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The Unusual Paramagnetic Mixed-Metal Carbonyl Chalcogenide Clusters: $[E_2Cr_2Fe(CO)_{10}]^{2-}$ (E = Te, Se)

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The rare examples of electron-rich mixed-metal carbonyl telluride and selenide clusters $[E_2Cr_2Fe(CO)_{10}]^{2-}$ (E = Te, Se) have been demonstrated. These two novel carbonyl complexes exhibit the unusual paramagnetic behavior.

In the field of transition metal clusters, it is of great interest and challenge to study the nature of heteronuclear metal–metal interaction.[1] Whereas the chemistry of homonuclear transition metal clusters bridged by main group elements has been well-developed, the heteronuclear metal clusters of the similar types are comparatively less explored. In such heteronuclear metal carbonyl complexes, only very few electron-deficient or electron-rich species have been reported,[1,2] and most studies are focused on structural determinations but not on their cooperative magnetism as to possibly probe for the metal–metal bonding. The synthesis of mixed-metal carbonyl clusters usually involves complicated metal-substitution or cluster-expansion processes; however, direct routes remain rare due to lack of the practical methodology.[1] We wish to report herein the direct synthesis, structures, and magnetic properties of two unusual electron-rich mixed-metal carbonyl chalcogenide clusters $[E_2Cr_2Fe(CO)_{10}]^{2-}$ (E = Te, **1**; E = Se, **2**) which are formed from the treatment of chalcogen powder with a mixture of $Cr(CO)_6$ and $Fe(CO)_5$ in the concentrated KOH/MeOH solutions at specifically 35–40 °C. Anions **1** and **2** represent as well the first examples of selenium- and tellurium-bridged chromium–iron carbonyl clusters with direct Cr–Fe bonds.

Clusters **1** and **2** can be isolated as the $[PPN]^+$ salts and are fully characterized by spectroscopic methods and X-ray structure determinations.[3,4] According to the X-ray analysis, **1** contains a distorted Te_2Cr_2Fe trigonal bipyramidal core with two μ_3-Te atoms in the apical positions and one carbonyl bridging the Cr–Cr bond (Figure 1). Cluster **2** is isostructural

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(3) Crystal structure analysis of $[PPN]_2[\mathbf{1}]$ follows. $C_{82}H_{60}Cr_2FeN_2O_{10}P_4Te_2$: $M = 1772.25$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 12.7126(2)$ Å, $b = 16.3892(1)$ Å, $c = 20.7383(4)$ Å, $V = 3802.3(1)$ Å^3, $\rho_{calcd} = 1.548$ g cm^{-3}, Mo Kα, $\lambda = 0.71073$ Å, crystal dimensions about 0.25 × 0.20 × 0.15 mm^3; CCD SMART diffractometer, and Sadabs absorption correction ($T_{min} = 0.672$, $T_{max} = 0.928$), were used. A total of 25295 reflections were measured, and 11545 unique reflections ($2\theta < 50°$, $R_{int} = 0.0735$) were used in the refinement. All the non-hydrogen atoms were refined with anisotropic temperature factors. Full-matrix least-squares refinement on F^2 converged to $R = 0.1641$ (all data), 0.0821 ($I > 2\sigma(I)$); wR = 0.2541 (all data), 0.2063 ($I > 2\sigma(I)$). All calculations were performed using SHELXTL packages. Crystal structure data for $[PPN]_2[\mathbf{2}]$ follow. $C_{82}H_{60}Cr_2FeN_2O_{10}P_4Se_2$: $M = 3779.7$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 12.734(4)$ Å, $b = 16.417(5)$ Å, $c = 20.568(4)$ Å, $V = 3779.7(18)$ Å^3, $\rho_{calcd} = 1.472$ g cm^{-3}, Mo Kα, $\lambda = 0.70930$ Å, $\mu = 1.58$ mm^{-1}, transmission range 0.60–0.70, crystal dimensions about 0.45 × 0.40 × 0.30 mm^3. A total of 13284 unique reflections were collected on a Nonius (CAD-4) diffractometer at 298 K with 2θ between 2.0° and 50° using $\theta/2\theta$ scans, and an absorption correction by azimuthal (ψ) scans was applied. The structure was solved by direct methods and refined with NRCC-SDP-VAX packages with R (R_w) = 0.042 (0.044) for 7773 observed reflections ($I > 2\sigma(I)$), non-hydrogen atoms anisotropy.

(4) $[PPN]_2[\mathbf{1}]$: To a mixture of 0.26 g (2.01 mmol) of Te powder, 0.44 g (2.01 mmol) of $Cr(CO)_6$, and 7.35 g (130 mmol) of KOH was added slowly 0.26 mL (1.98 mmol) of $Fe(CO)_5$ in 15 mL of MeOH in the ice–water bath. The mixed solution was allowed to stir at 35–40 °C for 90 h. The resulting solution was filtered, the solvent was concentrated, and a solution of 1.20 g (2.09 mmol) of PPNCl in 10 mL of MeOH was then added to give the precipitate. The precipitate was then washed with deionized water and MeOH several times, extracted with THF, and recrystallized with $CH_2Cl_2/Et_2O = 1:2$ to collect the filtrate. The filtrate was dried and washed with Et_2O to give the brown sample, 0.08 g (0.12 mmol) of $[PPN]_2[\mathbf{1}]$ (12% based on Te). IR (ν_{CO}, CH_2Cl_2): 1999 w, 1975 w, 1949 w, 1900 s, 1872 m, 1852 m cm^{-1}. Anal. Calcd (Found) for $[PPN]_2[\mathbf{1}]$: C, 55.57 (55.40); H, 3.41 (3.42); N, 1.58 (1.58); Te, 14.40 (12.00); Cr, 5.87 (5.56); Fe, 3.15 (3.18). MS (ESI negative-ion MS): m/e 687.2, $m/2e$ 343.7. ^{125}Te NMR (DMSO-d_6, 297 K): δ 188. $[PPN]_2[\mathbf{2}]$: The preparation and purification of $[PPN]_2[\mathbf{2}]$ is similar to that for $[PPN]_2[\mathbf{1}]$, and the yield is 55% (based on Se). IR (ν_{CO}, CH_2Cl_2): 1983 w, 1915 s, 1903 vs, 1864 m cm^{-1}. Anal. Calcd (Found) for $[PPN]_2[\mathbf{2}]$: C, 58.80 (59.10); H, 3.61 (3.89); N, 1.67 (1.49); Cr, 6.20 (5.79); Fe, 3.34 (3.00). ^{77}Se NMR (DMSO-d_6, 297 K): δ −383.

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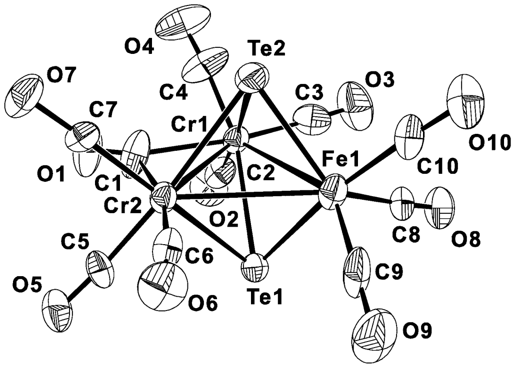

Figure 1. ORTEP diagram of anion **1**. Selected bond distances [Å] and angles [deg]: Te1−Fe1 2.548(2), Te1−Cr2 2.654(2), Te1−Cr1 2.677(2), Te2−Fe1 2.500(2), Te2−Cr2 2.653(2), Te2−Cr1 2.682(2), Fe1−Cr1 2.977(2), Fe1−Cr2 3.006(2), Cr1−Cr2 2.777(3); Cr1−Fe1−Cr2 55.30(6), Cr2−Cr1−Fe1 62.88(6), Cr1−Cr2−Fe1 61.82(6).

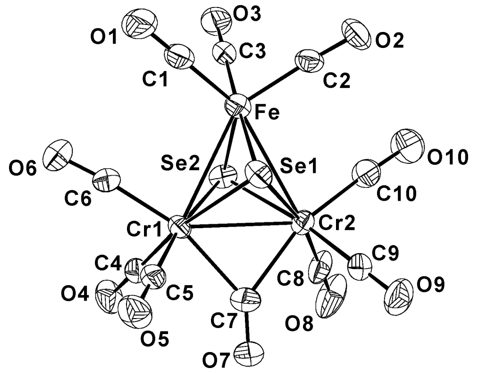

Figure 2. ORTEP diagram of anion **2**. Selected bond distances [Å] and angles [deg]: Se1−Fe 2.378(1), Se1−Cr1 2.495(1), Se1−Cr2 2.514(1), Se2−Fe 2.322(1), Se2−Cr1 2.487(1), Se2−Cr2 2.500(1), Fe−Cr1 2.912(2), Fe−Cr2 2.914(2), Cr1−Cr2 2.725(2); Cr1−Fe−Cr2 55.78(4), Fe−Cr1−Cr2 62.15(4), Fe−Cr2−Cr1 62.08(4).

to **1** except for the two bridging Te atoms replaced by two Se atoms (Figure 2).

The X-ray analysis shows that the Te−Cr bond lengths lying from 2.653 to 2.682 Å are significantly shorter than those found in $[Te_4Cr(CO)_5]^{2-}$ (2.726 Å),[5] $[Te_3\{Cr(CO)_5\}_4]^{2-}$ (2.763 Å),[6] $[Te_2Cr_4(CO)_{18}]^{2-}$ (2.721 Å),[6] $[Te_2\{Cr(CO)_5\}_4]^{2-}$ (2.749 Å),[6] and $Te\{Cr(CO)_3Cp\}_2$ (2.806 Å),[7] and a bit longer than that in $[Te_4\{Cr(CO)_5\}_4]$ (2.587 Å).[8] The Cr−Fe bonds are 2.977(2) and 3.006(2) Å, which are a bit long as compared to the covalent bond radii for Cr (1.28 Å)[9] and Fe (1.25 Å)[10] but are compared with that (2.901 Å) in $Cp_2CrFe(CO)_5$,[11] suggestive of significant metal−metal interaction.

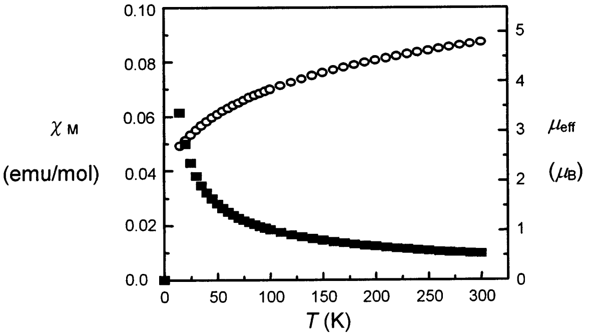

Figure 3. Temperature-dependent magnetic susceptibility data for $[PPN]_2$**1**: χ_M vs T (■) and μ_{eff} vs T (○) plots.

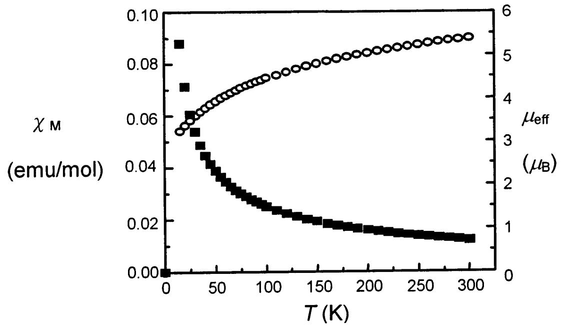

Figure 4. Temperature-dependent magnetic susceptibility data for $[PPN]_2$**2**: χ_M vs T (■) and μ_{eff} vs T (○) plots.

The Cr−Cr bond of 2.777(3) Å of **1** is evidently shorter than those (average 2.875 Å) in the related electron-precise cluster $[Se_2Cr_3(CO)_{10}]^{2-}$ mainly due to the bridging CO.[12] In **2**, the average Se−Cr bond is 2.499 Å, the Se−Fe bonds are normal, and the Cr−Fe bond of 2.913 Å is comparable to that in **1**, also indicative of the significant bonding interaction between Fe and Cr atoms.

Clusters **1** and **2** are both 50-electron species, each of which possesses two more electrons than that (48 electrons) for the conventional M_3 clusters. Besides, clusters **1** and **2** have seven skeletal bonding pairs each for the trigonal bipyramid geometry, which does not obey Wade's rules and would have two more electrons than what is expected. Since clusters **1** and **2** are both electron-rich species, their magnetic properties are investigated with a SQUID magnetometer. The magnetic data, in the form of χ_M versus T and μ_{eff} versus T plots for **1** and **2**, are shown in Figures 3 and 4. At 300 K, **1** has the effective magnetic moment $\mu_{eff} = 4.80\ \mu_B$, and **2** has the μ_{eff} value of 5.38 μ_B. Both values are close to the spin-only value ($\mu_{eff} = 4.90\ \mu_B$) predicted for a simple $S = 2$ species. At low temperatures, the SQUID analysis showed that **1** gave the μ_{eff} value of 2.83 at 20 K and **2** gave the value of 2.89 μ_B at 5 K, respectively, values which correspond to that for an $S = 1$ species.

Clusters **1** and **2** are even-electron species but highly paramagnetic, which is unusual due to the existence of the carbonyls. Further, the mixed chromium−iron carbonyl clusters with the heteronuclear metal−metal bonds are observed only in their sulfur analogue but not in the selenium

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and tellurium congeners. The related sulfur-containing complexes with carbonyl ligands are limited to $[SFeCr(CO)_4Cp]_2$,[13] $\{S_4Cr_2Fe_2(CO)_6Cp_2(S^tBu)\}Fe$,[14] and $S_2Cr_2Fe(CO)_3(S^tBu)Cp_2$.[15] The limited number of mixed chromium−iron or chromium-containing carbonyl clusters compared to their Mo analogues may be related to the lability of Cr.[16]

In addition, **1** and **2** exhibit unusual chemical shifts in the ^{125}Te and ^{77}Se NMR spectra, respectively. Complex **1** shows the ^{125}Te NMR resonance at 188 ppm whereas the related electron-precise square pyramidal clusters $Te_2Fe_3(CO)_9$ and $Te_2Fe_2W(CO)_{10}$ give values at 1123 and 467 ppm, respectively.[17,18] On the other hand, the ^{77}Se NMR of **2** gave the resonance at −383 ppm, largely shifted from those for the related electron-precise complexes $[Se_2Cr_3(CO)_{10}]^{2-}$ (22 ppm),[12] $[Se_2Fe_2W(CO)_{10}]$ (372 ppm),[18] and $[Se_2Fe_3(CO)_9]$ (778 ppm).[18]

The SQUID studies show that clusters **1** and **2** exhibit different Curie magnetic moments at different temperatures. This is highly unusual in metal carbonyl clusters, and the change of magnetic moments with temperature may be caused by a number of possible mechanisms.[19] Clusters **1** and **2** provide good examples for the insight study on this important issue.

We demonstrate herein the facile and direct synthesis of the first examples of the electron-rich Cr−Fe−CO telluride and selenide clusters that exhibit unusual magnetism. The detailed theoretical study to elucidate the orbital interactions and electronic demands of these two clusters is challenging and being undertaken.

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Supporting Information Available: X-ray crystallographic files in CIF format and magnetic measurements (PDF) for complexes $[PPN]_2[\mathbf{1}]$ and $[PPN]_2[\mathbf{2}]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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