

Synthesis and structural characterisation of the dianion $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$ as its tetramethylammonium salt

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The dianion $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$ **1** ($[\text{NMe}_4]^+$ salt) has been obtained by pyrolysis of $[\text{NMe}_4][\text{Co}_6\text{C}(\text{CO})_{14}]$ in diglyme (2,5,8-trioxanonane) at 130 °C, and, as the parent compound, is paramagnetic. The salt $[\text{NMe}_4]_2[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]$ has been characterised by single crystal X-ray diffraction. The $\text{Co}_9(\text{C}_2)$ core of the anion can be described as a D_{3h} tricapped trigonal prism of Co atoms with stretched interbasal edges encapsulating an acetylide C_2 unit [$\text{C}-\text{C}$ 1.39(2) Å]. Nine CO ligands are linearly bonded, one per metal atom, six are edge bridging and four semibridging. The overall molecular symmetry is C_{2v} or, more accurately, C_2 .

The chemistry of the carbidocarbonyl clusters of the Group 9 metals, discovered in 1973,¹ is far from being exhausted and still new molecular architectures are being characterised. The stabilising effect of the carbide atoms yields unique polyhedra that are a compromise between the tendency of the metal atoms towards closely packed arrangements and the need for suitable cavities for the allocation of the interstitial atoms. This is particularly evident for the high-nuclearity species containing more than one carbide atom. Compounds of the latter kind are more numerous for rhodium than cobalt, for which the species reported to date are $[\text{Co}_{11}(\text{C}_2)(\text{CO})_{22}]^{3-}$,² $[\text{Co}_{13}\text{C}_2(\text{CO})_{24}]^{4-3}$ and $[\text{Co}_{13}\text{C}_2(\text{CO})_{24}]^{3-}$,⁴ all obtained by pyrolysis of the trigonal-prismatic dianion $[\text{Co}_6\text{C}(\text{CO})_{15}]^{2-}$.^{5,6} To extend the research in this field we decided to investigate the products originating from pyrolysis of the paramagnetic species $[\text{Co}_6\text{C}(\text{CO})_{14}]^-$,^{7,8} and report here the first product that we have been able to isolate, the $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$ anion.

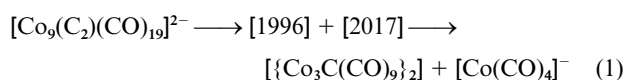
Results and Discussion

Synthesis and reactivity

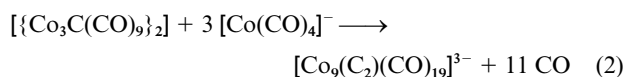
The anion $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$ **1** has been synthesized by pyrolysis under nitrogen of $[\text{NMe}_4][\text{Co}_6\text{C}(\text{CO})_{14}]$ in diglyme (2,5,8-trioxanonane) at 130 °C. Infrared checking shows that in a few hours the typical bands of the starting material disappear, being replaced by new bands centred at *ca.* 1989 and 1832 cm^{-1} ; some uncharacterised insoluble black material is also formed. Separation of the products is achieved by precipitation of the $[\text{NMe}_4]^+$ salts, followed by extraction with tetrahydrofuran (thf) which selectively dissolves the new anion. Interestingly, the residue of the extraction contains, besides some other unidentified products, substantial amounts of $[\text{Co}_{11}(\text{C}_2)(\text{CO})_{22}]^{3-}$, previously obtained only in small yields as a by-product of the synthesis of $[\text{Co}_{13}\text{C}_2(\text{CO})_{24}]^{4-}$. Crystals of $[\text{NMe}_4]_2[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]$ have been obtained from the thf solution by layering a mixture of propan-2-ol and *n*-hexane. The IR spectrum of $[\text{NMe}_4]_2[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]$ in thf shows bands at 2045w, 1989vs, 1832m and 1812 (sh) cm^{-1} .

The anion, having an odd number of cluster valence electrons, is paramagnetic, as shown by the appearance in the ESR spectrum in thf at 123 K of an intense symmetric signal at $g = 2.027$ with a peak-to-peak linewidth of 200 G (1 G = 10^{-4} T) and no evidence of hyperfine structure.

The $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$ dianion is reactive towards carbon monoxide which induces degradation of the cluster. Infrared monitoring of the course of the reaction, performed in thf solution on the $[\text{NMe}_4]^+$ salt under a CO atmosphere (100 kPa), shows, within minutes, disappearance of the dianion with formation of $[\text{Co}(\text{CO})_4]^-$, traces of $[(\text{OC})_9\text{Co}_3\text{C}-\text{CCo}_3(\text{CO})_9]$,^{9,10} **2**, and two unidentified products having the main stretching band of the terminal CO at, respectively, 1996 and 2017 cm^{-1} . These intermediate species upon further exposure to CO eventually disappear and yield a mixture of apparently only two products, the dimeric species **2** (bands at 2080, 2062 and 2026 cm^{-1}) and $[\text{Co}(\text{CO})_4]^-$ (1887 cm^{-1}), equation (1).



The isolation of compound **2** from this reaction confirms the presence of a strong bond between the two interstitial carbon atoms, and suggests its possible use as a source of interstitial C_2 units for the synthesis of clusters through suitable condensation reactions. Thus we have tried the synthesis of the hypothetical even-electron species $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{3-}$, on the basis of the simple stoichiometry (2), but found that the product is still the



dianionic Co_9 species in place of the expected trianion; this result confirms the possible role of **2** as a source of C_2 units, but clearly indicates that also apparently simple 'rational' syntheses as reaction (2) are not so easily achieved in cluster chemistry. Furthermore, the result seems to indicate a higher stability of the paramagnetic dianion with respect to the expected diamagnetic trianion. Interestingly, we have also found that this attempted reaction runs, among others, through the same two intermediate compounds observed in the degradation of

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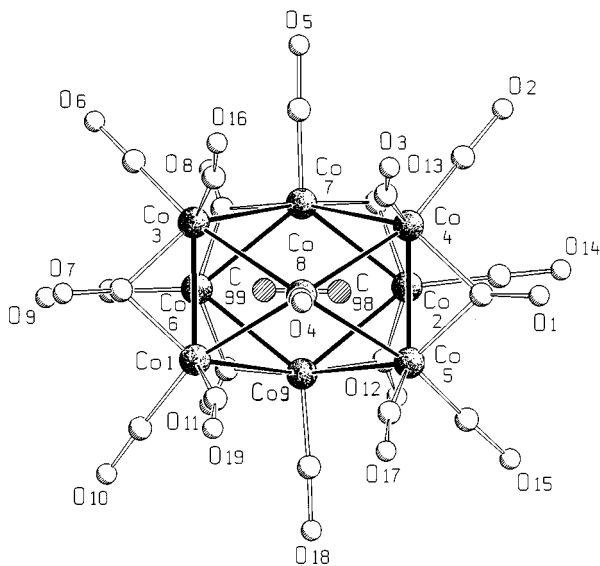


Fig. 1 Molecular stereogeometry of $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$ with atom labelling. The carbonyl carbons are numbered according to their oxygen atoms

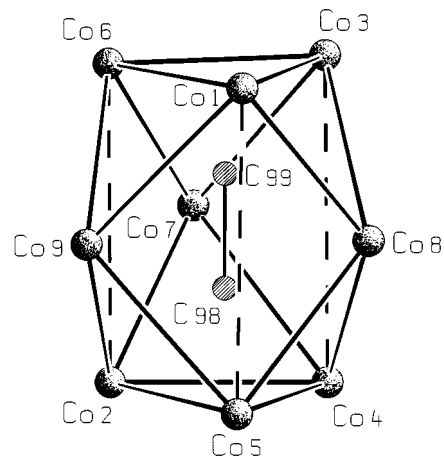


Fig. 2 The Co_9C_2 core in $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$

Table 1 Relevant bond distances (Å) for compound 1

| | | | |
|----------|----------|-----------|----------|
| Co1–Co3 | 2.516(4) | Co3–Co8 | 2.642(3) |
| Co1–Co8 | 2.567(4) | Co3–Co7 | 2.753(3) |
| Co1–Co6 | 2.628(4) | Co4–Co5 | 2.516(4) |
| Co1–Co9 | 2.775(4) | Co4–Co8 | 2.575(4) |
| Co2–Co7 | 2.514(3) | Co4–Co7 | 2.780(4) |
| Co2–Co9 | 2.532(3) | Co5–Co8 | 2.634(3) |
| Co2–Co4 | 2.620(4) | Co5–Co9 | 2.735(3) |
| Co2–Co5 | 2.626(3) | Co6–Co7 | 2.530(4) |
| Co3–Co6 | 2.620(3) | Co6–Co9 | 2.515(3) |
| C98–C99 | 1.39(2) | C99–Co1 | 1.96(2) |
| C98–Co2 | 1.97(2) | C99–Co3 | 1.96(2) |
| C98–Co4 | 1.95(2) | C99–Co6 | 1.97(2) |
| C98–Co5 | 1.96(1) | C99–Co7 | 2.04(2) |
| C98–Co7 | 2.06(2) | C99–Co8 | 2.03(2) |
| C98–Co8 | 2.03(2) | C99–Co9 | 2.05(2) |
| C98–Co9 | 2.03(2) | Co6–C11 | 1.88(2) |
| Co4–C1 | 1.92(2) | Co9–C11 | 1.97(2) |
| Co5–C1 | 1.93(2) | Co2–C12 | 1.81(2) |
| Co4–C2 | 1.71(2) | Co9–C12 | 2.13(2) |
| Co4–C3 | 1.74(2) | Co2–C13 | 1.89(2) |
| Co8–C4 | 1.72(2) | Co7–C13 | 1.94(2) |
| Co7–C5 | 1.73(2) | Co2–C14 | 1.75(2) |
| Co3–C6 | 1.76(2) | Co5–C15 | 1.72(2) |
| Co1–C7 | 1.95(2) | Co3–C16 | 1.75(2) |
| Co3–C7 | 1.90(2) | Co5–C17 | 1.73(2) |
| Co6–C8 | 1.83(2) | Co9–C18 | 1.72(2) |
| Co7–C8 | 2.07(2) | Co1–C19 | 1.77(2) |
| Co6–C9 | 1.67(2) | Co8...C19 | 2.52(2) |
| Co1–C10 | 1.77(3) | | |
| mean C–O | 1.17(3) | | |

$[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$ with CO. Work is in progress to isolate the intermediate species and to clarify the mechanism of both reactions.

The solid state molecular structure

The structure of the dianion $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$, illustrated in Fig. 1 (relevant bond distances in Table 1), contains a Co_9 cluster consisting of a three-layer stacking of triangles. The external triangles are bonded [mean Co–Co distance 2.588(4) Å] and eclipsed; the central triangle is non-bonded [mean $\text{Co}\cdots\text{Co}$ contact 3.313(4) Å] and staggered with respect to the other triangles. The resulting polyhedron is a D_{3h} tricapped trigonal prism with stretched interbasal edges [average length 3.935(4) Å], as shown in Fig. 2. The surface of the polyhedron

is defined by eight triangular faces and three re-entrant atoms. This metal atom arrangement can also be related to a bisoctahedron, a fragment of hexagonal close packing of atoms, from which it derives by stretching the central triangle. The cavity of the polyhedron is similar to that of a barrel and perfectly fits the C_2 acetylide unit placed in its middle. The average Co–C (acetylide) distances are 1.96(2) and 2.04(2) Å for the outer and central Co atoms, respectively. The shorter value is close to the expected one, as one can infer from the values found in $[\text{Co}_8\text{C}(\text{CO})_{18}]^{2-6}$ in which a large tetragonal antiprismatic cavity is distorted to allow the formation of four short contacts (mean 1.99 Å) and four longer ones (mean 2.15 Å). The C (acetylide)–C (acetylide) distance [1.39(2) Å] is one of the shortest among the interstitial C_2 units reported so far, comparable to those found in $[\text{Ni}_{16}(\text{C}_2)_2(\text{CO})_{23}]^{4-11}$ (1.38 Å) and $[\text{Ni}_{10}(\text{C}_2)(\text{CO})_{16}]^{2-12}$ (1.40 Å), but shorter than those found in $[\text{Co}_{11}(\text{C}_2)(\text{CO})_{22}]^{3-1}$ (1.62 Å), in other nickel and Ni–Co compounds,^{13–15} and in $[\text{Rh}_{12}(\text{C}_2)(\text{CO})_{25}]^{16}$ [1.48(2) Å]. Therefore it is fully justified to name this interstitial ligand acetylide.

It is of interest to analyse the distribution of the nineteen CO ligands on the cluster surface. The ligand stereogeometry does not conform to the idealised D_{3h} symmetry of the Co_9C_2 core. Only a C_{2v} subset is retained with the twofold axis passing through Co8 and its ligand CO4. Nine ligands are linearly bonded, one per cobalt atom; six are edge bridging and four semibridging. The bridging ligands span the four edges of the diamond Co2,7,6,9 and the edges in the outer triangles Co4,5 and Co1,3. The semibridging ligands involve the unique Co8 atom. If the latter ligands are attributed to the metal atoms to which they are primarily bonded (Co1,3,4,5) all the metals but Co8 are three-connected to the ligands. The deficiency of electron donation to Co8 is saturated by the four semibridging ligands that belong to two subsets: CO3 and CO19 establish a stronger interaction with Co8 [mean Co–C 2.49(2) Å], CO16 and CO17 a weaker one [mean Co–C 2.72(2) Å]. This feature affects the underlying Co–Co distances, the mean values of which are 2.571(4) and 2.638(4) Å, respectively. The remaining Co–Co interactions comprise six short edges supported by bridging ligands [mean 2.521(4) Å] and eight longer and unbridged distances [mean 2.692(4) Å].

A more accurate analysis of the cobalt–cobalt distances and ligand geometry would reveal that the anion better conforms to C_2 rather than C_{2v} symmetry. This fact is consistent with the packing of the anions in a dissymmetric space group (see Experimental section).

Conclusion

The actual stereogeometry clearly shows that the best ligand distribution on a cluster surface is the one that realises a well

balanced charge donation to the metal atoms. In many cases this primary need is associated to the steric regularity, *i.e.* the same co-ordination geometry around all the metal atoms. On the other hand, since the number of surface ligands is controlled by the number of cluster bonding orbitals, the geometric regularity is sometimes impossible to achieve. In the latter case the CO ligands take advantage of their extreme flexibility and an even charge distribution is always attained through a variety of semibringing co-ordination geometries.

From the synthetic point of view it is interesting to compare the different behaviour in the pyrolysis when starting from the diamagnetic $[\text{Co}_6\text{C}(\text{CO})_{14}]^{2-}$ or from the paramagnetic $[\text{Co}_6\text{C}(\text{CO})_{14}]^-$. In the first case the main product obtained is the dicarbido species $[\text{Co}_{13}\text{C}_2(\text{CO})_{24}]^{4-}$, with only traces of $[\text{Co}_{11}(\text{C}_2)(\text{CO})_{22}]^{3-}$ which contains a bonded C–C moiety. In the second case both the major products, $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$ and $[\text{Co}_{11}(\text{C}_2)(\text{CO})_{22}]^{3-}$, contain a C–C unit. This suggests that the more open paramagnetic $[\text{Co}_6\text{C}(\text{CO})_{14}]^-$ (a distorted octahedron with a stretched edge) easily loses cobalt fragments to give an intermediate species with exposed carbon, required for C–C bond formation. On the basis of the known M_5 species with exposed carbides, we could think of a Co_5C unit which, after 'dimerisation' to a $\text{Co}_{10}(\text{C}_2)$ cluster, would yield $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$ and/or $[\text{Co}_{11}(\text{C}_2)(\text{CO})_{22}]^{3-}$ by loss or addition of a cobalt fragment, respectively.

Finally, the odd electron count of $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$ confirms the tendency of cobalt, even in heterometallic Co–M compounds, to give stable paramagnetic carbido clusters such as $[\text{Co}_6\text{C}(\text{CO})_{14}]^-$, $[\text{Co}_{13}\text{C}_2(\text{CO})_{24}]^{4-}$ and $[\text{Co}_3\text{Ni}_7(\text{C}_2)(\text{CO})_{16}]^{2-}$,¹⁴ also the silicon-containing $[\text{Co}_9\text{Si}(\text{CO})_{21}]^{2-}$ ¹⁷ could be included in this group. This has no counterpart in rhodium cluster carbide chemistry, where all the known species, except the rather unstable $[\text{Rh}_{12}\text{C}_2(\text{CO})_{23}]^{3-}$,¹⁸ are diamagnetic. An explanation of this peculiarity could be that an extra electron occupying an antibonding frontier orbital has the beneficial effect of enlarging the cavity in the cobalt clusters in order to optimise the cobalt–carbide interactions. The carbide atoms, on the other hand, perfectly fit the larger cavities of the rhodium clusters and therefore no stretching mechanism is necessary.

Experimental

All operations were carried out under nitrogen with a standard Schlenk-tube apparatus. Tetrahydrofuran was distilled from sodium–benzophenone and propan-2-ol from aluminium isopropoxide. All other analytical grade solvents were degassed in vacuum and stored under nitrogen. The compounds $[\text{Co}_6\text{C}(\text{CO})_{14}]^{7,8}$ and $[\{\text{Co}_3\text{C}(\text{CO})_9\}_2]^9$ were prepared by the published methods. Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrometer, using 0.1 mm CaF_2 cells previously purged with nitrogen.

Synthesis of $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$ from $[\text{Co}_6\text{C}(\text{CO})_{14}]^-$

The salt $[\text{NMe}_4][\text{Co}_6\text{C}(\text{CO})_{14}]$ (389 mg, 0.47 mmol) was placed under nitrogen in a large Schlenk tube equipped with a small condenser and a magnetic stirring bar; the use of a large vessel (up to 250 cm³ in volume) is important in order to favour the CO evolution. After addition of diglyme (15 cm³), the resulting solution was heated, while stirring, at 130 °C till, after *ca.* 6–7 h, IR monitoring showed replacement of the reagent bands (2012 and 1855 cm⁻¹) by two bands at *ca.* 1989 and 1832 cm⁻¹. After the pyrolysis some precipitate was removed by filtration and the clear solution was treated dropwise, while stirring, with NMe_4Cl (2.0 g in 80 cm³ of water). The black precipitate was filtered off, washed with water (10 cm³ in four portions) and vacuum dried. The crude product was extracted from the septum with the minimum amount of thf (8 cm³) and carefully layered with propan-2-ol–*n*-hexane (1 : 1) to yield in a few days

crystals suitable for X-ray diffraction; yield 85.3 mg {Found: C, 27.83; H, 2.11; N, 2.53. Calc. for $[\text{NMe}_4]_2[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]$: C, 28.21; H, 1.96; N, 2.27%}.

Reaction of $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{2-}$ with CO

A solution of $[\text{NMe}_4]_2[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]$ in thf was subjected to CO at atmospheric pressure; within 15 min the IR spectra showed the initial appearance of terminal CO stretching bands first at 1996 then at 2017 cm⁻¹ together with those characteristic of $[\{\text{Co}_3\text{C}(\text{CO})_9\}_2]$ (2080, 2062, 2026 cm⁻¹) and $[\text{Co}(\text{CO})_4]^-$ (1887 cm⁻¹). On further reaction the intermediate bands at 2017 and 1996 cm⁻¹ disappeared, yielding within 24 h a solution containing essentially the above two species.

Attempted synthesis of $[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]^{3-}$ from $[\{\text{Co}_3\text{C}(\text{CO})_9\}_2]$ and $[\text{Co}(\text{CO})_4]^-$

The dimer $[\{\text{Co}_3\text{C}(\text{CO})_9\}_2]$ (104 mg, 0.12 mmol) and $\text{Na}[\text{Co}(\text{CO})_4]$ (75.5 mg, 0.39 mmol) were dissolved in thf (10 cm³) and heated at 60 °C with stirring. Several intermediate steps could be observed with IR monitoring, among which were two having main bands at 2017 and 1996 cm⁻¹, eventually yielding after *ca.* 10 h the characteristic bands of compound **1** (1989, 1832 cm⁻¹) together with some excess of $[\text{Co}(\text{CO})_4]^-$ (1890 cm⁻¹). After cooling at room temperature the solution was filtered to remove some precipitate which was washed with thf (1 + 1 cm³), prior to being discarded. The solution with the collected washings was treated for metathesis with a solution of NMe_4Cl (0.5 g in 30 cm³ of water), giving a brown precipitate which was filtered off, thoroughly washed with water (10 cm³, six times) and vacuum dried for about 1.5 h. Extraction with thf (5 cm³), followed by layering with propan-2-ol (20 cm³), gave, after solvent diffusion (about 1 week), crystals of pure $[\text{NMe}_4]_2[\text{Co}_9(\text{C}_2)(\text{CO})_{19}]$.

Crystallography

Crystal data. $\text{C}_{29}\text{H}_{24}\text{Co}_9\text{N}_2\text{O}_{19}$, **1**, $M = 1234.9$, orthorhombic, space group $P2_12_12_1$, $a = 11.652(8)$, $b = 16.679(6)$, $c = 20.892(6)$ Å, $U = 4060.2(5)$ Å³, $Z = 4$, $D_c = 2.02$ g cm⁻³, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, $T = 293(2)$ K, $\mu = 3.50$ mm⁻¹, $\theta = 2\text{--}25^\circ$, 3546 reflections collected, of which 2254 unique with $I > 2\sigma(I)$, $R1 = 0.0507$, $wR = 0.0535$, goodness of fit = 1.17. The absolute configuration was checked by running the final refinement also with the inverted set of coordinates and comparing the R factors; the lowest R factor was obtained with the structure reported here.

Data were collected on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods and refined by full-matrix least squares (SHELX 76¹⁹). Data were corrected for absorption by an azimuthal scan of reflections with $\chi > 80^\circ$ (minimum and maximum transmission 0.704 and 1.00). The metal atoms were refined anisotropically, while the limited number of observations prevented an extension of the anisotropic treatment to the remaining atoms. The Me groups of one of the two $[\text{NMe}_4]^+$ cations were found disordered around the N atom, with occupancy ratio of 3:2. Hydrogen atoms were added in calculated positions, and a single isotropic thermal parameter (0.106 Å²) was refined in the case of the ordered cation, while a fixed value of 0.09 Å² was used for the H atoms of the disordered cation. The program SCHAKAL 92²⁰ was used for all graphical representations.

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