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First selenium-capped carbonyltrichromium complex $[Se_2Cr_3(CO)_{10}]^{2-}$: a novel Cr_3 ring cluster

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$[Se_2Cr_3(CO)_{10}]^{2-}$, the first selenium-capped trichromium carbonyl cluster, has been prepared and its reaction with $Mo(CO)_6$ studied.

Although numerous carbonylchromium complexes have been reported, they have little tendency to form clusters with Cr–Cr bonds.[1] Up to now, only three homometallic chromium carbonyl clusters with a Cr_3 ring have been structurally characterized.[2–6] The rare Cr–Cr bonds in these clusters are made possible with the stabilizing ligands such as μ_3-S,[4,6] μ_3-PR,[5] and diphosphene,[6] and importantly, with the aid of the existence of the bridging carbonyls in each case.[4–6] Nevertheless, no fully characterized carbonylchromium cluster with Cr–Cr bonds stabilized with heavier main group elements has been known.[7,8] We have prepared the first example of the selenium-capping trichromium carbonyl cluster complex $[Et_4N]_2[Se_2Cr_3(CO)_{10}]$ **1**, in which three Cr–Cr bonds are present and all the carbonyls are terminally coordinated.

Numerous attempts to gain entry to the Se–Cr–CO system using SeO_2 with $Cr(CO)_6$ in basic KOH–MeOH solutions were not successful. However, it was found that use of the highly concentrated NaOH–MeOH solutions followed by cation metathesis with $[Et_4N]Br$ resulted in **1**. Note that the isolation of **1** succeeds only in the NaOH–MeOH solutions but not in the KOH–MeOH solutions due to alkali metal cation effects on the stabilization of the cluster anion. The Mo-substituted dichromium cluster complex $[Et_4N]_2[Se_2Cr_2Mo(CO)_{10}]$ **2** was obtained by treatment of the parent compound **1** with $[Mo(CO)_6]$ in acetone.† The anionic clusters of **1** and **2** represent rare examples of carbonylchromium clusters which possess three and one chromium–chromium bonds, respectively.

The anion of cluster **1** exhibits a trigonal bipyramidal structure with the Cr_3 ring capped above and below by μ_3-Se atoms, in which the Se atom donates four electrons to the Cr_3 ring making it a 48e$^-$ species, in accord with three chromium atoms with three Cr–Cr bonds. The anion possesses two mirror planes: one passing through the Cr_3 ring and the other one lying in the $Cr(1)Se_2$ plane (Fig. 1).‡ The Cr–Cr distances of 2.849(2) and 2.926(3) Å are somewhat longer than predicted from the covalent radius of Cr (1.28 Å).[9] However, they are comparable to Cr–Cr bonds found for $[SCr_3(CO)_{12}\{Cr(CO)_5\}]^{2-}$ (average 2.850 Å),[4] $[(Bu^tP)Cr_3(CO)_{10}(Bu^tPPBu^t)]$ (2.814–2.851 Å),[5] $[SCr_3(CO)_{12}]^{2-}$ (average 2.828 Å),[6] and $[Cr_6Se_8(PEt_3)_6]$ (average 2.81 Å),[10] and are slightly shorter than that in $[\{TeCr(CO)_5\}_2Cr_2(CO)_8]^{2-}$ (3.052 Å).[11] The fairly long Cr–Cr bonds reflect their weakness and may account for the rarity of carbonylchromium clusters. Unlike the previously reported carbonyltrichromium clusters,[4–6] the anion of **1** possesses only terminal carbonyls, with two Cr atoms coordinated with three carbonyls and the unique Cr(1) attached to four carbonyls. Of interest is that the four Cr(1)–C distances [1.832(9)–1.917(9) Å] are somewhat greater than those for Cr(2) [1.816(9)–1.855(7) Å], indicative of weaker Cr–C bonding for the Cr(1) atom with four coordinated carbonyls. The same effect is also observed in the larger Se–Cr(1) distance [2.575(2) Å] compared with the Se–Cr(2) distance [2.387(1) Å].

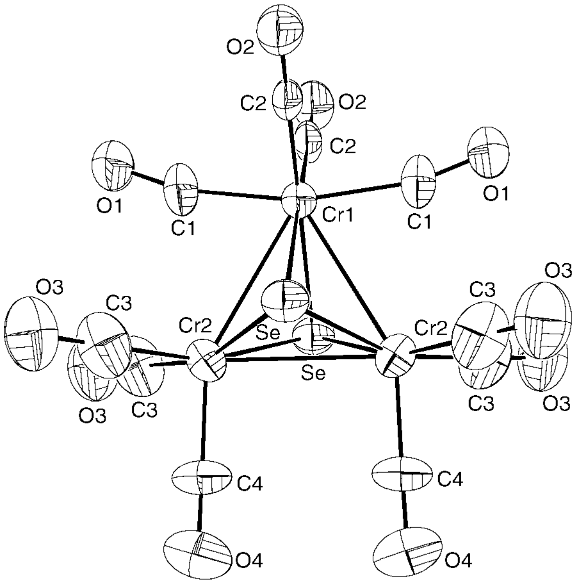

Fig. 1 Crystal structure of the dianion of **1** showing 30% thermal ellipsoids and the atom labelling scheme. Important bond lengths (Å) and angles (°): Se–Cr(1) 2.575(2), Se–Cr(2) 2.387(1), Cr(1)–Cr(2) 2.849(2), Cr(2)–Cr(2a) 2.926(3), Cr(1)–C(1) 1.917(9), Cr(1)–C(2) 1.832(9), Cr(2)–C(3) 1.855(7), Cr(2)–C(4) 1.816(9); Cr(2)–Cr(1)–Cr(2a) 61.81(7), Cr(1)–Cr(2)–Cr(2a) 59.09(3).

Employing a similar methodology to the Se–Mo–CO system failed, and we therefore treated **1** with $[Mo(CO)_6]$ in acetone to see if any carbonylchromium fragment can be replaced by an incoming molybdenum moiety. This was found to be so; the $Cr(CO)_4$ fragment in **1** can be exchanged by $Mo(CO)_4$ to form the mixed-group 6 metal complex **2**, $[Et_4N]_2[Se_2Cr_2Mo(CO)_{10}]$. X-Ray analysis shows that the anion of **2** is structurally similar to that of **1**, with the Cr(1) atom replaced by the Mo(1) atom (Fig. 2).‡ The formulation of **2** was further substantiated by ICP metal analysis. While the Cr–Cr bond of 2.947(2) Å is still long and similar to the Cr–Mo distances (average 2.9512 Å), the average Se–Cr length (2.4157 Å) is significantly shorter than that of the Se–Mo distances (2.6744 Å).

In summary, the first synthesis of a trichromiumcarbonyl cluster anion by the stabilization of the μ_3-Se atoms has been achieved. The ease of replacing one Cr moiety of **1** with the Mo fragment suggests the possibility in making other mixed-metal carbonylchromium clusters which may help elucidate the bonding characteristics of the Cr–Cr and Cr–M bonds. Further investigation is under way.

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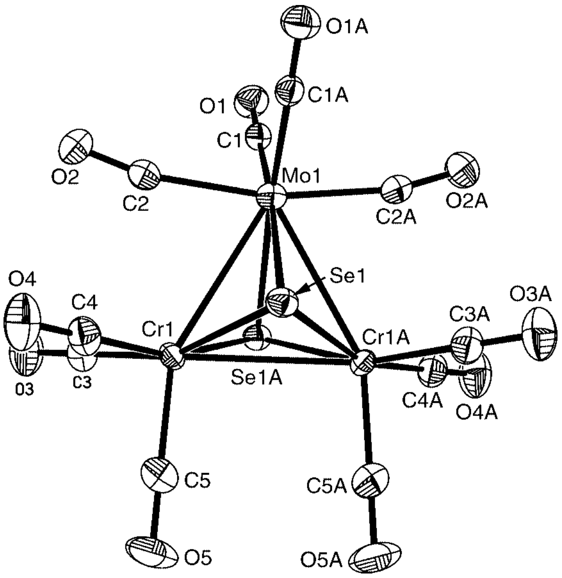

Fig. 2 Crystal structure of the anion of **2** showing 30% thermal ellipsoids and the atom labelling scheme. Important bond lengths (Å) and angles (°): Se(1)–Cr(1A) 2.4123(9), Se(1)–Cr(1) 2.4190(9), Se(1)–Mo(1) 2.6745(7), Se(1A)–Mo(1) 2.6743(7), Mo(1)–Cr(1) 2.9511(9), Mo(1)–Cr(1A) 2.9513(9), Cr(1)–Cr(1A) 2.947(2), Cr(1)–C(3) 1.845(6), Cr(1)–C(4) 1.850(5), Cr(1)–C(5) 1.815(7); Cr(1)–Mo(1)–Cr(1A) 59.92(3), Cr(1A)–Cr(1)–Mo(1) 60.04(2).

Notes and references

† *Synthetic procedure:* All experiemnts were performed under N_2 atomsphere. A mixed solution of MeOH (30 mL) and hexanes (7.5 mL) was added to a mixture of SeO_2 (0.21 g, 1.89 mmol) and $[Cr(CO)_6]$ (0.8 g, 3.64 mmol), and NaOH (3.0 g, 82.5 mmol). The mixed solution was heated to reflux in an oil-bath at 70 °C for 12 h to give a dark-red solution which was filtered and concentrated, and a MeOH solution of $[Et_4N]Br$ (3.0 g, 14.3 mmol) was added dropwise, precipitating the solid. The solid was washed several times with MeOH and CH_2Cl_2. The residue was recrystallized from diethyl ether–MeCN several times to give purplish-red **1** (0.42 g, 0.49 mmol) (52% based on Se). IR (ν_{CO}, MeCN): 1990w, 1914s, 1869m cm^{-1}. Anal. Found for **1**: C, 36.55; H, 4.67; N, 3.31%. Calc.: C, 36.55; H, 4.72; N, 3.28. Compound **1** is soluble in MeCN and acetone, but insoluble in other organic solvents. Crystals suitable for X-ray analysis were grown from CH_2Cl_2–MeCN solution.

Acetone (25 mL) was added to a mixture of **1** (0.23 g, 0.269 mmol) and $[Mo(CO)_6]$ (0.10 g, 0.379 mmol). The mixed solution was stirred at room temperature for 11 days and the color changed from dark-red to brown. The resultant solution was filtered and solvent was removed under vacuum. The residue was washed with CH_2Cl_2, extracted with MeCN, and then recrystallized with CH_2Cl_2–MeCN several times to give purplish-red **2** (0.16 g, 0.178 mmol) (66% based on **1**). IR (ν_{CO}, MeCN): 2068w, 2002m, 1916vs, 1868s, 1827m cm^{-1}. Anal. Found for **2**: C, 35.22; H, 4.56; N, 3.14; Cr, 11.20; Mo, 9.09. Calc.: C, 34.76; H, 4.49; N, 3.12; Cr, 11.57; Mo, 10.68%. Complex **2** is soluble in MeCN and acetone. Crystals suitable for X-ray analysis were grown from diethyl ether–MeCN solution.

‡ *Crystal structure data*: for **1**: $C_{26}H_{40}Cr_3N_2O_{10}Se_2$: $M = 854.51$, orthorhombic, space group *Cmcm*, $Z = 4$, $a = 8.607(3)$, $b = 24.591(8)$, $c = 15.941(4)$ Å, $V = 3374.0(18)$ Å^3, $D_c = 1.682$ g cm^{-3}, λ(Mo-Kα = 0.70930 Å, $\mu = 3.16$ mm^{-1}. A total of 1656 unique reflections were collected on a Nonius (CAD-4) diffractometer at 298 K in the 2θ range 2.0–50° using θ–2θ scans, and an absorption correction by azimuthal (ψ) scans was applied. The structure was solved by direct methods and refined both with NRCC-SDP-VAX and SHELXL-97 packages. Both refinements gave the similar results; however, the latter gave the lower *R* values and smaller esds on distances and angles. Therefore, the results of the SHELXL-97 refinement were used here. The $[Et_4N]^+$ cations are disordered and the H atoms were placed in calculated positions and refined with a riding model. All the other non-hydrogen atoms were refined with anisotropic temperature factors. Full-matrix least squares on F^2 converged to $R = 0.1123$ (all data), 0.0406 [$I > 2\sigma(I)$]; $wR = 0.1142$ (all data), 0.1037 [$I > 2\sigma(I)$].

For **2**: $C_{26}H_{40}Cr_2MoN_2O_{10}Se_2$: $M = 898.46$, orthorhombic, space group *Pnna*, $Z = 4$, $a = 24.8153(3)$, $b = 16.0695(3)$, $c = 8.6204(2)$ Å, $V = 3437.55(11)$ Å^3, $D_c = 1.736$ g cm^{-3}, λ(Mo-Kα) = 0.71073 Å; CCD SMART diffractometer, and SADABS absorption correction ($T_{min} = 0.569$, $T_{max} = 0.634$). A total of 22975 reflections were measured, and 3957 unique reflections ($2\theta < 55°$, $R_{int} = 0.0406$) 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 $R = 0.0774$ (all data), 0.0495 [$I > 2\sigma(I)$]; $wR = 0.1697$ (all data), 0.1442 [$I > 2\sigma(I)$]. All calculations were performed using SHELXTL packages.

CCDC 159098 and 159099. See http://www.rsc.org/suppdata/cc/b1/b101283p/ for crystallographic data in .cif or other electronic format.

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