

## Communications

## Formation of a Hydrogen Oxide Bridging Ligand in the Hydrolysis of a Mononuclear Iron(III) Complex: Support by Mössbauer Spectroscopy

Sir:

The mechanism of hydrolysis of metal aquo ions  $M(OH_2)^{n+}$ , specifically ferric ion, has been of interest for many years because of its biological implications.<sup>1,2</sup> The primary hydrolysis product  $M(OH)^{(n-1)+}$  normally undergoes condensation reactions to yield  $\mu$ -hydroxo- or  $\mu$ -oxo-bridged dimers and polymers.<sup>3</sup> The process by which these form, however, has not yet been elucidated. It has been proposed<sup>4</sup> that the hydrogen oxide bridging ligand ( $H_3O_2^-$ ) may be an important intermediate in the hydrolytic process. This work provides Mössbauer spectroscopic evidence for such a bridge in the hydrolysis of a mononuclear iron complex.

Figure 1 shows Mössbauer spectra of  $Fe(EHGS)^5$  frozen solutions in 5:1 glycerine/water at 4.2 K. An external magnetic field of 130 mT is applied perpendicular to the  $\gamma$ -beam direction. At low and high pH (Figure 1a,c) the Mössbauer spectra show one species of iron with well-defined paramagnetic hyperfine structure. Comparison of the high- and low-pH spectra shows that the high-pH spectrum has significantly narrower absorption lines, larger zero-field splittings, and a slightly larger magnetic hyperfine field at the nucleus.<sup>6</sup> At neutral pH (Figure 1b) we observe three types of iron sites, one that is fast relaxing, as seen by the narrow peaks at the center of the spectrum, and two that are slow relaxing with magnetic hyperfine fields typical of a high-spin ferric iron. The slow-relaxing spectrum is a mixture of two: the spectrum at low pH and the one at high pH. The solid line in Figure 1b is not a fit but a composite of (a) 56% of the spectrum at pH 4.9, (b) 23% of the spectrum at pH 9.8, and (c) 21% of a quadrupole doublet with isomer shift  $\delta = 0.52$  mm/s, quadrupole splitting  $\Delta E = 0.95$  mm/s, and line width  $\Gamma = 0.36$  mm/s. There is no evidence of the fast-relaxing component at pH 4.9 or 9.8.

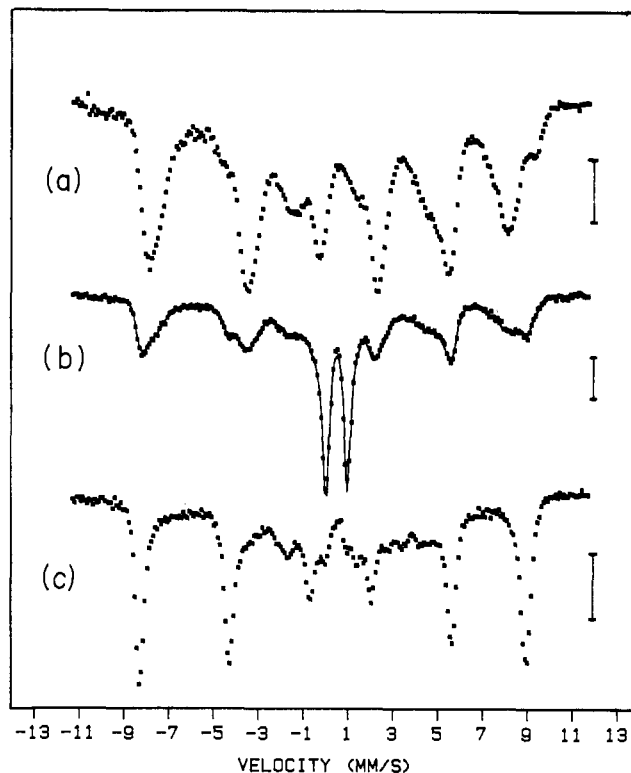


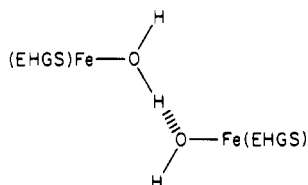
Figure 1. Mössbauer spectra of frozen  $Fe(EHGS)$  in 5:1 glycerine/water at 4.2 K. An external field of 130 mT is applied parallel to the  $\gamma$  beam: (a) pH 4.9; (b) pH 7.2 (see text for explanation of solid line); (c) pH 9.8. Vertical bars indicate 1% absorption.

The pH dependence in the Mössbauer spectra was reproducible to within our ability to determine pH for a 5:1 glycerine/water solution. In particular, the fast-relaxing component appears only around neutral pH values and is not present at low or high pH. We assign a water molecule to the sixth ligand position in the low-pH complex.<sup>7</sup> At high pH the water molecule is deprotonated to form a hydroxo complex. The  $pK_a$  of this process has been measured by spectrophotometric titration to be 6.7. At pH near the  $pK_a$  we have the coexistence of the aquo and hydroxo forms and a site that shows fast electronic relaxation.<sup>8</sup>

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- EHGS: *N*-[2-(salicylidenimino)ethyl](*o*-hydroxyphenyl)glycine.
- The spin Hamiltonian parameters for the low- and high-pH spectra have been found to be appropriate for high-spin  $Fe(III)$ ,  $g = 4.3$  complexes. They will be discussed in detail in a future paper. We note, however, that the quadrupole splittings are unusual:  $\Delta E = 1.6$  mm/s for the low-pH complex and  $\Delta E = 0.4$  mm/s for the high-pH complex.

- The formulation of  $Fe(EHGS) \cdot H_2O$  as a monomer with water occupying the sixth coordination site is supported by elemental analysis, infrared and optical spectroscopy, and conductivity and is consistent with magnetic measurements. An X-ray diffraction analysis on the methanol solvate has also been completed.

We interpret the spectrum at neutral pH as the sum of contributions from the aquo complex, the hydroxo complex, and a fast-relaxing species for which the magnetic hyperfine field at the nucleus is time averaged to zero. The fast-relaxing component indicates the formation of a dimer, bridged at the sixth coordination site. A plausible scheme requires the existence of a hydrogen oxide bridge of the type recently reported<sup>4,9</sup> for some trinuclear cluster ions. The hydrogen oxide bridge is formed by a strong hydrogen bond between a hydroxide ligand on one complex with an aquo ligand on the other.



Fast relaxation may occur via spin-spin interaction between the electronic distributions of the two iron atoms in the dimer. The values for the isomer shift and quadrupole splitting are characteristic of the iron in this particular dimer environment and fall within the usual range for high-spin Fe(III). However, spin-spin relaxation effects in specimens of high-spin Fe(III) usually give rise to poorly defined hyperfine structure with broad-winged absorption lines. The sharpness of the quadrupole pair in Figure 1b may indicate another mechanism for fast relaxation. As the bridging proton is shared between the two atoms, it is possible that each iron site in the dimer fluctuates between the aquo and hydroxo states. Rapid relaxation between the two states causes the magnetic hyperfine field at the nucleus to average to zero because the aquo and hydroxo states are not expected to have hyperfine fields that are identical in magnitude and direction. Furthermore, in the fast-relaxation regime, the quadrupole splitting is expected to have a value that is the numerical average of the values of the aquo and the hydroxo states. Because the value 0.95 mm/s is as close to the average of 1.6 and 0.4 mm/s as one hopes to get and because the central quadrupole pair shows narrow lines of Lorentzian line shape, we favor the second relaxation mechanism as the most likely explanation for the fast-relaxing component.

Regardless of the relaxation mechanism, bridges of this type are expected to be pH dependent.<sup>9</sup> At low pH, Fe(EHGS) is entirely in the aquo form; at higher pH, near the  $pK_a$ , the aquo and hydroxo forms coexist and may form hydrogen oxide bridged dimers; at pH higher than the  $pK_a$ , only the hydroxo form exists and the dimer disappears. This pattern is predicted by the model of Bino and Gibson<sup>9</sup> who have proposed that the  $H_3O_2^-$  bridge may be a general feature in the hydrolysis of mononuclear metal ions such as  $Fe(H_2O)_6^{3+}$ . Our results support this view.

- (8) The presence of an isosbestic point during the spectrophotometric titration of the aquo complex indicates that, under these conditions (10<sup>-4</sup> M, 25 °C), only two species are present, the aquo and hydroxo complexes. Dimer formation was promoted in the Mössbauer samples, which were 5-10 times more concentrated than the samples for the optical spectra. On the basis of the percentages from Figure 1b, we have calculated the equilibrium constant for dimer formation to be approximately 350. From this we calculate that the concentration of dimer in the optical samples is 2 orders of magnitude below that of the monomers. Thus, even if the dimer has its own optical spectral signature, it would not be observable.
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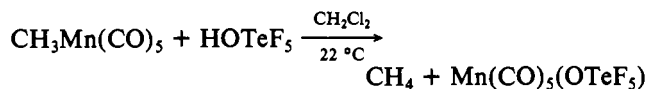
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## Low-Valent Metal Teflates: Preparation and Characterization of $Mn(CO)_5(OTeF_5)$

Sir:

The pentafluoroorthotellurate ( $OTeF_5$ ) group has been substituted for fluorine or chlorine in a wide variety of main-group and high-valent transition-metal compounds.<sup>1-3</sup> By the use of various physicochemical criteria, including molecular structures (group site preference),<sup>4,5</sup> NMR chemical shifts,<sup>5-7</sup> Mössbauer isomer shifts,<sup>7</sup> chemical reactivities,<sup>8</sup> and the thermal stabilities<sup>9</sup> of some main-group  $OTeF_5$  derivatives, it has been repeatedly demonstrated that the electronegativity of  $OTeF_5$  and fluorine are practically equal. We are currently extending this chemistry to include low-valent transition-metal compounds by exploring the use of the  $OTeF_5^-$  anion (hereafter referred to as teflate) as a ligand for organometallic and coordination complexes. To assess the promise of this bulky and electronegative pseudohalide (which seems to be incapable of bridging two elements<sup>1-3</sup>), one must ascertain (i) how strongly teflate can coordinate to low-valent metals (M) in these types of compounds, (ii) whether geometric constraints or strong  $O \rightarrow Te \pi$  bonding<sup>1,2,10</sup> will preclude  $O \rightarrow M \pi$  donation, and (iii) whether the combination of low-valent M and high-valent Te(VI) is intrinsically unstable with respect to intramolecular electron transfer.<sup>11</sup> We have accomplished these three things in an initial study and herein report our results.

The title compound was prepared by treating a 0.1 M  $CH_2Cl_2$  solution of  $CH_3Mn(CO)_5$  with a slight excess of  $HOTeF_5$ :<sup>9b</sup>



A 0.96-equiv amount of  $CH_4$  (based on  $CH_3Mn(CO)_5$ ) was measured by Toepler pump analysis and identified by its IR spectrum. A first crop of orange crystals (>25% yield) can be isolated by simply cooling the reaction mixture to -15 °C. Note that this compound is the first that can be considered a *low-valent* transition-metal teflate. The next lowest valent transition-metal teflates are those of Ti(IV).<sup>12</sup> The compound is stable in the solid state under a  $N_2$  atmosphere for long periods of time (>weeks). In  $CH_2Cl_2$  it slowly (days) evolves CO with precipitation of a pink solid. The teflate ligand is rapidly replaced by added  $Cl^-$  in  $CH_2Cl_2$  at 22 °C ( $t_{1/2} < 1$  min). Initial results indicate that this substitution occurs by facile CO dissociation and not by facile teflate dissociation.

The mass spectrum shows the parent ion and progressive loss of CO ligands down to  $MnOTeF_5^+$ . The <sup>19</sup>F NMR spectrum<sup>13</sup> and  $\nu(TeO)$ <sup>13</sup> are consistent with the teflate group

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 (11) (a) Intra- or intermolecular electron transfer plagues the chemistry of phosphorus(III) teflates. The compound  $P(OTeF_5)_3$  slowly decomposes to tellurium metal<sup>11b</sup> and a variety of phosphorus(V) species containing P-F bonds.<sup>11c</sup> (b) Lentz, D.; Seppelt, K. *Z. Anorg. Allg. Chem.* 1983, 502, 83-88. (c) Abney, K. D.; Strauss, S. H., unpublished observations, 1983.  
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