An excellent fit was obtained from the following set of parameters: $J_1 = 17.5$ cm^{-1}, $J_2 = J_3 = -22$ cm^{-1}, $g = 2.0$ (solid line of Figure 3). The fitted g value seems too low, but in other similar nickel clusters a value of 2.00 has also been found.[6] To confirm the validity of this fit, in particular the presence of ferromagnetic exchange interactions, the data were fit to a noninteracting dimer model (i.e. J_1 was set to be 0) giving $J = -12.5$ cm^{-1} and $g = 2.05$. As can be seen in Figure 3 (dashed line) this model is completely unable to reproduce the position of the maximum in χ_m. Therefore, the exchange network of this cluster is formed by four ferromagnetic exchange interactions (J_1) and two antiferromagnetic ones (J_2 and J_3).

The different sign of these interactions can be attributed to the presence of two types of Ni–O–Ni angles as a consequence of the distortions within the [Ni_4O_4] unit produced by the bridging tzdt molecules. Thus, in the four faces of the cube containing tzdt ligands the Ni–O–Ni angles (95–96°) are in the range in which the Ni-Ni-exchange interactions are ferromagnetic.[4] In the other two faces the Ni–O–Ni angles are 103°. These angles are unusually large for a cubane framework, giving rise to a resultant antiferromagnetic exchange interaction. There is only one other example, $[Ni_4(OMe)_4(O_2CMe)_2(tmb)_4]^{2+}$,[6] in which similar distortions in the cubane framework have been found. In this complex, the presence of two bridging acetates leads to two ferromagnetic exchange interactions (≈18 cm^{-1}), associated with Ni–O–Ni angles of ca. 93°, and to four antiferromagnetic ones (≈−9 cm^{-1}), associated with angles of ca. 101°. A comparison of the exchange parameters of this compound with those found in $[Ni_4(OH)_4(tzdt)_4(py)_4]$ allow us to notice that while the ferromagnetic exchange interaction is similar in both compounds, the antiferromagnetic one is significantly stronger in the latter (−22 compared to −9 cm^{-1}). This result emphasizes the sensitivity of the antiferromagnetic exchange interactions with respect to the Ni–O–Ni angles.

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Registry No. $[Ni(tzdt)_2]$, 30798-12-0; $[Ni(tzdt)_2(py)_2]$, 140875-45-2; $[Ni_4(OH)_4(tzdt)_4(py)_4]\cdot 2py$, 140875-47-4.

Supplementary Material Available: Tables of complete crystal and refinement data, calculated atomic coordinates and anisotropic thermal parameters, and bond distances and angles (6 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Group VI Metal Carbonyl Tellurides: Structures of $[M_4(CO)_{18}(\mu_3\text{-}Te)_2]^{2-}$ (M = Cr, W), $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_2)]^{2-}$, and $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]^{2-}$

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The reactions of group 6 metal carbonyls with soluble polytellurides, Te_x^{2-} ($x = 1$–4), have been investigated using a 3-fold excess of the metal carbonyls. Several novel products have been isolated and characterized as their PPh_4^+ salts, including $[M_4(CO)_{18}(\mu_3\text{-}Te)_2]^{2-}$, (M = Cr, Mo, W), $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_2)]^{2-}$, and $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]^{2-}$. The reaction of Te_2^{2-} with 3 equiv of $M(CO)_6$ generates $[M_4(CO)_{18}(\mu_3\text{-}Te)_2]^{2-}$ in good yield. The molecule contains a four-membered M_2Te_2 ring with a transannular metal–metal bond, which renders the molecules diamagnetic. One remaining lone pair on each of the Te atoms is donated to an out of plane $M(CO)_5$ fragment. The ring metal atoms are formally oxidized to M(I) states. Reaction of Te^{2-} with excess $Cr(CO)_6$ leads to formation of $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_2)]^{2-}$, which contains four $Cr(CO)_5$ fragments bound to lone pairs on a Te_2^{2-} chains. Reaction of any long chain Te_x^{2-} fragment, where $x \geq 3$, with excess $Cr(CO)_6$ leads to formation of $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]^{2-}$, containing a Te_3^{2-} chain with two $Cr(CO)_5$ fragments bound to lone pairs on each terminal tellurium. Two polymorphs of this anion have been isolated and characterized. No evidence of similar reactivity could be obtained with $W(CO)_6$ or $Mo(CO)_6$. All compounds have been characterized by IR and ^{125}Te NMR spectroscopy in addition to single-crystal diffraction. Structural data: for $[(C_6H_5)_4P]_2[W_4(CO)_{18}(\mu_3\text{-}Te)_2]$ (I), triclinic, $P\bar{1}$, $a = 10.026$ (4) Å, $b = 12.411$ (4) Å, $c = 14.404$ (5) Å, $\alpha = 81.21$ (3)°, $\beta = 87.45$ (3)°, $\gamma = 69.28$ (3)°, $V = 1657$ (1) Å^3, $Z = 1$, $R(F_o) = 0.0266$; for $[(C_6H_5)_4P]_2[Cr_4(CO)_{18}(\mu_3\text{-}Te)_2]$ (II), triclinic, $P\bar{1}$, 10.039 (3) Å, $b = 12.287$ (4) Å, $c = 14.275$ (5) Å, $\alpha = 81.54$ (3)°, $\beta = 88.00$ (3)°, $\gamma = 70.14$ (3)°, $V = 1637.9$ (9) Å^3, $Z = 1$, $R(F_o) = 0.0382$; for $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_2)]\cdot CH_2Cl_2$ (III), triclinic, $P\bar{1}$, $a = 11.753$ (6) Å, $b = 12.656$ (7) Å, $c = 26.670$ (15) Å, $\alpha = 76.63$ (4)°, $\beta = 85.30$ (4)°, $\gamma = 70.78$ (4)°, $V = 3644$ (3) Å^3, $Z = 2$, $R(F_o) = 0.0482$; for $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]$ (IVa), triclinic, $P\bar{1}$, $a = 10.610$ (3) Å, $b = 13.890$ (4) Å, $c = 14.425$ (4) Å, $\alpha = 115.14$ (2)°, $\beta = 91.98$ (2)°, $\gamma = 106.83$ (2)°, $V = 1812$ (1) Å^3, $Z = 1$, $R(F_o) = 0.0395$; for $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]\cdot CH_2Cl_2$ (IVb), orthorhombic, *Pbca*, $a = 14.557$ (3) Å, $b = 29.074$ (8) Å, $c = 35.995$ (8) Å, $V = 15234$ (16) Å^3, $Z = 8$, $R(F_o) = 0.0872$.

Introduction

Historically the chemistry of transition metal complexes containing telluride ligands has been a relatively unexplored area, although recently the chemistry has been expanding very quickly.[1-4] This is due in part to the use of metal telluride clusters as sources of new solid-state materials.[5] In addition, the enormous role of sulfide atoms[6] and other p-block elements[7] in cluster building suggests that the heavy chalcogenides would also be suitable for this purpose.[8] Recent results show that tellurides are quite active in metal cluster building reactions[9] but that they often display chemistry considerably different from that displayed by sulfides due to the large size, increased nucleophilicity, and

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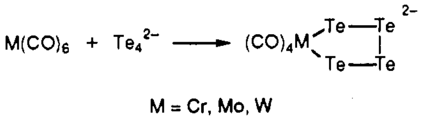
metallic character of the tellurium atoms.

We are currently investigating the coordination chemistry of soluble polychalcogenides with simple metal carbonyls.[10-13] These systems have an extraordinarily rich chemistry which is belied by their stoichiometric simplicity. In particular, the polysulfides and polyselenides readily induce oxidation of low-valent metal centers with formation of higher valent metal chalcogenide complexes.[11]

$$M(CO)_6 + E_4{}^{2-} \rightarrow ME_4{}^{2-}$$

$$M = Mo, W \qquad E = S, Se$$

In contrast polytellurides show a much decreased tendency to induce oxidative decarbonylation. For example we found that polytellurides react with an equimolar amount of group 6 metal carbonyls with simple substitution of CO ligands to form a tetratelluride chelate ring.[12]



These are extremely stable molecules and have resisted attempts to thermally induce oxidative decarbonylation. Recently, however, we found that changes in initial stoichiometry and reaction conditions lead to very diverse reactivity.[13] This paper is a report of some further chemistry of group 6 metal carbonyls with soluble polytellurides.

Experimental Section

The polytelluride anions are extremely air sensitive in solution and were handled in purified argon under rigorously anaerobic conditions, using standard Schlenk techniques. All solvents were the highest available grade, dried over activated sieves and bubbled with argon. All solids were handled in a Vacuum Atmospheres glovebox under argon. The metal carbonyls and other fine chemicals were purchased from commercial houses and used as received. The ^{125}Te NMR spectra were obtained on a Bruker AC300 instrument in sealed 10-mm tubes, in DMF with 0.5 mL of CD_3CN added to obtain lock. The spectra were referenced to an external sample of 1 M $Te(OH)_6$ in D_2O, and shifts are reported relative to Me_2Te = 0 ppm by adding 712 to our measured values. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. Magnetic susceptibility measurements were performed using the Gouy technique at 21 °C.

Preparation of Polytellurides. All polytellurides were prepared in a similar fashion. Tellurium powder and potassium were combined in a flask in the correct stoichiometry to produce approximately 5 g of product. Dry NH_3 (ca. 20 ml) was distilled into the flask and the reaction stirred at −78 °C for 4 h and the NH_3 removed by distillation. Fresh NH_3 was added to the flask and the reaction stirred again for 4 h to insure complete reaction of the potassium. Removal of the NH_3 resulted in formation of a black microcrystalline product.

Preparation of Polytellurides in Situ. In a typical reaction, a solution containing $Te_3{}^{2-}$ was prepared by stirring K (0.076 g, 1.94 mmol) and Te (0.375 g, 2.94 mmol) in 10 mL of DMF for 8 h at 25 °C to yield a violet solution. All other polytelluride solutions were prepared in a similar manner.

Synthesis of $[(C_6H_5)_4P]_2[Te_4]$. The procedure used was a modification of literature methods.[14] A sample of K_2Te_2 (0.750 g, 2.25 mmol), prepared as described above, was dissolved in DMF (30 mL) and stirred for 30 min. The solution was filtered and the solid washed with two 5-mL portions of DMF to dissolve any polytelluride remaining of the frit. A solution of PPh_4Br (1.887 g, 4.50 mmol) in 10 mL of DMF was added to the polytelluride solution. Slow addition of THF (10 mL) and overnight storage at 4 °C produced a black crystalline product in 74% yield, which was isolated by filtration.

Synthesis of $[(C_6H_5)_4P]_2[W_4(CO)_{18}(\mu_3\text{-}Te)_2]$ (I). A solution of K_2Te_2 (0.100 g, 0.300 mmol) and $W(CO)_6$ (0.317 g, 0.901 mmol) in 10 mL of DMF was stirred under static vacuum at 100 °C for 24 h. The brown solution was filtered, PPh_4Br (0.19 g, 0.45 mmol) was added, and the DMF was removed under vacuum. The resultant oily solid was washed with 5 mL of CH_2Cl_2 and a red brown crystalline product remained. This solid was redissolved in 2 mL of DMF and layered with 10 mL of diethyl ether. Overnight storage at 4 °C produced red brown crystals, which were isolated by filtration. Yield: 65% based on $W(CO)_6$. IR, Nujol mull (cm^{-1}): $\nu(CO)$ = 2047 (s), 2017 (w), 1997 (s), 1963 (m), 1924 (s, br), 1901 (m), 1892 (m), 1859 (s). Anal. Calcd for $C_{66}H_{40}O_{18}P_2Te_2W_4$: C, 36.47; H, 1.85. Found: C, 36.09; H, 1.85. ^{125}Te NMR (CD_3CN): $\delta = -508.0$; $\omega_{1/2}$ = 137 Hz.

Synthesis of $[(C_6H_5)_4P]_2[Mo_4(CO)_{18}Te_2]$. As described above, a solution of K_2Te_2 (0.100 g, 0.300 mmol) and $Mo(CO)_6$ (0.238 g, 0.900 mmol) in 10 mL of DMF was stirred under static vacuum at 100 °C for 24 h. The brown solution was filtered, treated with 0.19 g (0.45 mmol) of PPh_4Br, and worked up as described above. Recrystallization from 2 mL of DMF and 10 mL of diethyl ether results in formation of red brown crystals in 37% yield. IR, Nujol mull (cm^{-1}): $\nu(CO)$ = 2047 (s), 1997 (s), 1968 (m), 1931 (s, br), 1901 (m), 1889 (m), 1860 (m). Anal. Calcd for $C_{66}H_{40}Mo_4O_{18}P_2Te_2$: C, 43.51; H, 2.21. Found: C, 42.90; H, 2.06.

Synthesis of $[(C_6H_5)_4P]_2[Cr_4(CO)_{18}(\mu_3\text{-}Te)_2]$ (II). A solution containing $Te_2{}^{2-}$ (0.600 mmol) was prepared in situ by stirring the appropriate amount of K and Te metals in 10 mL of DMF as described above. A 0.396-g (1.80-mmol) sample of $Cr(CO)_6$ was added and the solution stirred under static vacuum at 100 °C for 24 h. The red solution was filtered, and 0.30 g (0.70 mmol) of PPh_4Br was added. Upon slow addition of ether (10 mL), and storage overnight at 4 °C, a tan powder formed, which was removed by filtration. The solvent was removed from the filtrate under vacuum, and the oily solid was dissolved in CH_2Cl_2 (5 mL) and layered with diethyl ether. Overnight storage at 5 °C produced red crystals, which were isolated by filtration. Yield: 24%. IR, Nujol mull (cm^{-1}): $\nu(CO)$ = 2029 (s), 1979 (s), 1924 (s, br), 1896 (s), 1879 (m), 1865 (m). Anal. Calcd for $C_{66}H_{40}Cr_4O_{18}P_2Te_2$: C, 48.16; H, 2.45. Found: C, 47.87; H, 2.38. ^{125}Te NMR (CD_3CN): $\delta = 1454$; $\omega_{1/2}$ = 147.5 Hz.

Synthesis of $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_2)]\cdot CH_2Cl_2$ (III). Method A. A solution containing 0.200 g (0.99 mmol) of K_2Te was prepared in situ as described above. A 0.641-g (2.90-mmol) sample of $Cr(CO)_6$ was added and the solution stirred under static vacuum at 100 °C for 24 h. The dark green solution was filtered and PPh_4Br was added. Upon slow addition of 10 mL of diethyl ether and storage overnight at 4 °C, a tan powder formed and was removed by filtration. The solvent was removed from the filtrate under vacuum and the brown oily solid redissolved in 5 mL of CH_2Cl_2 and layered with 5 mL of diethyl ether. Overnight storage at 4 °C resulted in formation of green-brown hexagonal-shaped crystals, which were isolated by filtration. Yield 15%. IR, Nujol mull (cm^{-1}): $\nu(CO)$ = 2030 (s, br), 1983 (w), 1966 (w), 1923 (s, br), 1862 (s, br). Anal. Calcd for $C_{69}H_{42}Cl_2Cr_4O_{20}P_2Te_2$: C, 46.37; H, 2.31. Found: C, 46.59; H, 2.33. ^{125}Te NMR (CD_3CN): $\delta = -281$.

Synthesis of $[(C_6H_5)_4P]_2[Cr_4(CO)_{18}(\mu_3\text{-}Te)_2]$ and $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_2)]$. Method B. A flask was charged with 0.200 g of either K_2Te or K_2Te_2, and 0.641 g (2.91 mmol) of $Cr(CO)_6$ and 10 mL of DMF were added. The mixture was stirred under static vacuum at 100 °C for 24 h. The resultant brown solution was filtered, and 0.30 g (0.70 mmol) of PPh_4Br was added. Slow addition of 10 mL of diethyl ether and overnight storage at 4 °C resulted in formation of a tan powder,

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Table I. Crystallographic Data for I, II, III, IVa, and IVb

	I	II	III	IVa	IVb
chem formula	$C_{66}H_{40}O_{18}P_2Te_2W_4$	$C_{66}H_{40}O_{18}P_2Cr_4Te_2$	$C_{67}H_{42}O_{20}P_2Cl_2Cr_4Te_2$	$C_{68}H_{40}O_{20}P_2Cr_4Te_3$	$C_{69}H_{42}O_{20}P_2Cl_2Cr_4Te_3$
fw	2173.60	1646.20	1763.13	1829.78	1914.75
a/Å	10.026 (4)	10.039 (3)	11.753 (6)	10.610 (3)	14.557 (3)
b/Å	12.411 (4)	12.287 (4)	12.656 (7)	13.890 (4)	29.074 (8)
c/Å	14.404 (5)	14.275 (5)	26.670 (15)	14.425 (4)	35.995 (8)
α/deg	81.21 (3)	81.54 (3)	76.63 (4)	115.14 (2)	90
β/deg	87.45 (3)	88.00 (3)	85.30 (4)	91.98 (2)	90
γ/deg	69.28 (3)	70.14 (3)	70.78 (4)	106.83 (2)	90
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
V/Å^3	1657 (1)	1637.9 (9)	3644 (3)	1812 (1)	15234 (16)
Z	1	1	2	1	8
D_{calc}/g cm^{-3}	2.18	1.67	1.61	1.68	1.67
μ/cm^{-1}	80.5	16.2	15.4	18.7	18.5
transm coeff	0.48–1.00	0.86–1.00	0.81–1.00	0.89–1.00	0.71–1.00
$R(F_o)^a$	0.0266	0.0382	0.0482	0.0395	0.0872
$R_w(F_o)^b$	0.0322	0.0398	0.0616	0.0564	0.0898

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o) = [(\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2)]^{1/2}$.

which was removed by filtration. The solvent was removed from the filtrate under vacuum, and the oily solid was dissolved in 5 mL of CH_2Cl_2 and layered with 5 mL of ether. Overnight storage at 4 °C produced red brown crystals of $[(C_6H_5)_4P]_2[Cr_4(CO)_{18}Te_2]$, which were isolated by filtration. After these were harvested, the filtrate was layered with a second 5-mL aliquot of ether. Overnight storage at 4 °C produced brown crystals of $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te)_2]$. The yields varied from reaction to reaction but were typically 5% and 15%, respectively.

Synthesis of $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]$ (IVa). Method A. A 0.200-g (0.600-mmol) sample of powder of nominal composition K_2Te_3 and 0.396 g (1.8 mmol) of $Cr(CO)_6$ were reacted as described above. The brown solution was filtered, and 0.300 g (0.70 mmol) of PPh_4Br was added. Slow addition of 10 mL of diethyl ether and overnight storage at 4 °C yielded a tan powder, which was removed by filtration. The solvent was removed under vacuum and the oily solid dissolved in 5 mL of CH_2Cl_2 and layered with 5 mL of diethyl ether. Overnight storage at 4 °C yielded a gray powder, which was assumed to be elemental tellurium and was removed by filtration. Slow addition of a fresh 5-mL aliquot of diethyl ether followed by overnight storage at 4 °C resulted in brown crystals, which were isolated by filtration. Yield: 42%. IR, Nujol mull (cm^{-1}): ν(CO) = 2043 (m), 2027 (s), 1968 (m), 1953 (m), 1918 (s, br), 1858 (s, br). Anal. Calcd for $C_{68}H_{40}Cr_4O_{20}P_2Te_3$: C, 44.63; H, 2.20. Found: C, 44.26; H, 2.10. ^{125}Te NMR (DMF with external D_2O lock): δ = −160 (2 Te), 404 (1 Te) (J_{Te-Te} = 1640 Hz). The reaction proceeds in identical fashion if K_2Te_4 is used as the initial telluride source.

Synthesis of $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]$. Method B. A flask was charged with 0.250 g (0.210 mmol) of $(PPh_4)_2Te_4$ and 0.139 g (0.631 mmol) of $Cr(CO)_6$, 10 mL of DMF added, and the mixture stirred under static vacuum at 100 °C for 24 h. The resultant brown solution was filtered and layered with 10 mL of a diethyl ether. Following workup as described above, brown crystals of the product could be isolated in 55% yield.

Synthesis of $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]\cdot CH_2Cl_2$ (IVb). A 10-mL solution of composition Te_3^{2-} (0.43 mmol) was prepared by dissolving the appropriate amounts of K and Te in 10 mL of DMF in situ as described above. A 0.286-g (1.30–mmol) sample of $Cr(CO)_6$ was added and the solution stirred under static vacuum at 100 °C for 24 h. The brown solution was filtered and 0.27 g (0.65 mmol) of PPh_4Br added. Upon slow addition of 10 mL of diethyl ether and overnight storage at 4 °C, a tan powder formed, which was removed by filtration. The solvent was removed from the filtrate under vacuum, and the brown oily solid was redissolved in 5 mL of CH_2Cl_2. Workup with diethyl ether and storage at 4 °C produced red brown crystals, which were isolated by filtration. Yield: 50%.

X-ray Crystallography. Intensity measurements were made at ambient temperature (21 °C) on a Nicolet R3mV diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073). Data were measured using $\omega/2\Theta$ scans for compounds I, II, and IVa, and ω scans for III and IVb to a maximum 2Θ value of 45.0° for I - IVa and 40.0° for IVb. The data were corrected for Lorentz and polarization effects; in addition, the data for IVb were corrected for a 13% decay in the intensities of three standard reflections. An empirical absorption correction, based on azimuthal scans of several moderately intense reflections, was applied for each compound. The structures were solved by direct methods and refined by full-matrix least-squares methods using the SHELXTL+ package of programs. For I, II, and IVa, the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included as a riding model at idealized positions with a refined isotropic group thermal parameter. The phenyl rings of the cations for III and IVb were treated as rigid groups with the individual atoms refined isotropically; all other non-hydrogen atoms were refined anisotropically. Methylene chloride solvent molecules were included in the lattices of III and IVb. Relevant crystallographic data for all five compounds are listed in Table I. Important atomic coordinates and isotropic thermal parameters for I, II, III, IVa, and IVb are listed in Tables II–VI, respectively. Full crystallographic details and complete structure information are given in the supplementary material.

Table II. Selected Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for I

	x	*y*	*z*	*U*(eq)^a
W(1)	621 (1)	985 (1)	8 (1)	44 (1)
W(2)	1469 (1)	−1445 (1)	3078 (1)	48 (1)
Te(1)	−473 (1)	−25 (1)	1596 (1)	43 (1)
O(1)	−2516 (8)	2804 (6)	−351 (7)	99 (4)
O(2)	1782 (7)	2640 (5)	−1379 (5)	79 (3)
O(3)	3814 (8)	−757 (7)	211 (5)	86 (4)
O(4)	1317 (11)	2303 (8)	1500 (6)	129 (6)
O(5)	−917 (8)	−584 (8)	4560 (6)	100 (4)
O(6)	469 (9)	−3578 (6)	2983 (5)	86 (4)
O(7)	4278 (8)	−2534 (7)	1940 (5)	95 (4)
O(8)	2327 (9)	696 (7)	3347 (7)	111 (5)
O(9)	3449 (9)	−2767 (8)	4781 (6)	109 (4)
C(1)	−1391 (11)	2140 (8)	−216 (7)	64 (4)
C(2)	1359 (9)	2024 (7)	−879 (6)	53 (4)
C(3)	2637 (10)	−152 (8)	170 (6)	57 (4)
C(4)	1045 (12)	1807 (9)	961 (8)	78 (5)
C(5)	−101 (10)	−866 (8)	4000 (7)	63 (4)
C(6)	821 (10)	−2808 (8)	2995 (6)	59 (4)
C(7)	3211 (11)	−2102 (7)	2283 (7)	63 (4)
C(8)	2011 (10)	−55 (9)	3186 (7)	69 (4)
C(9)	2698 (11)	−2286 (8)	4146 (7)	65 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Discussion

Structure of $[(C_6H_5)_4P]_2[M_4(CO)_{18}(\mu_3\text{-}Te)_2]$ (M = Cr, Mo, W). The structure of the tungsten and chromium species have been fully determined (I and II, respectively), and the molybdenum analogue has been determined to be isomorphous with the other two. Each structure contains a metal–metal bonded dimer of two metal tetracarbonyl fragments (see Figure 1). The dimer is bridged by two tellurides generating a planar four membered ring. Each telluride also donates a lone pair of electrons to a metal pentacarbonyl fragment, one above and one below the ring (see Figure 2). The overall effect is two open edge-sharing tetrahedra in a trans conformation. The shape of the molecule is somewhat similar to an iron thallium carbonyl cluster reported recently,[15]

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(15) Whitmire, K. H.; Cassidy, J. M.; Rheingold, A. L.; Ryan, R. R. *Inorg. Chem.* **1988**, *27*, 1347.

Table III. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for II

	x	*y*	*z*	*U*(eq)[a]
Cr(1)	606 (1)	980 (1)	18 (1)	53 (1)
Cr(2)	1484 (1)	-1444 (1)	3010 (1)	57 (1)
Te(1)	-363 (1)	-83 (1)	1546 (1)	50 (1)
O(1)	-2380 (6)	2721 (5)	-259 (5)	108 (3)
O(2)	1692 (6)	2609 (5)	-1321 (4)	83 (3)
O(3)	3662 (6)	-657 (5)	212 (4)	85 (3)
O(4)	1280 (9)	2265 (7)	1462 (5)	137 (5)
O(5)	-830 (6)	-559 (6)	4408 (4)	104 (4)
O(6)	506 (7)	-3512 (5)	2934 (4)	94 (3)
O(7)	4139 (7)	-2510 (5)	1916 (5)	109 (3)
O(8)	2325 (7)	615 (6)	3299 (6)	122 (4)
O(9)	3363 (7)	-2709 (6)	4673 (5)	114 (4)
C(1)	-1263 (9)	2052 (7)	-146 (6)	75 (4)
C(2)	1269 (7)	1963 (6)	-834 (5)	56 (3)
C(3)	2481 (9)	-79 (7)	146 (5)	61 (3)
C(4)	1004 (10)	1757 (8)	926 (6)	87 (5)
C(5)	4 (8)	-883 (7)	3852 (6)	66 (4)
C(6)	849 (9)	-2706 (7)	2936 (5)	68 (4)
C(7)	3077 (9)	-2065 (6)	2253 (6)	73 (4)
C(8)	1988 (8)	-131 (7)	3123 (6)	77 (4)
C(9)	2608 (9)	-2237 (8)	4030 (7)	78 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

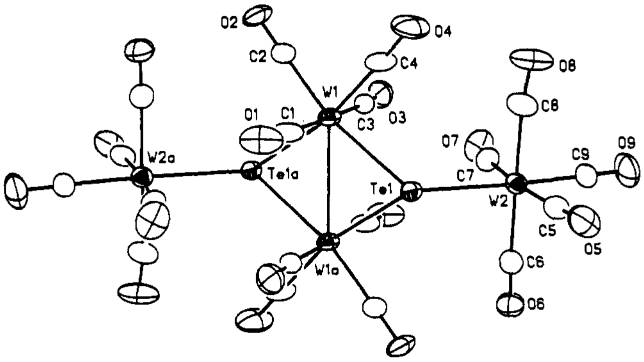

Figure 1. Thermal ellipsoid plot (35% probability) of $[W_4(CO)_{18}(\mu_3\text{-}Te)_2]^{2-}$, anion of molecule I.

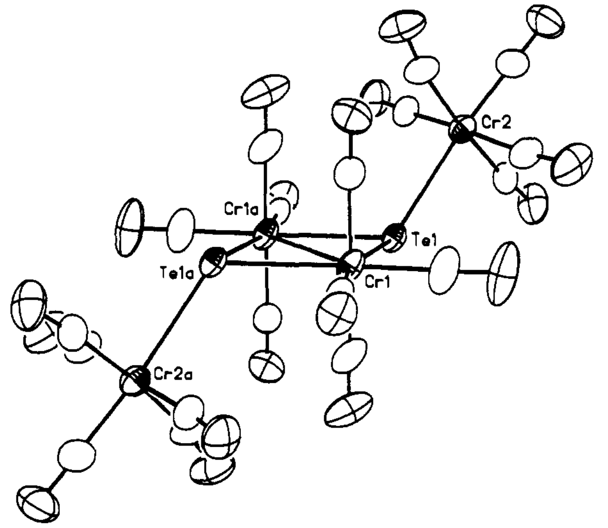

Figure 2. Thermal ellipsoid plot (35% probability) of $[Cr_4(CO)_{18}(\mu_3\text{-}Te)_2]^{2-}$, anion of molecule II.

Table IV. Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for III

	x	*y*	*z*	*U*(eq)[a]
Te(1)	5394 (1)	7299 (1)	2937 (1)	42 (1)
Te(2)	3239 (1)	7311 (1)	2569 (1)	41 (1)
Cr(1)	5615 (1)	9402 (1)	2476 (1)	58 (1)
Cr(2)	2431 (1)	5796 (1)	3301 (1)	43 (1)
Cr(3)	7358 (1)	5381 (1)	2922 (1)	47 (1)
Cr(4)	3265 (1)	7055 (1)	1573 (1)	49 (1)
O(11)	2954 (7)	10497 (7)	2252 (3)	88 (4)
O(12)	8328 (8)	8480 (9)	2670 (5)	141 (6)
O(13)	5889 (10)	11720 (7)	2063 (4)	131 (6)
O(14)	5993 (9)	8889 (7)	1404 (4)	101 (5)
O(15)	5141 (9)	9907 (9)	3542 (4)	111 (6)
O(21)	1298 (7)	4254 (6)	4037 (3)	74 (3)
O(22)	3864 (6)	5933 (6)	4165 (3)	67 (3)
O(23)	468 (7)	7899 (7)	3511 (3)	94 (4)
O(24)	4426 (7)	3683 (7)	3124 (3)	91 (4)
O(25)	805 (7)	5547 (7)	2547 (3)	89 (4)
O(31)	9594 (7)	3341 (7)	3016 (4)	102 (4)
O(32)	6229 (6)	4246 (6)	3861 (3)	78 (3)
O(33)	8584 (7)	6270 (7)	3617 (3)	90 (4)
O(34)	6272 (8)	4267 (7)	2273 (3)	93 (5)
O(35)	8282 (7)	6621 (7)	1936 (3)	85 (4)
O(41)	3611 (7)	4507 (7)	1917 (3)	86 (4)
O(42)	572 (7)	7685 (7)	1726 (3)	84 (4)
O(43)	2990 (7)	6814 (7)	502 (3)	80 (4)
O(44)	2906 (8)	9599 (7)	1202 (3)	97 (4)
O(45)	5965 (6)	6564 (6)	1435 (3)	76 (4)
C(11)	3963 (10)	10046 (8)	2342 (4)	64 (5)
C(12)	7297 (12)	8813 (10)	2600 (6)	92 (7)
C(13)	5774 (12)	10818 (10)	2220 (5)	90 (6)
C(14)	5861 (10)	9054 (9)	1808 (5)	73 (5)
C(15)	5316 (10)	9710 (10)	3144 (5)	73 (6)
C(21)	1746 (8)	4860 (8)	3762 (4)	55 (4)
C(22)	3351 (8)	5892 (7)	3824 (4)	49 (4)
C(23)	1201 (9)	7127 (9)	3423 (4)	59 (5)
C(24)	3700 (9)	4499 (8)	3179 (4)	54 (4)
C(25)	1445 (8)	5666 (8)	2806 (4)	53 (4)
C(31)	8737 (9)	4118 (9)	2980 (4)	64 (5)
C(32)	6644 (8)	4685 (8)	3512 (4)	54 (4)
C(33)	8101 (8)	5967 (8)	3343 (4)	58 (4)
C(34)	6643 (10)	4700 (8)	2515 (4)	61 (5)
C(35)	7942 (8)	6166 (8)	2307 (4)	58 (4)
C(41)	3493 (8)	5456 (9)	1805 (4)	58 (4)
C(42)	1599 (9)	7427 (8)	1674 (4)	54 (4)
C(43)	3107 (9)	6913 (9)	916 (4)	61 (5)
C(44)	3064 (10)	8649 (9)	1345 (4)	64 (5)
C(45)	4960 (9)	6739 (8)	1501 (4)	52 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

though the bonding is considerably different.

The metal-metal bond distance in the tungsten compound, I, is 3.115 (1) Å (see Table VII), which is somewhat long for typical chalcogenide-bridged tungsten-tungsten distances. A tabulation of W-W bond distances in a variety of tungsten sulfides and selenides reveals bond distances in the vicinity of 2.90 Å.[16] However, there can be little doubt about the presence of a metal-metal bond in the present systems as magnetic susceptibility data clearly reveal the molecules to be diamagnetic. The long distance is probably due to the large size of the bridging tellurium atoms.

The tungsten-tellurium distances within the ring average 2.80 (1) Å, which is comparable to those in other tungsten carbonyl tellurides (average 2.837 Å in $[(CO)_4WTe_4]^{2-}$,[12] 2.763 Å in $[(W(CO)_3)_6(Te_2)_4]^{2-}$,[13] and 2.739 Å in $(W(CO)_5)_3Te_2$[9d]). The W-Te distance to the terminal $W(CO)_5$ fragment is somewhat longer (2.872 (1) Å) but is still reasonable. The W-Te-W angle within the ring is quite distorted from the ideal tetrahedron at 67.7 (1)°, which is probably the result of the metal-metal bond. The other angles around the telluride are considerably closer to the ideal tetrahedral angle.

All the metal-carbonyl distances are normal and angles are typical for octahedral coordination around the tungsten centers. The tetraphenylphosphonium counterions are well separated and structurally unremarkable.

The structure of the chromium molecule is virtually identical with that of the tungsten analogue. The Cr-Cr distance is also

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[16] Wardle, R. W. M.; Bhaduri, S.; Chua, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 1747.

Table V. Selected Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for IVa

	x	*y*	*z*	*U*(eq)^a
Te(1)	44 (1)	−3488 (1)	1335 (1)	52 (1)
Te(2)	−992 (1)	−5722 (1)	−71 (1)	66 (1)
Te(3)	1006 (1)	−5817 (1)	−1224 (1)	51 (1)
Cr(1)	−1805 (1)	−2536 (1)	1039 (1)	66 (1)
Cr(2)	217 (1)	−3514 (1)	3227 (1)	64 (1)
O(1)	−3053 (6)	−976 (5)	772 (5)	113 (4)
O(2)	−1536 (6)	−1105 (5)	3352 (4)	106 (3)
O(3)	−4406 (11)	−4064 (8)	1158 (7)	212 (7)
O(4)	−2379 (8)	−3936 (5)	−1295 (5)	129 (4)
O(5)	868 (7)	−1117 (6)	935 (6)	144 (4)
O(6)	−2578 (6)	−3516 (7)	3546 (6)	136 (5)
O(7)	872 (5)	−3073 (5)	5430 (4)	101 (3)
O(8)	−624 (6)	−6033 (5)	2542 (5)	116 (4)
O(9)	3004 (6)	−3520 (5)	2833 (5)	103 (4)
O(10)	1294 (6)	−999 (6)	3935 (6)	123 (4)
C(1)	−2597 (7)	−1590 (6)	881 (5)	76 (3)
C(2)	−1608 (7)	−1657 (6)	2487 (6)	77 (4)
C(3)	−3442 (11)	−3507 (7)	1097 (7)	114 (5)
C(4)	−2130 (8)	−3429 (6)	−419 (6)	84 (4)
C(5)	−136 (8)	−1657 (7)	993 (6)	92 (4)
C(6)	−1522 (8)	−3510 (7)	3407 (6)	89 (4)
C(7)	641 (7)	−3240 (6)	4580 (6)	72 (4)
C(8)	−329 (7)	−5096 (7)	2774 (6)	80 (4)
C(9)	1959 (8)	−3528 (5)	2969 (6)	71 (4)
C(10)	849 (7)	−1954 (7)	3649 (6)	82 (4)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthoganlized $\mathbf{U}_{ij}$ tensor.

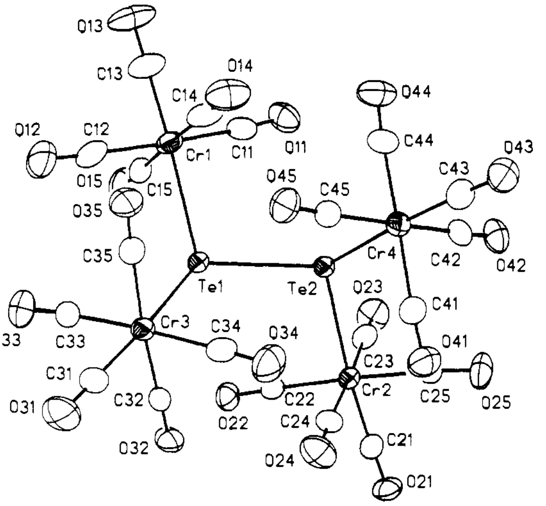

Figure 3. Thermal ellipsoid plot (35% probability) of $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_3\text{-}Te_2)]^{2-}$, anion of molecule III.

Table VI. Selected Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for IVb

	x	*y*	*z*	*U*(eq)^a
Te(1)	406 (1)	6680 (1)	1103 (1)	65 (1)
Te(2)	−44 (1)	8014 (1)	1252 (1)	64 (1)
Te(3)	1408 (2)	7444 (1)	1185 (1)	109 (1)
Cr(1)	1498 (3)	6238 (2)	603 (1)	67 (2)
Cr(2)	256 (3)	6310 (2)	1796 (1)	64 (2)
Cr(3)	−330 (4)	8281 (2)	530 (1)	74 (2)
Cr(4)	692 (4)	8656 (2)	1727 (1)	72 (2)
O(1)	1315 (20)	5331 (9)	996 (8)	105 (13)
O(2)	−197 (20)	5999 (11)	187 (7)	137 (16)
O(3)	1675 (21)	7094 (10)	137 (7)	128 (15)
O(4)	3126 (16)	6535 (8)	1044 (6)	90 (11)
O(5)	2689 (19)	5770 (11)	42 (6)	126 (15)
O(6)	1247 (20)	7074 (10)	2166 (7)	123 (15)
O(7)	−731 (17)	5561 (10)	1397 (6)	112 (13)
O(8)	−117 (14)	5831 (7)	2501 (6)	76 (9)
O(9)	−1515 (18)	6862 (12)	1872 (8)	139 (16)
O(10)	2119 (16)	5874 (10)	1724 (6)	110 (13)
O(11)	−576 (21)	7290 (9)	323 (8)	114 (13)
O(12)	−243 (23)	9300 (10)	701 (9)	141 (15)
O(13)	1691 (15)	8247 (11)	394 (8)	109 (13)
O(14)	−2383 (16)	8286 (10)	648 (6)	112 (12)
O(15)	−686 (16)	8488 (10)	−272 (6)	118 (13)
O(16)	−928 (19)	9227 (10)	1576 (8)	123 (15)
O(17)	2383 (17)	8113 (10)	1934 (7)	110 (13)
O(18)	1844 (19)	9023 (9)	1096 (7)	130 (14)
O(19)	−327 (18)	8180 (12)	2344 (8)	141 (16)
O(20)	1251 (19)	9366 (10)	2242 (7)	120 (14)
C(1)	1379 (28)	5709 (15)	859 (11)	95 (20)
C(2)	485 (29)	6087 (14)	359 (10)	105 (20)
C(3)	1638 (24)	6765 (13)	332 (10)	80 (18)
C(4)	2522 (25)	6413 (12)	870 (8)	76 (16)
C(5)	2208 (26)	5931 (15)	257 (8)	100 (21)
C(6)	841 (28)	6753 (14)	2004 (10)	94 (20)
C(7)	−328 (24)	5854 (12)	1558 (8)	75 (16)
C(8)	49 (22)	6032 (11)	2237 (9)	69 (14)
C(9)	−844 (23)	6645 (16)	1848 (8)	84 (18)
C(10)	1360 (23)	6045 (12)	1743 (8)	70 (15)
C(11)	−486 (28)	7669 (12)	390 (10)	80 (17)
C(12)	−261 (29)	8913 (13)	648 (10)	87 (17)
C(13)	937 (28)	8270 (14)	444 (9)	90 (18)
C(14)	−1586 (23)	8288 (12)	621 (8)	69 (14)
C(15)	−503 (25)	8418 (14)	38 (10)	120 (19)
C(16)	−248 (27)	9009 (16)	1610 (11)	108 (22)
C(17)	1722 (23)	8284 (15)	1846 (10)	92 (19)
C(18)	1366 (23)	8890 (12)	1347 (9)	81 (17)
C(19)	50 (27)	8362 (15)	2103 (10)	101 (20)
C(20)	979 (29)	9072 (16)	2029 (9)	110 (22)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VII. Selected Bond Distances (Å) and Angles (deg) for I

Distances			
W(1)–Te(1)	2.807 (1)	W(1)–W(1A)	3.115 (1)
W(1)–Te(1A)	2.788 (1)	W(2)–Te(1)	2.872 (1)
W–C(av)	2.00 (3)	C–O(av)	1.14 (2)
Angles			
Te(1)–W(1)–C(1)	86.0 (3)	Te(1)–W(1)–C(2)	163.9 (3)
Te(1)–W(1)–C(3)	96.2 (3)	Te(1)–W(1)–C(4)	80.9 (3)
Te(1)–W(1)–W(1A)	55.9 (1)	C(1)–W(1)–W(1A)	87.6 (3)
C(2)–W(1)–W(1A)	139.7 (3)	C(3)–W(1)–W(1A)	92.7 (3)
C(4)–W(1)–W(1A)	136.6 (3)	Te(1)–W(1)–Te(1A)	112.3 (1)
C(1)–W(1)–Te(1A)	91.3 (3)	C(2)–W(1)–Te(1A)	83.4 (3)
C(3)–W(1)–Te(1A)	86.8 (3)	C(4)–W(1)–Te(1A)	166.3 (3)
W(1A)–W(1)–Te(1A)	56.5 (1)	Te(1)–W(2)–C(5)	88.3 (2)
Te(1)–W(2)–C(6)	91.1 (2)	Te(1)–W(2)–C(7)	98.4 (2)
Te(1)–W(2)–C(8)	87.9 (3)	Te(1)–W(2)–C(9)	174.7 (3)
W(1)–Te(1)–W(2)	118.5 (1)	W(1)–Te(1)–W(1A)	67.7 (1)
W(2)–Te(1)–W(1A)	118.6 (1)	C–W–C(cis; av)	89 (3)
C–W–C(trans; av)	176 (2)	W–C–O(av)	176 (3)

quite long at 3.052 (2) Å (Table VIII), but this is shorter than the Cr–Cr distance in the prototype chromium dimer $(C_5H_5)_2Cr_2(CO)_6$ (3.281 (1) Å).[17] The long distance in the cyclopentadienyl compound was rationalized on the basis of steric repulsions. However, we feel that the long distance in our compound is due to the presence of the large telluride atom. The Cr–Te distances are somewhat shorter than in the tungsten analogue (ring distances average 2.691 (2) Å), but are still comparable to those in $[Cr(CO)_4Te_4]^{2-}$.[12] Again the Cr–Te distance to the terminal $Cr(CO)_5$ fragment is somewhat longer (2.781 (1) Å) and the Cr–Te–Cr angle in the ring is quite acute at 69.1°. All other structural aspects of the molecule are unremarkable.

Structure of $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_2)]$ (III). This structure consists of two well-separated tetraphenylphosphonium cations and an unusual $[Cr_4(CO)_{20}Te_2]^{2-}$ dianion. It has a Te_2^{2-} chain which is attached to four $Cr(CO)_5$ fragments, two on each tellurium atom (see Figure 3). The remaining lone pairs on each tellurium atom are in a gauche conformation (vida infra). The Te–Te distance is clearly within bonding distance at 2.784 (2) Å (see Table IX) (for comparison the Te–Te distance in $(C_6H_5)_2Te_2$ is 2.71 Å[18]) and is typical for Te–Te bonds in metal

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[17] Adams, R. D.; Collins, D. E.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749.

Table VIII. Selected Bond Distances (Å) and Angles (deg) for II

Distances			
Cr(1)-Te(1)	2.699 (2)	Cr(1)-Cr(1A)	3.052 (2)
Cr(1)-Te(1A)	2.684 (2)	Cr(2)-Te(1)	2.781 (2)
Cr-C(av)	1.87 (3)	C-O(av)	1.15 (1)
Angles			
Te(1)-Cr(1)-C(1)	86.4 (3)	Te(1)-Cr(1)-C(2)	166.1 (3)
Te(1)-Cr(1)-C(3)	95.1 (2)	Te(1)-Cr(1)-C(4)	81.4 (3)
Te(1)-Cr(1)-Te(1A)	110.9 (1)	Te(1)-Cr(1)-Cr(1A)	55.2 (1)
C(1)-Cr(1)-Te(1A)	91.4 (3)	C(2)-Cr(1)-Te(1A)	82.7 (3)
C(3)-Cr(1)-Te(1A)	87.5 (3)	C(4)-Cr(1)-Te(1A)	167.5 (3)
C(1)-Cr(1)-Cr(1A)	88.0 (3)	C(2)-Cr(1)-Cr(1A)	138.3 (3)
C(3)-Cr(1)-Cr(1A)	92.3 (3)	C(4)-Cr(1)-Cr(1A)	136.6 (3)
Te(1A)-Cr(1)-Cr(1A)	55.7 (1)	Te(1)-Cr(2)-C(5)	87.5 (2)
Te(1)-Cr(2)-C(6)	90.8 (2)	Te(1)-Cr(2)-C(7)	97.3 (2)
Te(1)-Cr(2)-C(8)	87.9 (2)	Te(1)-Cr(2)-C(9)	175.0 (3)
Cr(1)-Te(1)-Cr(2)	120.4 (1)	Cr(1)-Te(1)-Cr(1A)	69.1 (1)
Cr(2)-Te(1)-Cr(1A)	120.4 (1)	C-Cr-C(cis; av)	89 (2)
C-Cr-C(trans; av)	176 (2)	Cr-C-O(av)	175 (3)

Table IX. Selected Bond Distances (Å) and Angles (deg) for III

Distances			
Te(1)-Te(2)	2.784 (2)	Te(1)-Cr(1)	2.749 (2)
Te(1)-Cr(3)	2.750 (2)	Te(2)-Cr(2)	2.748 (2)
Te(2)-Cr(4)	2.747 (2)	Cr-C(av)	1.88 (3)
C-O(av)	1.14 (2)		
Angles			
Te(2)-Te(1)-Cr(1)	105.2 (1)	Te(2)-Te(1)-Cr(3)	116.7 (1)
Cr(1)-Te(1)-Cr(3)	118.1 (1)	Te(1)-Te(2)-Cr(2)	106.5 (1)
Te(1)-Te(2)-Cr(4)	116.5 (1)	Cr(2)-Te(2)-Cr(4)	115.7 (1)
Te(1)-Cr(1)-C(11)	92.3 (3)	Te(1)-Cr(1)-C(12)	90.2 (4)
Te(1)-Cr(1)-C(13)	175.5 (4)	Te(1)-Cr(1)-C(14)	93.0 (3)
Te(1)-Cr(1)-C(15)	84.9 (4)	Te(2)-Cr(2)-C(21)	174.4 (3)
Te(2)-Cr(2)-C(22)	92.7 (3)	Te(2)-Cr(2)-C(23)	84.8 (3)
Te(2)-Cr(2)-C(24)	93.7 (3)	Te(2)-Cr(2)-C(25)	90.5 (3)
Te(1)-Cr(3)-C(31)	173.4 (4)	Te(1)-Cr(3)-C(32)	85.2 (2)
Te(1)-Cr(3)-C(33)	85.6 (3)	Te(1)-Cr(3)-C(34)	96.8 (3)
Te(1)-Cr(3)-C(35)	90.5 (3)	Te(2)-Cr(4)-C(41)	91.2 (3)
Te(2)-Cr(4)-C(42)	83.3 (3)	Te(2)-Cr(4)-C(43)	173.8 (3)
Te(2)-Cr(4)-C(44)	88.4 (3)	Te(2)-Cr(4)-C(45)	93.4 (3)
C-Cr-C(cis; av)	90 (2)	C-Cr-C(trans; av)	177 (1)
Cr-C-O(av)	177 (1)		

complexes.[19] All of the $Cr(CO)_5$ fragments are oriented away from the Te-Te bond and are not involved in any bridging interactions.[9d,e]

This is a somewhat rare structural type for dichalcogenide fragments. There are several characterized metal ditellurides, which generally tend to be side bonded,[20] as well as several ditellurides, which are bonded to one metal center at each end.[5c,9c,i] There is a unique end-bonded μ_2,η^1 example,[21] as well as one other example of an unsupported ditelluride bonded to two dimolybdenum fragments in $[Mo_4Te_{16}(en)_4]^{2-}$.[9f]

The chromium-tellurium distances average 2.749 (2) Å, which is similar to the nonring Cr-Te distances in II described above. The telluride lone pair completes the octahedral coordination environment around each chromium atom, and all carbonyl distances and angles are reasonable. There does not appear to be any substantial distortion of the coordination environment due to steric congestion. This is somewhat surprising as intuition suggests that the molecule would be quite crowded.

Structure of $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]$ (IVa). The structure of IVa contains two well-separated tetraphenylphosphonium cations and a $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]^{2-}$ molecule. The dianion is similar to III in that it has four chromium pentacarbonyl fragments bound to two lone pairs at each end of a tritelluride chain (see Figure 4).

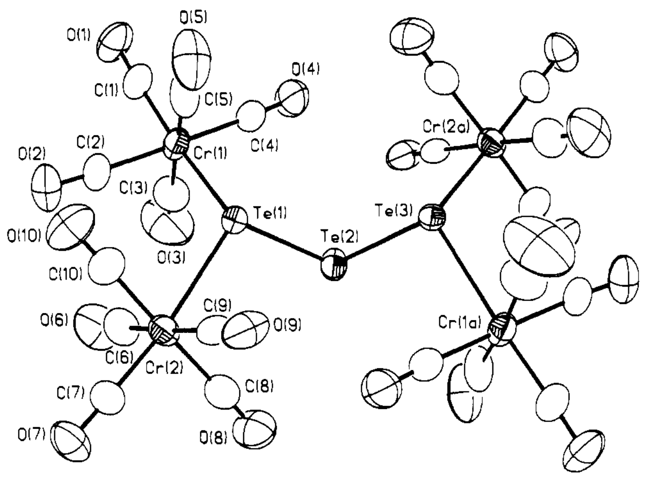

Figure 4. Thermal ellipsoid plot (35% probability) showing a top view of $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]^{2-}$, anion of molecule IVa.

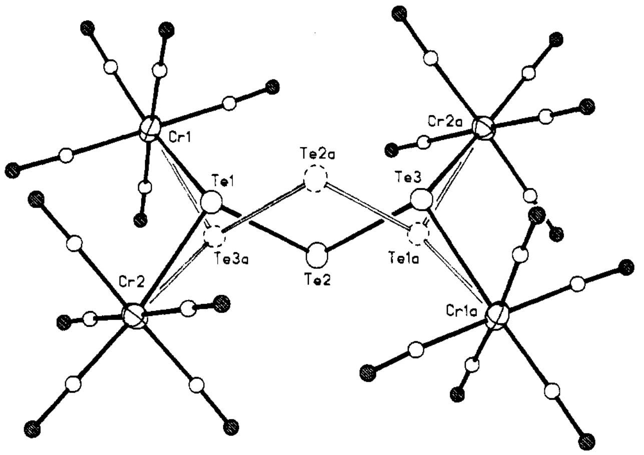

Figure 5. Side view of the anion of IVa showing the disorder involving the inverted Te_3^{2-} chain.

Table X. Selected Bond Distances (Å) and Angles (deg) for IVa

Distances			
Te(1)-Te(2)	2.734 (1)	Te(1)-Cr(1)	2.776 (2)
Te(1)-Cr(2)	2.745 (2)	Te(2)-Te(3)	2.738 (2)
Te(3)-Cr(1A)	2.765 (2)	Te(3)-Cr(2A)	2.767 (2)
Cr-C(av)	1.88 (2)	C-O(av)	1.14 (1)
Angles			
Te(2)-Te(1)-Cr(1)	105.3 (1)	Te(2)-Te(1)-Cr(2)	103.8 (1)
Cr(1)-Te(1)-Cr(2)	113.3 (1)	Te(1)-Te(2)-Te(3)	98.4 (1)
Te(2)-Te(3)-Cr(1A)	101.6 (1)	Te(2)-Te(3)-Cr(2A)	105.4 (1)
Cr(1A)-Te(3)-Cr(2A)	112.9 (1)	Te(1)-Cr(1)-C(1)	163.8 (2)
Te(1)-Cr(1)-C(2)	91.3 (3)	Te(1)-Cr(1)-C(3)	102.9 (4)
Te(1)-Cr(1)-C(4)	91.8 (3)	Te(1)-Cr(1)-C(5)	72.7 (3)
C(1)-Cr(1)-Te(3A)	171.2 (2)	C(2)-Cr(1)-Te(3A)	94.3 (3)
C(3)-Cr(1)-Te(3A)	78.3 (4)	C(4)-Cr(1)-Te(3A)	87.5 (3)
C(5)-Cr(1)-Te(3A)	97.3 (3)	Te(1)-Cr(2)-C(6)	95.8 (3)
Te(1)-Cr(2)-C(7)	167.3 (2)	Te(1)-Cr(2)-C(8)	99.9 (3)
Te(1)-Cr(2)-C(9)	81.1 (3)	Te(1)-Cr(2)-C(10)	79.1 (3)
C(6)-Cr(2)-Te(3A)	78.0 (3)	C(7)-Cr(2)-Te(3A)	166.8 (2)
C(8)-Cr(2)-Te(3A)	82.8 (3)	C(9)-Cr(2)-Te(3A)	98.9 (2)
C(10)-Cr(2)-Te(3A)	97.2 (3)	C-Cr-C(cis; av)	90 (2)
C-Cr-C(trans; av)	176 (1)	Cr-C-O(av)	177.4 (9)

The Cr-Te distances are slightly different at 2.776 (2) and 2.745 (2) Å (see Table X). However, the average of 2.76 (1) Å is similar to distances in III. The Te-Te distances are also quite normal at 2.734 (1) and 2.738 (1) Å.[18] The angle between the three tellurium atoms is 98.4 (1)°, which is somewhat compressed from the ideal tetrahedral angle. The Cr-Te-Cr angle is somewhat expanded from the ideal tetrahedral angle at 113.3 (1)°, and this is probably due to steric repulsion of the metal penta-

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(18) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, England, 1984.

(19) See table in ref 8, p 164.

(20) (a) DiVaira, M.; Peruzzini, M.; Stoppioni, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 916. (b) Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1981**, *20*, 3583. (c) DiVaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc., Chem. Commun.* **1986**, 374.

(21) Eichhorn, B. W.; Haushalter, R. C.; Merola, J. S. *Inorg. Chem.* **1990**, *29*, 728.

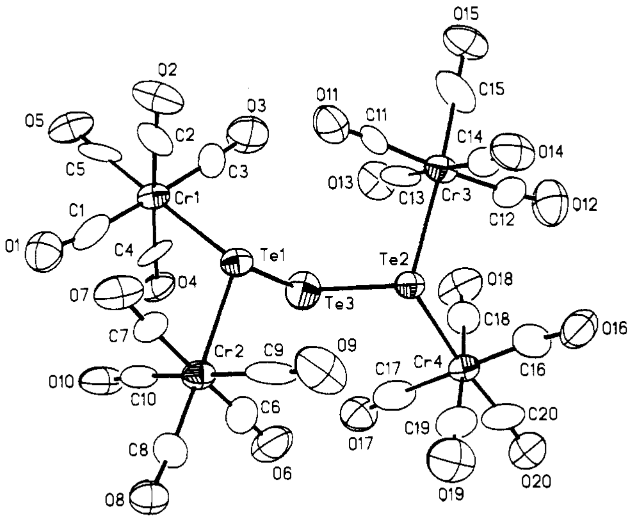

Figure 6. Thermal ellipsoid plot (35% probability) showing a top view of $[Cr_4(CO)_{20}(\eta^2-\mu_2-Te_3)]^{2-}$, anion of molecule IVb.

Table XI. Selected Bond Distances (Å) and Angles (deg) for IVb

	Distances		
Te(1)–Te(3)	2.673 (4)	Te(1)–Cr(1)	2.724 (6)
Te(1)–Cr(2)	2.728 (5)	Te(2)–Te(3)	2.697 (3)
Te(2)–Cr(3)	2.743 (5)	Te(2)–Cr(4)	2.748 (6)
Cr–C(av)	1.82 (6)	C–O(av)	1.17 (4)
	Angles		
Te(3)–Te(1)–Cr(1)	98.4 (1)	Te(3)–Te(1)–Cr(2)	105.7 (1)
Cr(1)–Te(1)–Cr(2)	117.7 (2)	Te(3)–Te(2)–Cr(3)	102.0 (1)
Te(3)–Te(2)–Cr(4)	99.6 (1)	Cr(3)–Te(2)–Cr(4)	117.1 (2)
Te(1)–Te(3)–Te(2)	95.3 (1)	Te(1)–Cr(1)–C(1)	90.5 (13)
Te(1)–Cr(1)–C(2)	87.6 (13)	Te(1)–Cr(1)–C(3)	91.2 (12)
Te(1)–Cr(1)–C(4)	89.8 (10)	Te(1)–Cr(1)–C(5)	178.3 (13)
Te(1)–Cr(2)–C(6)	93.6 (13)	Te(1)–Cr(2)–C(7)	83.8 (10)
Te(1)–Cr(2)–C(8)	173.8 (11)	Te(1)–Cr(2)–C(9)	87.3 (10)
Te(1)–Cr(2)–C(10)	89.9 (9)	Te(2)–Cr(3)–C(11)	90.2 (11)
Te(2)–Cr(3)–C(12)	93.2 (11)	Te(2)–Cr(3)–C(13)	90.1 (10)
Te(2)–Cr(3)–C(14)	89.2 (9)	Te(2)–Cr(3)–C(15)	176.0 (13)
Te(2)–Cr(4)–C(16)	86.8 (14)	Te(2)–Cr(4)–C(17)	93.6 (12)
Te(2)–Cr(4)–C(18)	89.8 (11)	Te(2)–Cr(4)–C(19)	86.9 (12)
Te(2)–Cr(4)–C(20)	171.5 (15)	C–Cr–C(cis; av)	90 (2)
C–Cr–C(trans; av)	177 (2)	Cr–C–O(av)	176 (4)

carbonyl fragments. The dianion contains a very interesting disorder involving an inversion of the bent tritelluride fragment about a crystallographic center of symmetry ($x = 0, y = y - {}^1/_2, z = 0$) (see Figure 5). Because the disorder is crystallographic, the populations of the two forms are equal. This disorder can be modeled quite cleanly without changing the position of any of the chromium centers or CO ligands. The environment around the chromium centers is only slightly distorted from octahedral. The carbonyl distances and angles are normal, and the thermal parameters reflect only slight distortion due to the disorder.

Structure of $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2-\mu_2-Te_3)]\cdot CH_2Cl_2$ (IVb). The structure of IVb contains a dianion which is similar to that in IVa (see Figure 6). However the crystal lattice contains a CH_2Cl_2 molecule of solvation and there is no disorder of the tritelluride. In addition the orientation of the metal pentacarbonyl fragments relative to each other is different (vida infra). The average Te–Te bond distances in IVb (2.68 (2) Å) are nearly equivalent to those in IVa (2.76 (1) Å) (see Table XI), as are the Cr–Te distances (2.736 (2) Å for IVb and 2.76 (1) Å for IVa). The central Te–Te–Te angle is again quite acute at 95.3 (1)°.

There have been several stable tritellurides reported, all of which contain bulky terminal groups.[22] They typically display Te–Te distances comparable to those in IV but have somewhat larger central Te–Te–Te angles (usually greater than 130°).

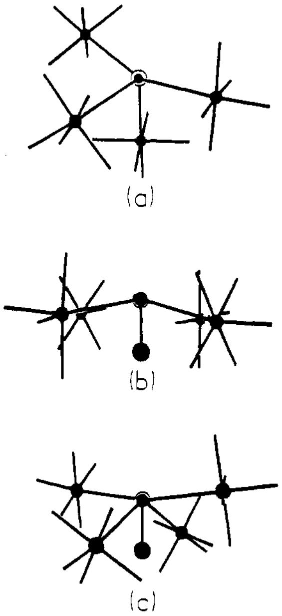

Figure 7. View of the anions of molecules III, IVa, and IVb (a, b, and c respectively) looking down the axis formed by the terminal tellurium atoms in each case. The different orientations of the $Cr(CO)_5$ and the tellurium lone pairs can be clearly discerned.

All of the metal complexed tellurium atoms in clusters III, IVa, and IVb contain one lone pair of electrons and their relative orientations are worthy of comment. In molecule III, the lone pairs are clearly gauche relative to the Te–Te bond axis (see Figure 7). In molecule IVa, the lone pairs are eclipsed relative to an axis through the terminal tellurides (see Figure 7), as are the metal pentacarbonyl fragments. However in IVb, the lone pairs again are gauche. The reasons for these steric preferences are not understood.

Synthesis of Group 6 Metal Carbonyl Tellurides. We have previously reported that the group 6 carbonyls react with an equimolar amount of soluble polytellurides to form metal tetracarbonyl fragment chelated by tetratelluride and that the reaction does not seem to be influenced by the nature of the polytelluride used as starting material.[12] However extensions of these reactions show that further chemistry is considerably more complex. We have found that the reaction of a 3-fold excess of metal carbonyl with soluble polytelluride leads to a variety of products, depending on the stoichiometry and nature of starting materials, as well as the reaction conditions employed.

Reaction of a 3-fold excess of group 6 metal carbonyl with a solution containing a reduced telluride anion of nominal composition Te_2^{2-} leads to formation and isolation of I. Mild pyrolysis speeds up the reaction considerably. A possible balanced equation is given as follows:

$$4M(CO)_6 + Te_2^{2-} \rightarrow [Cr_4(CO)_{18}(\mu_3\text{-}Te)_2]^{2-} + 6CO$$

$$M = \underset{\text{I}}{\text{Mo}}, \underset{\text{II}}{\text{W}}, \text{Cr}$$

The reaction appears to involve the oxidative addition of a ditelluride unit to a metal carbonyl with subsequent formation of a metal–metal bond.

The IR spectrum is quite distinctive in the carbonyl region for all three carbonyls, and the spectrum of the initial reaction mixture is very similar to that of the isolated product. This leads to the conclusion that I is the dominant carbonyl-containing product in solution for both molybdenum and tungsten. However, in our early experiments, the IR spectrum of the original reaction mixture of solutions containing chromium carbonyls appeared much more complex, leading to the conclusion that several other species were present. In hindsight this is not surprising considering the long, and presumably weak, Cr–Cr bond in II. It should be noted that

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[22] (a) Sladky, F.; Bildstein, B.; Rieker, C.; Gieren, A.; Betz, H.; Hübner, *J. Chem. Soc., Chem. Commun.* **1985**, 1800. (b) Hamor, T. A.; Al-Salim, N.; West, A. A.; McWhinnie, W. R. *J. Organomet. Chem.* **1986**, *310*, C5. (c) Kuhn, N.; Schumann, H.; Boese, R. *J. Chem. Soc., Chem. Commun.* **1987**, 1257.

to obtain pure II, an in situ preparation of Te_2^{2-}, made by reduction of Te metal by potassium in DMF, is required. Use of premade K_2Te_2 always leads to a mixture of II and III.

Subsequent experimentation showed that use of a more reduced telluride solution, namely that of nominal composition Te^{2-}, with $Cr(CO)_6$, leads to formation of III as the only isolable product.

$$4Cr(CO)_6 + 2Te^{2-} \xrightarrow{-2e} [(Cr(CO)_5)_4Te_2]^{2-}$$

We postulate that Te^{2-} forms a dimer dianion $[Cr(CO)_5–Te–Cr(CO)_5]^{2-}$, which is oxidized in solution with formation of a Te–Te bond. We have no evidence for the nature of the oxidant.

In contrast to the above reactions, when a less reduced form of polytelluride is used, such as salts of nominal composition K_2Te_3, K_2Te_4, Te_3^{2-}, Te_4^{2-} prepared in situ, or crystalline $[(C_6H_5)_4P]_2[Te_4]$, product IV forms readily.

$$\text{excess } Cr(CO)_6 + Te_n^{2-} \rightarrow [(Cr(CO)_5)_4Te_3]^{2-}$$

$$n = 3,4$$

It should be noted in all cases that the nature of the polytelluride solutions is still unclear. Even when crystalline tetratelluride salts, such as $[(C_6H_5)_4P]_2[Te_4]$, are used as starting materials, equilibration reactions can take place upon dissolution, generating a variety of polytellurides. So it is not known whether the chromium carbonyl fragments are selectively trapping Te_3^{2-} or are merely being isolated because they are the least soluble species. However, it is clear that less reduced, longer chain polytellurides, in the presence of $Cr(CO)_6$, produce IV in good yield as the only isolable product.

Product IV is reasonably stable. It slowly extrudes elemental tellurium to form III, either in room light or upon thermolysis at 125 °C. This reaction can be observed in a sealed NMR tube over several days. Also it is fairly air stable. It can remain intact in solution in the air for several hours. We attribute at least part of this stability to steric protection by the large carbonyl fragments. Product III is somewhat less stable, decomposing rapidly in the air to insoluble gray powders. This is probably caused by a large amount of steric strain, leading to bond dissociation.

The nature of the polytelluride solution has a significant effect on the chemistry in the chromium–telluride system. If the polytellurides are prepared in situ by the reaction of elemental potassium with elemental tellurium in DMF, as described, the products are considerably cleaner and can obtained in higher yield. If the polytelluride source is a premade potassium salt, such as K_2Te_2 or K_2Te_3, the reaction is more complex and it is difficult to obtain pure products. Furthermore it is obvious that equilibria are occurring in the reaction flask. It is well-known that the chemistry of polytellurides is quite complex in solution. Careful work by Schultz has shown that Te_2^{2-} and Te_3^{2-} can be prepared pure in liquid ammonia, but they were able to find no evidence for the existence of higher tellurides in the presence of alkali metal counterions.[23] However, higher tellurides such as Te_4^{2-} and Te_5^{2-} seem to be the dominant species in polar organic solvents, particularly in the presence of large organic counterions.[14] We conclude that the complexity of the polytelluride behavior in solution is responsible for much of the unusual chemistry observed in these metal carbonyl systems.

The tungsten and molybdenum carbonyls show no apparent tendency to form analogues of III and IV. We have been unable to observe any indications of their formations on the basis of IR spectra or through crystallization. It is known however that there is more chemistry in these systems, based on the previous isolation of a novel 14 vertex tungsten telluride cluster from the reaction[13]

$$3W(CO)_6 + Te_4^{2-} \rightarrow [W_6(CO)_{18}(Te_2)_4]^{2-}$$

Conversely, no evidence for Cr or Mo analogues to this cluster have been observed. Extensions of this chemistry are under investigation.

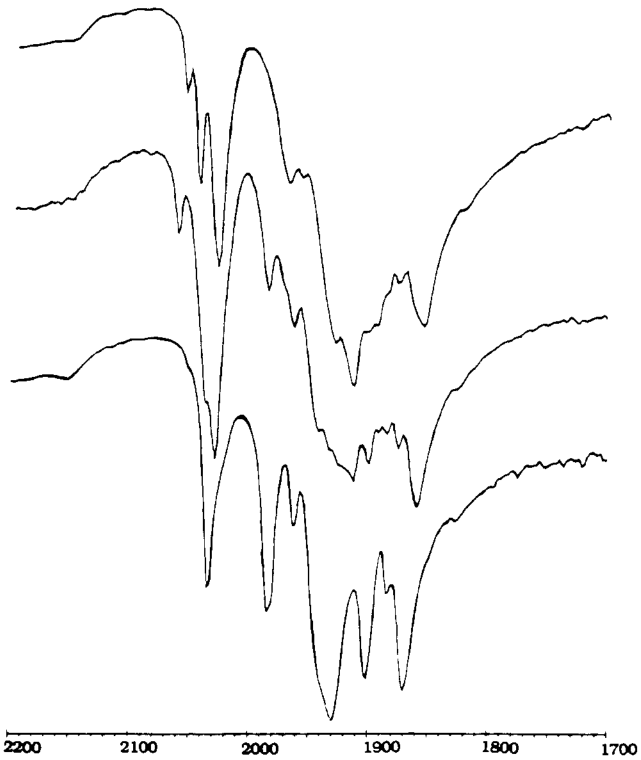

Figure 8. IR spectra of Nujol mulls of the CO stretching region of chromium carbonyl telluride clusters. From top to bottom the spectra represent II, III, and IVa.

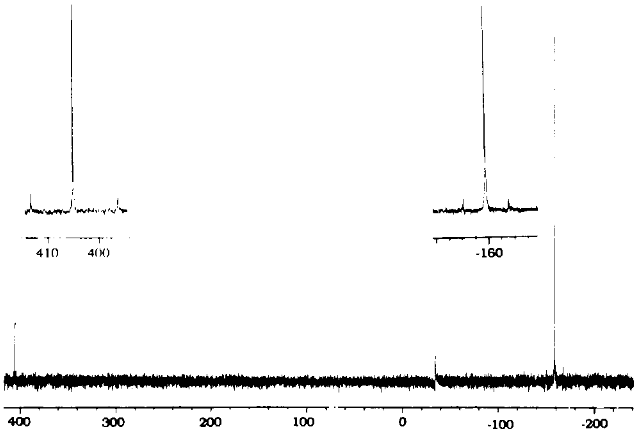

Figure 9. ^{125}Te NMR spectrum of $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]^{2-}$ in DMF solution. The satellites due to Te–Te coupling can be clearly discerned in each case. The greater intensity of the terminal resonance relative to the internal Te atom is probably due to faster relaxation of the terminal atoms caused by direct bonding to the transition metal. The small peak at center is due to an impurity.

Spectroscopy. The IR spectra of the carbonyl stretching region of these molecules are quite complex and distinctive (see Figure 8). The spectra for I, II, and their molybdenum analogue are nearly superimposable. The spectra for III and IV are also complex and possess a signature pattern.

The ^{125}Te NMR spectra have been obtained for molecules I, II, III, and IV (see Figure 9) with shifts given in the Experimental Section. The few ^{125}Te shifts which have been reported have a wide range of values.[14c,24,25] The shifts of I, III, and IV are all at reasonably low field but are within the range of observed values for complex tellurides.[25,26] Complex II has a shift of 1454 ppm, which is considerably downfield of any previously observed coordinated tellurides. Though impurities appear sporadically in

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(23) (a) Schultz, L. D.; Koehler, W. T. *Inorg. Chem.* **1987**, *26*, 1989. (b) Schultz, L. D. *Inorg. Chim. Acta* **1990**, *176*, 271.

(24) Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1983**, *22*, 1854.

(25) Herrmann, W. A.; Kneuper, H.-J. *J. Organomet. Chem.* **1988**, *344*, 193.

(26) See table in ref 8, p 175.

all the spectra, there is no evidence for observable isomers of IV in solution.

Preliminary T_1 measurements on I and III indicate that they have fast relaxation times of 16 and 23 ms, respectively, and spectra were obtained with no pulse delay. Despite this, the peaks of I and II were still somewhat broadened (about 140 Hz at half height). Since III and IV also had short relaxation times but had sharp peaks, we attribute the broadening of I and II to some molecular fluxionality in solution. The low solubility of I and II precludes variable-temperature studies. The low-field shift for II suggests some slight paramagnetic nature to the molecule in solution. The extremely long Cr–Cr bond may allow some thermal population of the low-lying metal–metal antibonding orbital. However, the obvious stability of compound II, along with the fact that a ^{125}Te NMR signal could be easily observed, leads us to conclude that there is no substantial dissociation occurring in solution.

Bonding. The bonding in I and II is fairly straightforward. Each telluride can be viewed as donating one lone pair of electrons to each metal tetracarbonyl fragment in the ring. If each telluride is considered to bear a 2– charge, then each ring metal center is formally 1+. This leads to the formation of the metal–metal bond, completing the 18-electron count around each metal center and rendering the molecule diamagnetic, as observed from Gouy measurements of I and II in the solid state. One of the remaining lone pairs of each telluride is donated to a neutral metal pentacarbonyl fragment exo to the ring.

Similarly, the bonding in III and IV can be explained by classical valence arguments. The Te_2^{2-} and Te_3^{2-} chains have three lone pairs and formal charges of 2– localized on the terminal tellurides. These terminal atoms each donate two lone pairs to $Cr(CO)_5$ fragments, completing the 18-electron count around the metal centers.

Conclusions

We have shown that the reaction of excess group 6 carbonyls with various polytellurides in solution is quite complex and leads to variety of unusual metal-rich products. We had previously demonstrated that equimolar amounts of metal carbonyl and polytelluride leads to simple substitution products and that excess tungsten carbonyl is susceptible to oxidation by Te_4^{2-}, leading to cluster formation.[13] In this paper we extend this chemistry using excess metal carbonyls and a variety of polytelluride starting materials. The identity of the products is extremely sensitive to the reaction conditions and stoichiometry employed, which is understandable given the complexity of the polytelluride equilibria in solution. The nature of these products highlights the ability of tellurides to act as excellent cluster building species.

The polytellurides can induce some oxidation of the low-valent metal centers upon coordination. However there is significantly less electron transfer than is the case with polyselenides or polysulfides, presumably because of the lower electron affinity of tellurium. However it is clear that under the proper conditions a large number of stable and interesting metal tellurides can be prepared.

Acknowledgment. We are indebted to the National Science Foundation for support of this work (Grant CHE-9102548). We are also grateful to Dr. Dan Bearden for assistance in obtaining ^{125}Te NMR data.

Supplementary Material Available: Tables of complete crystallographic data and complete listings of distances and angles, atomic coordinates, anisotropic thermal parameters, and hydrogen atom coordinates for structures I, II, III, IVa, and IVb (30 pages); tables of observed and calculated structure factors for all five structures (110 pages). Ordering information is given on any current masthead page.

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Reactions of [Pt(dien)Cl]Cl and [Pt(trpy)Cl]Cl with Thiols, Thioethers, and Dialkyl Disulfides: A ^{195}Pt NMR Study

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The reactions of monofunctional platinum compounds [Pt(dien)Cl]Cl (dien = 1,5-diamino-3-azapentane) and [Pt(trpy)Cl]Cl (trpy = 2,2′,2″-terpyridine) with thiols (RSH), thioethers (RSR), and disulfides (RSSR) have been investigated by ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopy. Empirical trends in ^{195}Pt NMR chemical shifts are noted in terms of the classes sulfur functional groups coordinated to platinum. It appears that neither the steric bulk nor the electronic character of the alkyl group makes a significant contribution to the ^{195}Pt nuclear shielding. Reactions of dialkyl disulfides with [Pt(dien)Cl]Cl initially lead to a monodentate complex $[Pt(dien)(RSSR)]^{2+}$ which can be isolated as the ClO_4^- or PF_6^- salts. In the presence of [Pt(dien)Cl]Cl, the monodentate disulfido complex undergoes further reaction to cleave the S–S bond in the disulfide ligand, via a redox process.

Introduction

The chemistry of transition metal complexes containing metal–sulfur bonds has become of considerable biological, environmental, and industrial importance during the past decade.[1-3] Organosulfur compounds are present in kerogens and crude oils, and they play an important role in coal processing. A knowledge of the distribution of various sulfur functional groups in petroleum fractions, coal, and coal-derived liquids is also very important to further our understanding of the role of sulfur in the generation of oil and natural gas.[4] A motivation behind our current interest in sulfur coordination to platinum is the possibility of developing a ^{195}Pt NMR method to identify organically bound sulfur (thiols, thiophenes, thioethers, disulfides) in coal materials.[5] As part of our strategy to make model complexes with sulfur ligands for ^{195}Pt

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