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[7] Part of a Diplomarbeit by *S. K.*; X-ray structure analysis by *G. M.*
[8] The formation of cyclobutadienes as intermediates cannot be ruled out, but, in our opinion, seems highly unlikely for energetic reasons.
[9] **4a**: Orthorhombic, $a=9.446(3)$, $b=19.937(4)$, $c=21.416(7)$ Å, $\alpha=\beta=\gamma=90°$; space group $Pca2_1$, $Z=8$ (two independent molecules), $\rho_{calc}=1.276$ g cm^{-3}. Data collection: Enraf-Nonius CAD4 diffractometer, 2633 independent reflections with $2.00<\theta<22.00°$. Refinement: $R=0.087$, $R_w=0.081$ (2279 reflections with $I>2\sigma(I)$, $w=1/(\sigma^2+(0.023F_0)^2)$, heavy atoms anisotropic, disordered O atoms of the sulfoxide group isotropic, H atoms with $B=7.0$ Å^2 (only in calculation of structure factors). Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 50698, the names of the authors, and full citation of the journal.

Synthesis and Crystal Structure of the Dicarbido Bimetallic Cluster $[Co_6Ni_2C_2(CO)_{16}]^{2-}$**

By *Aurora Arrigoni, Alessandro Ceriotti, Roberto Della Pergola, Giuliano Longoni*, Mario Manassero*, Norberto Masciocchi,* and *Mirella Sansoni*

Recently, we reported the synthesis and structural characterization of the carbido cluster $[Co_3Ni_9C(CO)_{20}]^{3-}$ **1**[1,2]. We report here the synthesis and crystal structure of a chemically related bimetallic dicarbido cluster, namely the dianion $[Co_6Ni_2C_2(CO)_{16}]^{2-}$ **2**, which is the first simple-hexagonal array of metal atoms whose cavity is completely filled by carbido C atoms.

The dicarbido cluster **2** was originally detected by IR spectroscopy, together with several other species, in the reaction of $[Co_3(CO)_9CCl]$ **3** with $[Ni_6(CO)_{12}]^{2-}$ **4** when **3** and **4** are allowed to react in a molar ratio greater than that used previously to synthesize **1**[1,2]. **2** can be synthesized selectively from **1** and **3** according to equation (a) or by slow addition of **4** to **3** (ca. 1:2 molar ratio) in tetrahydrofuran (THF) [equation (b)]. The dianion **2** has been isolated in more than 70% yield with several tetrasubstituted ammonium or phosphonium counterions; the $Et_4N^{\oplus}$ salt has been crystallized from acetone/heptane[3].

$$2\,[Co_3Ni_9C(CO)_{20}]^{3-} + 4\,[Co_3(CO)_9CCl] \longrightarrow \underset{\mathbf{1}}{} \qquad \underset{\mathbf{3}}{}$$

$$3\,[Co_6Ni_2C_2(CO)_{16}]^{2-} + 2\,NiCl_2 + 7\,Ni(CO)_4 + 3\,Ni \qquad \text{(a)}$$
$$\mathbf{2}$$

$$2\,[Co_3(CO)_9CCl] + [Ni_6(CO)_{12}]^{2-} \longrightarrow \qquad \text{(b)}$$
$$\mathbf{3} \qquad \mathbf{4}$$

$$[Co_6Ni_2C_2(CO)_{16}]^{2-} + NiCl_2 + 3\,Ni(CO)_4 + 2\,CO$$
$$\mathbf{2}$$

The structure of the $Et_4N^{\oplus}$ salt of **2** has been elucidated by X-ray diffraction (Fig. 1)[4]. Dianion **2** has a crystallographic C_i-$\bar{1}$ and an idealized C_{2h}-2/m symmetry and originates from the condensation of two trigonal-prismatic moieties sharing a common square face. An idealized mirror plane is defined by atoms Co1, Co1′, Ni3, and Ni3′. The metal framework of **2** represents a fragment of a simple hexagonal metal lattice, which is stabilized by filling each of the two trigonal prismatic cavities with two carbido C atoms[5]. Previously described clusters having this type of trigonal prismatic building unit are, for instance, $[Rh_6C(CO)_{15}]^{2-}$[6], and the pseudo one-dimensional oligomers $[Pt_3(CO)_6]_n^{2-}$ $(n=2-5)$[7].

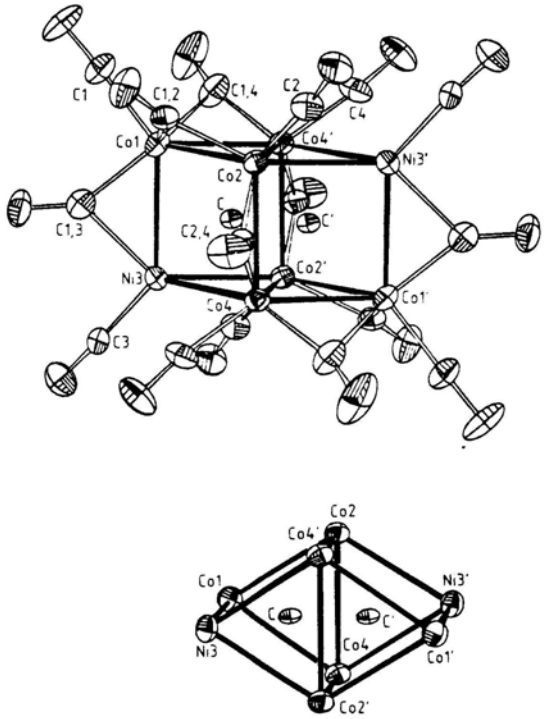

Fig. 1. ORTEP view of the structure of **2** in the crystal. Complete dianion (top) and naked metal framework with the two interstitial C atoms (bottom). Most important distances [Å]: M–M: Co1-Co2 = 2.577(1), Co1-Co4 = 2.528(1), Co1-Ni3 = 2.548(1), Co2-Co4 = 2.775(1), Co2-Co4′ = 2.559(1), Co2-Ni3′ = 2.647(1), Ni3-Co4′ = 2.590(1). - M–$C_{carbido}$: Co1-C = 1.953(5), Co2-C = 2.048(6), Ni3-C = 1.885(5), Co4-C = 2.031(5), Co2′-C = 2.017(6), Co4′-C = 2.023(6). - M–$CO_{terminal}$: Co1-C1 = 1.755(8), Co2-C2 = 1.753(8), Co4-C4 = 1.739(8), Ni3-C3 = 1.774(8). - M–$CO_{bridging}$: Co1-C1,3 = 1.845(8), Co1-C1,2 = 2.317(8), Co1-C1,4 = 2.034(7), Co2-C1,2 = 1.797(8), Co2-C2,4 = 1.956(7), Ni3-C1,3 = 1.967(7), Co4-C1,4 = 1.866(7), Co4-C2,4 = 1.929(7). - C–O: C1-O1 = 1.131(8), C2-O2 = 1.160(8), C3-O3 = 1.117(8), C4-O4 = 1.149(8), C1,3-O1,3 = 1.142(8), C1,2-O1,2 = 1.169(8), C1,4-O1,4 = 1.163(8), C2,4-O2,4 = 1.157(8). - C–C′ = 1.494(11).

In accord with analytical data[3], two atoms of **2** are less coordinated by CO ligands, and we presume that they are Ni atoms. The distance between the two carbido C atoms of 1.49 Å is shorter than typical CC single bonds in hydrocarbons (1.54 Å) and than most C···C interatomic separations in other dicarbido clusters[8,9]. Only the neutral Rh cluster $[Rh_{12}C_2(CO)_{25}]$ and the $[Co_{11}C_2(CO)_{22}]^{3-}$ trianion[10,11], whose metal frameworks originate from condensation of square-antiprismatic and trigonal prismatic moie-

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ties, respectively, show comparably short CC interatomic separations (1.48 and 1.62 Å, respectively); an even shorter distance (1.41 Å) is exhibited by the trianion $[Co_3Ni_7C_2(CO)_{15}]^{3-}$[1]. In both $[Rh_{12}C_2(CO)_{25}]$ and $[Co_{11}C_2(CO)_{22}]^{3-}$, the calculated distances between the centers of the two idealized cavities (with edge length equal to the overall mean value of the M–M bonds) are longer than the experimentally determined CC distances (1.98 and 1.80 Å, respectively)[11]. In contrast, in **2** the corresponding calculated and experimental distances (1.49 Å) almost coincide. Such a short interatomic CC separation would be in keeping with the presence of a localized CC bonding interaction in **2**. However, the number of valence electrons (n_{CVE}) of the known carbonylmetal clusters of the first transition series systematically conforms to the relationship $n_{CVE} \geq 18N - 2n_{M-M}$ (where N and n_{M-M} are, respectively, the number of metal atoms and M–M bonds). Furthermore, EHMO calculations on a naked cluster having the idealized metal geometry of the title compound predict 58 cluster valence MOs[12]. **2** would therefore require at least 116 cluster valence electrons, which is fulfilled only if each interstitial C atom contributes four skeletal electrons. In accord with this, the thermal ellipsoids of the two carbido C atoms elongated in the CC direction appear to argue against the presence of a localized C–C bond in **2** and suggest a delocalized CC interaction supported by the metal atoms.

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2·2Et$_4$N, 89462-35-1; **3**, 13682-02-5; Ni, 7440-02-0; Co, 7440-48-4

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[3] *Procedure:* A solution of $Co_3(CO)_9CCl$ (0.24 g) in 9 mL acetone was added dropwise to a stirred solution of $[NEt_4]_3[Co_3Ni_9C(CO)_{30}]$ (0.42 g) in 20 mL acetone. After 3 h, the reaction solution was evaporated to dryness in vacuo to eliminate $Ni(CO)_4$, and the residue was taken up in acetone (20 mL). Precipitation by slow diffusion of *n*-heptane (30 mL) afforded 0.31 g of the Et$_4$N$^{\oplus}$ salt of **2** as black crystals. **2** as its Et$_4$N$^{\oplus}$ salt is diamagnetic and its ^{1}H-NMR spectrum shows no signals other than those of the cation (30 and −75°C). Carbonyl absorptions occur at 2040 (vw), 2010 (vs), 1987 (sh), 1977 (s), 1931 (ms), 1829 (m), and 1797 (w) cm^{-1} in the IR spectrum (THF). Elemental analysis: Calcd. Et$_4$N$^{\oplus}$ 21.62, Co 29.38, Ni 9.76, CO 37.26; Et$_4$N$^{\oplus}$: Co : Ni = 1 : 3 : 1. Found: Et$_4$N$^{\oplus}$ 21.3, Co 29.2, Ni 9.3; Et$_4$N$^{\oplus}$: Co : Ni = 1 : 3.03 : 0.98.
[4] Monoclinic, space group $P2_1/c$; $a = 9.015(4)$, $b = 20.215(5)$, $c = 13.120(3)$ Å, $\beta = 113.10(4)°$, $V = 2199(3)$ Å^3, $\rho_{calc.} = 1.818$ g·cm^{-3} for $Z = 2$. CA4 four circle diffractometer (Enraf-Nonius), graphite-monochromatized $Mo_{K\alpha}$ radiation, $2\vartheta = 3-48°$, corrected for Lorentz polarization and absorption. Structure solved by direct methods and refined by full-matrix least-squares to $R = 0.029$, 1578 independent reflections ($I > 3\sigma(I)$). Further details of the crystal structure investigation are available on request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England on quoting the names of the authors and the journal citation.
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X-Ray Spectroscopic Studies of the Surface Species in Co–Mo–Al_2O_3 Hydrodesulphurization Catalysts

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Despite a number of investigations of Co–Mo–Al_2O_3 hydrodesulphurization catalysts carried out in recent years[1], a clear understanding of the active sites in these catalysts has not emerged. Accordingly, we have carried out a systematic study of Al_2O_3-supported, sulphided cobalt-molybdenum (Co–Mo) catalysts and their oxide precursors over a wide range of compositions together with a number of model oxides and sulphides of cobalt and molybdenum, including several samples of Co-MoS_2. For this purpose, we have employed X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy; in the latter, use was made of both X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) to determine coordination numbers and bond distances. The present study shows that Co^{II} and Mo^{IV} are present as sulphides on the surfaces of the active catalysts, each in octahedral coordination; furthermore, our results indicate the presence of disulphide bonds which may play a significant role in the hydrodesulphurization processes.

Co–Mo–Al_2O_3 precursors with Co : Mo ratios between 3 : 12 and 6 : 12 exhibit Mo($3d_{5/2}$) binding energies of 232.3 ± 0.1 eV (XPS) and a 3d spin-orbit splitting of 3.1 ± 0.1 eV, characteristic of Mo^{VI} species. The Co($2p_{3/2}$) binding energy is 781.7 ± 0.1 eV with a 2p spin-orbit splitting of 16.0 ± 0.1 eV and a satellite structure separated by ca. 6.2 eV from the main peak, showing that cobalt occurs as Co^{II}. The spectroscopic transition energies determined by XANES spectroscopy are similar to those of Co^{II} and Mo^{VI} oxides. The 1s→nd transitions show that Co is tetrahedrally coordinated whereas Mo is octahedrally coordinated in these oxide precursors. EXAFS spectra of the 4 : 12 and 6 : 12 oxide precursors confirm these coordinations and yield Co–O and Mo–O distances close to 2.0 and 1.80 Å, respectively (corresponding distances in CoO and MoO_3 are 2.12 and 1.86 Å).

Sulphided Co–Mo–Al_2O_3 catalysts with Co : Mo ratios between 2 : 12 and 12 : 12 show Mo($3d_{5/2}$) and Co($2p_{3/2}$) binding energies (228.9 ± 0.1 eV and 778.8 ± 0.1 eV, respectively) characteristic of Mo^{IV} and Co^{II}. The Co^{II} spectrum shows no satellites. In addition to these Mo^{IV} and Co^{II} species, the sulphided samples generally exhibit additional features due to Mo^{VI} and Co^{II} which are similar to those found in the oxide precursors. The S(2p)/Mo(3d) intensity ratio in XP spectra in the sulphided catalysts increases with increasing Co concentration. The Mo(3d)/Al(2p) intensity ratio also increases as the Co concentration increases, in contrast to the oxide precursors.

XANES spectroscopy suggests an octahedral coordination for both Co and Mo in their catalytically active sulphided state, the spectral transition energies being close to those of CoS and MoS_2. These coordinations are also corroborated by our EXAFS measurements. The Co–S and Mo–S distances found by EXAFS spectroscopy are 2.32 and 2.29 Å, respectively (the Co–S and Mo–S distances in

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