solvents is intriguing, and our preliminary studies show that the chemistry of these compounds is quite rich.

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Supplementary Material Available: For both the *C*2 and *C*2/*m* structures, ORTEP and Chem-X[35] drawings of **1** and complete listings of bond distances, bond angles, fractional coordinates, and anisotropic thermal parameters (25 pages); listings of calculated and observed structure factors for the *C*2 and *C*2/*m* structures (22 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Properties of $Fe_2Te_3(CO)_6{}^{2-}$ Containing the Unusual μ_2-η^1-$Te_2{}^{2-}$ Ligand

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$Fe(CO)_3(\eta^4$-butadiene) reacts with excess K_2Te_4 in ethylenediamine in the presence of crypt to form $[Fe_2Te_3(CO_6)][(K\cdot crypt)_2]\cdot {}^1/_2$en in good yield. The $Fe_2Te_3(CO)_6{}^{2-}$ anion (**1**) contains two square-pyramidal Fe centers joined along a common basal edge via μ-Te and μ_2-η^1-Te_2 ligands. The Fe–Fe distance in **1** is 2.63 (1) Å. IR spectroscopic studies are suggestive of at least two detectable transient species during the formation of **1** with an overall t_∞ of ca. 18 h. The complex does not form in the absence of crypt. The $Fe_2Te_3(CO)_6{}^{2-}$ anion remains intact when dissolved. Crystal data: a = 11.531 (7) Å, b = 22.098 (12) Å, c = 25.341 (13) Å; α = 85.22 (4)°, β = 84.60 (4)°, γ = 84.39 (5)°, space group $P\bar{1}$, and Z = 4.

Introduction

We have recently shown that soluble main-group polyanions can be used to form metalized polymers[1] and metastable solids with tunable conductivities[2] by soluble deposition techniques at ambient temperatures. As an extension of this work, we have been preparing transition-metal main-group polyanions to investigate their structures and properties as well as their utility in forming new metastable materials.[3,4] Of particular interest are transition-metal polytelluride complexes, which are currently few in number in contrast to the large family of transition-metal polysulfide complexes.[5] The virtue of using such molecular precursors in the formation of binary solids is exemplified by the convenient low-temperature synthesis of FeTe and $FeTe_2$ from $[Cp(Et_3P)(CO)Fe]Te_n$ compounds reported by Steigerwald.[6] As a result of the effects of ourselves and others, a few transition-metal polytelluride anions have recently been prepared including $Mo_4Te_{16}(en)_4{}^{2-}$,[7] $Pd(Te_4)_2{}^{2-}$,[8] *trans*-$Cr(CO)_2(\eta^2$-$Te_2)_2{}^{2-}$,[9] $NbTe_{10}{}^{3-}$,[10a] $Cr(Te_4)(CO)_4{}^{2-}$,[10b] and $Cr_3Te_{24}{}^{3-}$.[11] The complexes were synthesized from various transition-metal complexes in solution reactions with soluble polytelluride ions. These compounds provide an unusual assortment of clusters with unprecedented structures and, with the exception of $Pd(Te_4)_2{}^{2-}$, have no analogues in the polysulfide systems.[5] We report here the synthesis, structure, and properties of the unusual $Fe_2Te_3(CO)_6{}^{2-}$ ion, which extends this class of transition-metal polytelluride anions.

Experimental Section

General Data. All reactions were conducted in a Vacuum Atmospheres Co. drybox under dry oxygen-free He atmospheres. The IR spectra were recorded on a Perkin-Elmer 283 infrared spectrophotometer under an N_2 purge. The solid-state spectra were obtained from pressed KI pellets. The solution spectra were recorded in an airtight CaF_2 cell in ethylenediamine (en) solvent. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Chemicals. $Fe(CO)_3(\eta^4$-butadiene) was purchased from Aldrich Chemicals and used without further purification. The melt of nominal composition K_2Te_4 was prepared by fusing a stoichiometric ratio of the elements under a He atmosphere in a quartz tube. The ethylenediamine solvent was purchased from Aldrich (Gold Label, 99+%), distilled three times from CaH_2 and once from K_4Sn_9, and stored under He. Crypt[12] was purchased from Fluka and used without further purification.

Preparation of $[Fe_2Te_3(CO)_6][(K\cdot crypt)_2]\cdot {}^1/_2$en. K_2Te_4 (78 mg, ca. 0.13 mmol) was extracted into en (ca. 2 mL), producing a reddish purple solution. Approximately 80% of the intermetallic compound went into solution. $Fe(CO)_3(\eta^4$-butadiene) (52 mg, 0.27 mmol) was added dropwise to the polytelluride solution. While the mixture was being stirred, crypt (100 mg, 0.27 mmol) was added as a solid. A slight reddening of the solution was observed upon addition of crypt. The solution was stirred for 24 h at room temperature and then filtered twice. After an additional 24 h, long dark needles of $[Fe_2Te_3(CO)_6][(K\cdot crypt)_2]\cdot {}^1/_2$en were isolated by removing the solvent and washing with en (2 × 1 mL). The crystals were dried in vacuo (crystalline yield, 86 mg, 46%). Large, chunky crystals of $(K\cdot crypt)_2Te_x$ are often formed when large excesses of K_2Te_4 are employed in the synthesis.[13] This material is more soluble in en than the iron–telluride product and can be washed away. IR data (KI pellet), cm^{-1}: 1995 (s), 1950 (s), 1922 (s), 1898 (s), 1886 (s). IR data (en solution, CaF_2 cell), cm^{-1}: 2000 (m), 1971 (m), 1957 (s), 1924 (m), 1909 (m). Anal. Calcd for $K_2Fe_2Te_3C_{43}H_{76}O_{18}N_5$: Fe, 7.3; Te, 25.1; C, 33.8; H, 5.0; N, 4.6. Found: Fe, 7.3; Te, 25.4; C, 34.9; H, 5.3; N, 4.5.

Structural Studies. A dark, almost black, irregularly-shaped crystal of $[Fe_2Te_3(CO_6)][(K\cdot crypt)_2]\cdot {}^1/_2$en, having approximate dimensions of 0.2 × 0.3 × 0.5 mm, was mounted in a glass capillary with its long axis

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Table I. Selected Bond Distances (Å) and Angles (deg) in the $Fe_2Te_3(CO)_6^{2-}$ Ions

	ion A	ion B[a]
	Bond Distances	
Fe(1)-Fe(2)	2.614 (4)	2.638 (5)
Fe(1)-Te(1)	2.582 (4)	2.581 (4)
Fe(1)-Te(2)	2.554 (4)	2.560 (4)
Te(1)-Te(2)	3.215 (3)	3.238 (3)
Te(2)-Te(3)	2.705 (3)	2.715 (3)
Fe(2)-Te(1)	2.586 (3)	2.580 (4)
Fe(2)-Te(2)	2.568 (3)	2.569 (4)
Fe(1)-C(1A)	1.683 (23)	1.776 (26)
Fe(1)-C(1B)	1.772 (28)	1.705 (24)
Fe(1)-C(1C)	1.701 (27)	1.773 (29)
Fe(2)-C(2A)	1.688 (23)	1.773 (30)
Fe(2)-C(2B)	1.708 (24)	1.744 (29)
Fe(2)-C(2C)	1.814 (23)	1.771 (31)
	Bond Angles	
Fe(1)-Te(1)-Fe(2)	60.8 (1)	61.5 (1)
Fe(1)-Te(2)-Fe(2)	61.4 (1)	61.9 (1)
Fe(1)-Te(2)-Te(3)	114.6 (1)	114.6 (1)
Fe(2)-Te(2)-Te(3)	117.2 (1)	117.1 (1)
Te(1)-Te(2)-Te(3)	164.2 (1)	163.5 (1)
Te(1)-Fe(1)-C(1A)	88.6 (9)	85.4 (9)
C(1A)-Fe(1)-C(1B)	95.9 (11)	95.1 (11)
C(1A)-Fe(1)-C(1C)	97.9 (12)	101.6 (11)
Te(1)-Fe(1)-C(1C)	100.0 (10)	104.2 (8)
Te(2)-Fe(1)-C(1C)	100.0 (9)	94.5 (7)
Te(2)-Fe(1)-C(1B)	90.5 (7)	94.5 (7)
C(1B)-Fe(1)-C(1C)	104.0 (13)	100.8 (11)
Te(1)-Fe(1)-C(1B)	154.7 (8)	154.4 (8)
Te(2)-Fe(1)-C(1A)	159.0 (9)	159.3 (9)
Te(2)-Fe(2)-C(2A)	158.1 (7)	158.4 (9)
Te(1)-Fe(2)-C(2C)	156.6 (7)	158.5 (9)
Te(1)-Fe(2)-C(2A)	87.0 (7)	90.0 (10)
Te(1)-Fe(2)-C(2B)	98.4 (8)	101.1 (9)
Te(2)-Fe(2)-C(2C)	92.7 (7)	92.6 (10)
Te(2)-Fe(2)-C(2B)	96.0 (8)	100.1 (9)
C(2A)-Fe(2)-C(2B)	101.3 (11)	99.7 (13)
C(2A)-Fe(2)-C(2C)	96.2 (10)	92.4 (15)
C(2B)-Fe(2)-C(2C)	103.7 (11)	99.5 (13)
Fe(1)-Fe(2)-C(2B)	148.3 (8)	152.3 (9)
Fe(2)-Fe(1)-C(1C)	152.5 (10)	150.1 (7)

[a] To determine the atom numbers for anion B used in Table II and the supplementary material, the following conversions must be applied: Fe(1) = Fe(3); Fe(2) = Fe(4); Te(1) = Te(4); Te(2) = Te(5); Te(3) = Te(6); C(1A) = C(3A); C(1B) = C(3C); C(1C) = C(3B); C(2A) = C(4C); C(2B) = C(4A); C(2C) = C(4B).

roughly parallel to the ϕ axis of the goniometer. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on a Nicolet R3m/V computer-controlled diffractometer equipped with an oriented graphite-crystal monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, by using the setting angles of 25 reflections in the range $15° < 2\theta < 30°$. Details of the data collection experiment are listed in Table III. Statistical analysis of the intensities suggested the centrosymmetric space group $P\bar{1}$, and the structure was successfully solved in this space group.

The structure was solved by using direct methods (SHELXTL-Plus on a Microvax II), which revealed the positions of all of the heavy atoms. The remaining atoms were located in successive difference Fourier syntheses. All of the cluster atoms, the K, N, and O atoms from the cryptands, and the C and N atoms from the en were refined anisotropically. The carbon atoms from the cryptands were refined isotropically. No hydrogen atoms were included in the model. Due to the number of parameters to be refined in the last stages, the refinement was carried out in blocks. Neutral-atom scattering factors were taken from ref 14. Anomalous dispersion effects were included in F_c;[15] the values for f' and f'' were taken from ref 16. Table III also lists the important values from the solution and refinement of the structure. The data were corrected for absorption and extinction.

Table II. Selected Atomic Positional Parameters (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for $[Fe_2Te_3(CO)_6][(K\cdot crypt)_2]\cdot{}^1/_2en$

	x	*y*	*z*	*U*(eq)
Te(1)	7930 (1)	7642 (1)	1915 (1)	63 (1)
Te(2)	6089 (1)	8129 (1)	1064 (1)	65 (1)
Te(3)	4200 (2)	8297 (1)	494 (1)	94 (1)
Fe(1)	6484 (3)	7048 (1)	1490 (1)	57 (1)
Fe(2)	5709 (3)	7945 (1)	2077 (1)	52 (1)
C(1A)	6684 (21)	6482 (10)	1969 (10)	74 (10)
O(1A)	6684 (17)	6064 (8)	2297 (7)	103 (9)
C(1B)	5078 (23)	6873 (11)	1357 (10)	79 (11)
O(1B)	4201 (18)	6748 (9)	1298 (8)	121 (10)
C(1C)	7395 (26)	6735 (12)	998 (10)	90 (12)
O(1C)	8144 (21)	6521 (11)	651 (10)	149 (12)
C(2A)	5784 (18)	7581 (10)	2688 (9)	65 (9)
O(2A)	5846 (14)	7319 (7)	3120 (6)	86 (7)
C(2B)	5771 (22)	8685 (11)	2213 (10)	83 (11)
O(2B)	5714 (15)	9195 (8)	2337 (7)	94 (8)
C(2C)	4162 (19)	7886 (9)	2040 (8)	56 (8)
O(2C)	3256 (15)	7847 (7)	2029 (6)	83 (7)
Te(4)	3049 (1)	1948 (1)	3772 (1)	92 (1)
Te(5)	4574 (1)	3095 (1)	3815 (1)	66 (1)
Te(6)	6368 (2)	3802 (1)	3828 (1)	77 (1)
Fe(3)	4998 (3)	1990 (1)	4186 (1)	62 (1)
Fe(4)	4844 (3)	2256 (1)	3159 (1)	70 (1)
C(3A)	5075 (22)	1181 (12)	4228 (10)	86 (11)
O(3A)	5121 (15)	660 (8)	4301 (8)	100 (8)
C(3B)	4569 (20)	2147 (10)	4854 (12)	79 (10)
O(3B)	4330 (18)	2232 (9)	5304 (7)	120 (10)
C(3C)	6472 (21)	2027 (10)	4165 (9)	70 (10)
O(3C)	7497 (17)	2032 (8)	4175 (8)	111 (9)
C(4A)	4173 (25)	2639 (12)	2623 (12)	97 (13)
O(4A)	3714 (24)	2870 (10)	2247 (9)	169 (13)
C(4B)	6314 (27)	2400 (15)	2965 (10)	107 (14)
O(4B)	7220 (20)	2525 (13)	2792 (10)	186 (15)
C(4C)	5063 (29)	1511 (14)	2936 (11)	111 (14)
O(4C)	5148 (21)	1011 (9)	2793 (10)	155 (12)
K(1)	1130 (1)	5951 (1)	3907 (1)	51 (1)
K(2)	4007 (1)	4264 (1)	1274 (1)	69 (1)
K(3)	10241 (1)	9240 (1)	3814 (1)	51 (1)
K(4)	673 (1)	690 (1)	1172 (1)	58 (1)

Table III. Summary of Crystallographic Data for $[Fe_2Te_3(CO)_6][(K\cdot crypt)_2]\cdot{}^1/_2en$

empirical formula	$K_2Fe_2Te_3C_{43}H_{76}O_{18}N_5$
space group	$P\bar{1}$ (No. 2)
temp, K	298
cell dimens (at 298 K)	
a, Å	11.531 (7)
b, Å	22.098 (12)
c, Å	25.341 (13)
α, deg	85.22 (4)
β, deg	84.60 (5)
γ, deg	84.39 (5)
Z, molecules/cell	4
V, Å³	6380 (6)
d_{calcd}, g/cm³	1.507
wavelength, (Å)	0.71073
mol wt	1523.8
linear abs coeff, mm⁻¹	1.991
R(*F*)	0.0947
$R_w(F)$	0.1264

Synthesis

Ethylenediamine (en) extracts of a melt of nominal composition K_2Te_4 react with $Fe(CO)_3(\eta^4\text{-butadiene})$ in the presence of crypt[12] to form $Fe_2Te_3(CO)_6^{2-}$ (**1**) in good yield according to eq 1. The iron-telluride complex was isolated as a dark crystalline solid with two (K·crypt)⁺ cations and half an en solvate molecule per anion. The relative ratios of reagents in eq 1 do not affect the course

$$Fe(CO)_3(\eta^4\text{-butadiene}) + \text{excess } K_2Te_4 \xrightarrow{\text{en/crypt}} [Fe_2Te_3(CO)_6][(K\cdot crypt)_2]\cdot{}^1\!/_2en \quad (1)$$

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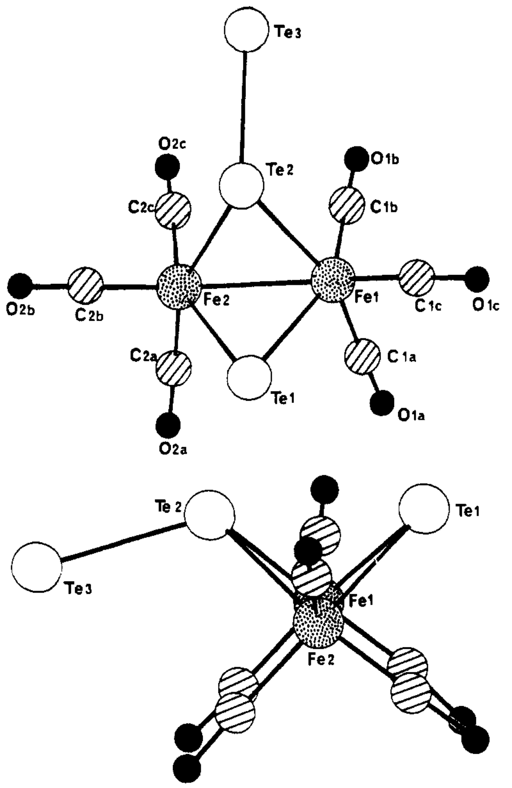

Figure 1. Two Chem-X[29] perspectives of the $Fe_2Te_3(CO)_6^{2-}$ ion.

of reaction in that **1** is the only iron-containing product isolated even when large excesses of polytellurides are employed. The complex is fairly air- and moisture-sensitive in en solutions but stable to air in the solid state for short periods of time. The crystalline material is moderately soluble in en and DMF. The K·crypt salt of **1** has been characterized by EDAX analysis, bulk elemental analysis, solid-state and solution IR spectroscopy, and single-crystal X-ray diffraction.

The rate of reaction of eq 1 is relatively slow, with $t_\infty \approx 18$ h at 25 °C in en solutions. When the synthesis is monitored by solution IR spectroscopy, several interesting features can be elucidated. First, when reaction 1 is conducted in the absence of crypt, **1** is not observed even after long reaction times. The IR spectrum of the crypt-free solution is invariant with time and contains two major carbonyl bands at 2047 and 1973 cm^{-1}, which are identical with those of the $Fe(CO)_3(\eta^4$-butadiene) starting material in the same solvent.[17] In addition, a new minor band at 1904 cm^{-1} is present and also does not change in intensity with time. Upon addition of crypt, new CO bands are observed at 1932 and 1839 cm^{-1} after 5 min along with the three other bands previously described. Over a 16-h period, all of these absorbances disappear as the bands for **1** emerge (see Figure 2). After 18 h, **1** is the only metal–carbonyl species detectable in solution—even in the presence of excess polytelluride. Although these unidentified transient complexes appear to be reduced $Fe(CO)_x^{n-}$ species, it is not known if they are intermediates in the formation of **1** or if they have any Te atoms associated with them.

Reaction 1 could be proceeding by various mechanisms including oxidative addition of a Te_x fragment in consort with diene displacement or by an initial reduction of the Fe center by a Te_x^{n-} ion (electron transfer) prompting diene elimination. Displacement of modified diene ligands from $Fe(CO)_3(\eta^4$-diene) complexes used in organic synthesis is often accomplished by using external oxidants, such as Ce(IV), ethanolic $FeCl_3$, or Me_3NO, but the diene ligands are tightly bound to the $Fe(CO)_3$ centers and these processes are not always efficient.[18] On the other hand, certain diene complexes such as $Fe(CO)_3(\eta^4$-cyclohexadiene) undergo reversible one electron reductions, but attempts to reduce $Fe(CO)_3(\eta^4$-butadiene) electrochemically rapidly leads to total decomposition.[19] The slow rate of $Fe(CO)_3(\eta^4$-butadiene) disappearance in the present reaction suggests that the formation of **1** is not proceeding by an initial outer-sphere electron transfer from the Te_x^{n-} species to the Fe center.

Figure 2. IR spectra of the $[Fe_2Te_3(CO)_6][(K\cdot crypt)_2]\cdot{}^1/_2$en complex recorded in en solution (a) and in the solid state (b).

Solid-State Structure

The compound crystallizes in the space group $P\bar{1}$ and contains two independent $Fe_2Te_3(CO)_6^{2-}$ anions, four $(K\cdot crypt)^+$ cations, and an en solvate molecule in the asymmetric unit (146 non-H atoms). Two views of the $Fe_2Te_3(CO)_6^{2-}$ ion are shown in Figure 1. Selected bond distances and angles are listed in Table I, and the fractional coordinates are given in Table II. A summary of the crystallographic data is given in Table III. As is common with most large transition-metal p-block polyanions with several cryptated countercations,[3,4,20] the final residuals are somewhat high with $R = 9.5$ and $R_w = 12.6\%$.

The two independent $Fe_2Te_3(CO)_6^{2-}$ anions are virtually identical as evidenced by the structural parameters listed in Table I. Each ion has C_s molecular symmetry with a virtual mirror plane defined by the three Te atoms. The Fe atoms are in square-pyramidal coordination environments with CO ligands occupying the apical positions. The two Fe centers are fused along a common basal edge by virtue of the μ-Te^{2-} and μ_2-η^1-Te_2^{2-} ligands. The $Fe_2Te_3(CO)_6$ core in **1** bears a striking resemblance to the $Fe_2S_3(CO)_6$ core in $Fe_4S_4(CO)_{12}^{2-}$ (**2**).[21] The Fe–Fe distance in **1** of 2.626 (12) Å (average) is identical with that observed in **2** and is consistent with an Fe–Fe single bond. Perhaps the most unusual feature in the structure of **1** is the μ_2-η^1-Te_2^{2-} ligand that spans the dimetal center. The Te(2)–Te(3) contact is 2.71 (2) Å, representing a typical Te–Te single bond. For comparison, the Te–Te distances in PhTeTePh[22] and $Pd(Te_4)_2^{2-}$[8] are 2.72 and 2.74 Å, respectively. The Te(1)–Te(2) separation of 3.23 (2) Å (average) is long relative to the Te(2)–Te(3) contact and can be considered nonbonding. The *exo*-Te atom Te(3) is not involved in any intermolecular interactions with the en solvate molecule, the cations, or the other anion in the solid state. The μ_2-η^1-Te_2^{2-} fragment is virtually identical with those found in $Mo_4Te_{16}(en)_4^{2-}$

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(17) IR data for $Fe(CO)_3(\eta^4$-butadiene) in en (CaF_2 cell): ν(CO) = 2047, 1973 cm^{-1}. The IR spectrum of the neat compound is somewhat different, with ν(CO) = 2055.9, 1990.0, and 1980.1 cm^{-1}. See: Davidson, G. *Inorg. Chim. Acta* **1969**, *3*, 596.

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and is reminiscent of the unusual, rare μ_2-η^1-S_2^{2-} ligand in $(C_5Me_5)_2Cr_2(\mu\text{-}S_2)_2(\mu\text{-}S)$.[23] The Fe–Te distances average 2.57 Å and are quite similar to those observed in other $(CO)_xFe$–Te species.[24,25] The Fe–C and C–O distances in **1** average 1.75 and 1.17 Å, respectively, but little significance can be given to these values.

Spectroscopic Studies

The solution and solid-state IR spectra for the K·crypt salt of **1** are shown in Figure 2. While some minor differences exist between the two spectra, the band frequencies and intensities suggest that the $Fe_2Te_3(CO)_6^{2-}$ ion remains intact in solution. The CO bands for **1** are shifted by ca. 60 cm^{-1} to lower energy relative to those of the parent $Fe(CO)_3(\eta^4$-butadiene) complex.[17] In contrast, the CO bands in the related $M_9Cr(CO)_3^{4-}$ ions (M = Sn, Pb)[3,26] and $M_7Cr(CO)_3^{3-}$ ions (M = As, Sb)[4,27] are red-shifted by 150–200 cm^{-1} relative to the $Cr(CO)_3(\eta^6$-arene) precursors. The trend in CO stretching frequencies among these main-group transition-metal ions is consistent with expectations based on charge per cluster and electronegativities of the main-group atoms.[28]

Conclusion

$Fe(CO)_3(\eta^4$-butadiene) reacts with en extracts of polytellurides in the presence of crypt to form $Fe_2Te_3(CO)_6^{2-}$ (**1**) in good yield. The rate of formation is relatively slow with $t_\infty \approx 18$ h, but **1** is the only carbonyl-containing product present in solution upon completion of reaction even when large excesses of polytellurides are used. The activation of the polytelluride ions by the addition of crypt is directly analogous to the crypt activations of the Sn_9^{4-} and As_7^{3-} ions necessary to form the corresponding $Sn_9Cr(CO)_3^{4-}$ and $As_7Cr(CO)_3^{3-}$ complexes.[3,4] Solution IR spectroscopic studies suggest that **1** maintains its integrity when dissolved. The structure of **1** consists of an $Fe_2(CO)_6$ core with a bridging Te^{2-} ion and an unusual μ_2-η^1-Te_2^{2-} ligand. The Fe–Fe separation is 2.63 (1) Å, which is indicative of an iron–iron single bond. It is interesting to note that **1** and Rauchfuss' $fe_2(\mu\text{-}Te_2)(CO)_6$ differ only by a single Te^{2-} ion.[28]

Supplementary Material Available: Complete crystallographic summary, ORTEP representations of each $Fe_2Te_3(CO)_6^{2-}$ anion, and complete listings of fractional coordinates, anisotropic thermal parameters, and bond distances and angles (15 pages); a listing of calculated and observed structure factors (58 pages). Ordering information is given on any current masthead page.

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Synthesis and Multinuclear NMR Studies of $[M\{o\text{-}C_6H_4(TeMe)_2\}X_2]$ (M = Pd, Pt; X = Cl, Br, I). The Presence of a Characteristic Ring Contribution to ^{125}Te NMR Chemical Shifts

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The complexes $[M\{o\text{-}C_6H_4(TeMe)_2\}X_2]$ (M = Pd, Pt; X = Cl, Br, I) and $[N^nBu_4][Ir\{o\text{-}C_6H_4(TeMe)_2\}X_4]$ (X = Cl, Br) have been prepared, and characterized by analysis and UV-visible, IR, and multinuclear (^1H, $^{195}Pt\{^1H\}$, $^{125}Te\{^1H\}$) NMR spectroscopy. Two isomers, *meso* and *dl* invertomers, are present in each complex. The coordination shifts in the ^{125}Te NMR spectra of the Pd and Pt complexes are compared with those reported for $[M\{PhTe(CH_2)_3TePh\}X_2]$ and for the analogous *cis*-$[M(TeMePh)_2X_2]$. It is found that, compared with the monodentate complexes, the chelate complexes having five-membered rings exhibit large high frequency coordination shifts and those having six-membered rings have small low frequency shifts. Data on complexes of $o\text{-}C_6H_4(TePh)_2$ and $MeTe(CH_2)_3TeMe$ compared with data for $TePh_2$ and $TeMe_2$ complexes show similar effects, which are rationalized in terms of a characteristic "chelate ring contribution", defined as Δ_R, to the shifts of the bidentate telluroethers. Similar phenomena are known for ^{31}P and ^{77}Se shifts in analogous complexes, but this is the first demonstration of the effect in ^{125}Te NMR.

Introduction

We have recently reported[1] palladium(II) and platinum(II) six-membered chelate ring complexes of two ditelluroethers, $RTe(CH_2)_3TeR$ (R = Me or Ph). Unfortunately $RTe(CH_2)_2TeR$ compounds have not been obtained,[2] but we report here similar complexes of $o\text{-}C_6H_4(TeMe)_2$[3] that contain five-membered chelate rings. In addition to providing a second series of rare chelated ditelluroether complexes,[4] this work allowed the investigation of the effect of ring size upon the ^{125}Te NMR chemical shifts. Many studies of chelating diphosphine complexes[5] have shown that $\delta(^{31}P)$ values are very dependent upon the ring size present. In comparison with the equivalent cis complex containing similar monodentate phosphines, it is observed that five-membered chelate ring diphosphines have large high-frequency coordination shifts, while four- or six-membered rings have small low-frequency shifts. This effect has been systematized in terms of a "chelate ring contribution" to the shifts by Garrou,[6] who also pointed out the usefulness of such an effect in structural assignments. We recently observed similar effects in the ^{77}Se NMR shifts in diselenoether complexes,[7-9] and here we report evidence for the same effect in a third nucleus—^{125}Te.

Experimental Section

Physical measurements were made as described previously.[1] In particular, ^{195}Pt NMR spectra are referenced to external 1 mol dm^{-3} Na_2-

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