexes having linear Fe–C–O motifs as is found in [Fe\(^{III}\)(CO)]\(^{3+}\).\(^{15,24}\) A possible explanation for this lower CO binding constant is that the energy difference between states \(S = 2\) and \(S = 0\) in distorted-octahedral symmetry significantly greater than the energy difference between states \(S = 2\) and \(S = 1\) in trigonal symmetry.\(^{25}\) The constrained microenvironment must also affect exogenous ligand binding, given the large structural reorganization effects observed upon CO binding for most Fe(II) complexes, especially for complexes having linear Fe–C–O motifs as is found in [Fe\(^{III}\)(CO)]\(^{3+}\). For a recent account of the relevance of linear Fe–C–O motifs see Reference 26. The magnitudes of these electronic and structural effects on exogenous ligand binding can be further examined because the design of [\(\text{Fe}^{III}\)(CO)]\(^{2+}\) allows for convenient access to ligands with cavities having different structural and physical properties.\(^{26}\) Studies to address the relative contributions of these effects are in progress.

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Supporting Information Available: Structure determination summaries and tables of X-ray structural data for [K\(^{III}\)(CO)]\(^{2+}\) and K\(^{III}\)(CO)\(^{3+}\); plots of \(P_{CO}\) vs % CO (wide CO dissociation); and a qualitative MO diagrams (Figures S1 and S2) (23 pages). See any current masthead page for ordering and Internet access instructions.

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1(14) K[Fe\(^{III}\)(CO)]\(^{2+}\) was synthesized by treating a DMF solution of K[Fe\(^{III}\)(CO)]\(^{3+}\) with excess CO. Diffusion of ether into this solution afforded deep blue crystals in 70% yield. Anal. Calc. (Found) for K[Fe\(^{III}\)(CO)]\(^{3+}\)-DMF·H\(_2\)O, C\(_{10}\)H\(_4\)FeKNO\(_3\)·C\(_{14}\)H\(_{33}\)FeCO\(_2\)·H\(_2\)O, C\(_{67}\)H\(_{60}\)O\(_{11}\); N, 13.37 (13.78); Br (Nujol, cm\(^{-1}\)), v(CO) 1940 (s), 1675 (MF), v(amide, s), \(\Delta_{\text{nu}}\) (DMF) 390 (sh), 590 (e, 670 M \(^{-1}\) cm\(^{-1}\)), 696 (sh); \(\mu_{\text{eff}} = 3.41(2)\ \mu_B\) (solid, average of three independent measurements at 298 K).

1(25) The release of CO from the trigonal bipyramidal [Fe\(^{III}\)(CO)]\(^{2+}\) complex requires promotion of only one electron to a \(d_2\) orbital to form the uncarbonylated high-spin TMP complex, whereas octahedral Fe(II) complexes require promotion of two electrons to the \(d_{xy}\) and \(d_{yz}\) orbitals. For a recent account of the relevance of linear Fe–C–O motifs in biomolecules with constrained microenvironments, see: Lim, M.; Jackson, T. A.; Anfinrud, P. A. Science 1995, 269, 962.

1(27) Note Added in Proof: Another \(S = 1\) Fe–CO complex has been isolated recently by S. A. Koch (submitted for publication).