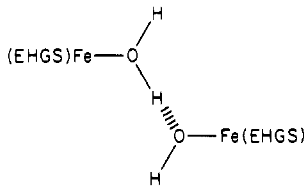
We interpret the spectrum at neutral pH as the sum of contributions from the aquo complex, the hydroxo complex, and a fast-relaxing species for which the magnetic hyperfine field at the nucleus is time averaged to zero. The fast-relaxing component indicates the formation of a dimer, bridged at the sixth coordination site. A plausible scheme requires the existence of a hydrogen oxide bridge of the type recently reported[4,9] 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.[9] 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[9] 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.

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(8) The presence of an isosbestic point during the spectrophotometric titration of the aquo complex indicates that, under these conditions (10^{-4} 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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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.[1-3] By the use of various physicochemical criteria, including molecular structures (group site preference),[4,5] NMR chemical shifts,[5-7] Mössbauer isomer shifts,[7] chemical reactivities,[8] and the thermal stabilities[9] 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[1-3]), 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 → Te π bonding[1,2,10] will preclude O → M π donation, and (iii) whether the combination of low-valent M and high-valent Te(VI) is intrinsically unstable with respect to intramolecular electron transfer.[11] 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 $HOTeF_5$:[9b]

$$CH_3Mn(CO)_5 + HOTeF_5 \xrightarrow[22\ ^\circ C]{CH_2Cl_2} CH_4 + Mn(CO)_5(OTeF_5)$$

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).[12] 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 ^{19}F NMR spectrum[13] and ν(TeO)[13] are consistent with the teflate group

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Table I. Vibrational Frequencies (cm^{-1}) and λ_{max} (nm) for $Mn(CO)_5X$ in CH_2Cl_2 at 22 °C

	ν(CO)			
X	A_1	E	A_1	λ_{max}
$OTeF_5$	2155	2070	2016	403
ClO_4[a]	2158	2074	2023	379
O_2CCF_3[b]	2149	2063	2012	
Cl	2143	2055	2007	377
Br	2138	2052	2007	383
I	2129	2045	2008	406

[a] Prepared by the method of: Wimmer, F. L.; Snow, M. R. *Aust. J. Chem.* 1978, *31*, 267–78. [b] IR data from ref 22.

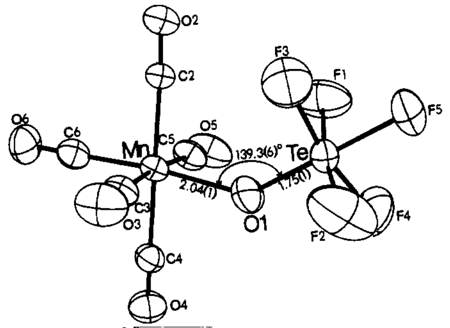

Figure 1. Structure of $Mn(CO)_5(OTeF_5)$ (25% probability ellipsoids) showing the angle and distances (Å) germane to the discussion in the text. Other distances (Å) are as follows: Mn–C2 = 1.88 (1), Mn–C3 = 1.89 (1), Mn–C4 = 1.93 (1), Mn–C5 = 1.91 (1), Mn–C6 = 1.82 (1), C2–O2 = 1.11 (1), C3–O3 = 1.09 (1), C4–O4 = 1.05 (2), C5–O5 = 1.09 (2), C6–O6 = 1.09 (2), Te–F1 = 1.84 (1), Te–F2 = 1.78 (1), Te–F3 = 1.82 (1), Te–F4 = 1.78 (1), Te–F5 = 1.82 (1).

in this compound having considerable ionic character (see below).[10,14] While ν(CO) data (Table I) clearly imply that teflate is a poorer σ-donor than Cl^-, visible spectral data (Table I) do not follow any intelligible trend. The electronic spectra of $Mn(CO)_5X$ (X = Cl, Br, I) have been studied by many investigators, but the nature of the lowest energy band ($^1A_1 \rightarrow {}^1E$; π X → Mn charge transfer and/or ligand field) is still incompletely understood.[15]

The NMR and IR spectral results are in harmony with the molecular structure[16] of the compound (Figure 1). The short Te–O distance of 1.75 (1) Å, indicative of O → Te π bonding, reflects the large degree of teflate ionic character in this compound. A normal-coordinate analysis[10] of $OTeF_5^-$ and vibrational data of other teflate derivatives[17] have shown that the Te–O stretching force constant is larger for free $OTeF_5^-$ than for either ion-paired $OTeF_5^-$ or covalent teflates. Thus, as the ionic character of the teflate group in a molecule increases, the Te–O bond becomes stronger and, presumably, shorter. The Te–O distance in free $OTeF_5^-$ is not known, since salts such as $Cs^+OTeF_5^-$ are at least threefold disordered in the solid state.[17] In the seven other structurally characterized teflates (all of which have hexavalent central metals), the Te–O distances range from 1.79 to 1.95 Å.[18] The Te–O distances in the monoclinic modification of $Te(OH)_6$ are all ~1.91 Å.[19]

A covalent radius of 1.40 ± 0.02 Å for the $Mn(CO)_5$ moiety can be calculated from the structures of $Mn(CO)_5CH_3$[20] and $Mn(CO)_5Cl$.[21] The covalent radius of the oxygen atom of $OTeF_5$ can be estimated to be 0.70 ± 0.02 Å from the structures of $U(OTeF_5)_6$, $Te(OTeF_5)_6$, and *trans*-$TeF_2(OTeF_5)_4$.[18] Thus the observed Mn–O bond distance of 2.04 (1) Å is readily described as a reasonably strong manganese–oxygen single bond.[22] The Mn–O–Te angle of 139.3 (6)° is near the more acute end of the range (134–173°) observed for structurally characterized teflates.[18] Since there is significant O → Te π bonding in our compound, the staggered conformation of the teflate group (with respect to the carbonyl ligands) prevents any possibility of O → Mn π bonding. Note that $F_5TeOTeF_5$ has a (gas-phase) structure with eclipsed fluorines,[18] presumably to achieve some degree of O → Te π bonding with both tellurium atoms. The lack of O → Mn π bonding in $Mn(CO)_5(OTeF_5)$ may lead to the unusually low-energy λ_{max} noted above. This possibility is being explored.

In summary, we have shown that the $OTeF_5^-$ ligand is compatible with *low-valent* transition-metal chemistry. Teflate is not a "noncoordinating" anion but is firmly bound to Mn in $Mn(CO)_5(OTeF_5)$ despite the ionic nature of the Mn–O bond. In contrast with $Mn(CO)_5(OSO_2CF_3)$,[23] our compound does not form $Mn(CO)_6^+$ in solution under an atmosphere of CO at room temperature, even after many hours. Other low-valent metal teflates have been prepared in this laboratory (including some platinum metal complexes) and are under investigation.

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Supplementary Material Available: Listings of positional and thermal parameters, bond lengths, and bond angles (2 pages). Ordering information is given on any current masthead page.

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(13) ^{19}F NMR (188.31 MHz, CH_2Cl_2 ($CFCl_3$ internal standard), 22 °C): AB_4X pattern (X = ^{125}Te, 7.0% NA, $I = {}^1/_2$) δ_A −30.8, δ_B −44.7, J_{AB} = 181 Hz, J_{BX} = 3646 Hz. ν(TeO) = 848 (Nujol mull), 841 cm^{-1} (CH_2Cl_2).

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(16) Orange crystals of $Mn(CO)_5(OTeF_5)$ suitable for diffraction were grown from CH_2Cl_2 by cooling a saturated solution. An irregularly shaped platelet with approximate dimensions 0.4 × 0.3 × 0.5 mm crystallized in the orthorhombic system, space group $Pna2_1$, a = 12.462 (3) Å, b = 7.612 (2) Å, c = 12.539 (2) Å, with Z = 4. Diffraction data (graphite-monochromatized Mo Kα radiation, λ = 0.710 73 Å) were collected on a Nicolet R3m diffractometer at room temperature. The intensities of 2876 reflections for which $3.5° \leqslant 2\theta \leqslant 60°$ and $h, k, l \geqslant 0$ were measured by θ–2θ scans (bisecting geometry). The Te atom position was derived from a Patterson map, and subsequent difference Fourier maps revealed the remaining atoms. A chirality test determined the correct enantiomorph. An empirical absorption correction (μ = 36.35 cm^{-1}) was performed on the basis of ψ scan data. Anisotropic least-squares refinement for all atoms converged at R = 0.0482 (R_w = 0.0527, GOF = 1.342) for 1905 unique observed reflections ($I > 2\sigma(I)$).

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