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Note

A structural isomer of the $[CoFe_3(CO)_{13}]^-$ anion

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Abstract

The crystal structure of $[Et_4N][CoFe_3(CO)_{13}]$ has been determined, and shown to contain an anion with the CO ligands adopting a very different arrangement about the tetrahedral $CoFe_3$ core to that found for the same anion, reported previously for the PPN^+ salt. The relationship between the two structures can be understood in terms of Johnson's Ligand Polyhedral Model. In contrast the anion in $[Et_4N][CoRu_3(CO)_{13}]$ has the same geometry as that described in the corresponding PPN^+ salt. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cluster; Isomer; Polyhedral; Iron; Cobalt; X-ray structure

1. Introduction

Clusters of the type $[M_4(CO)_{13}]^{n-}$ with a tetrahedral metal core are of interest because there is no uniquely obvious way of arranging 13 CO ligands equally over four metal centres [1–3]. The commonest structure to date for mixed-metal species is as shown in **1a**, where there are three doubly-bridging carbonyls along the edges to one apex, as found in the structures of $[CoFe_3(CO)_{13}]^-$ [4], $[CoRu_3(CO)_{13}]^-$ [5] and $[RhRu_3(CO)_{13}]^-$ [6] (all determined as $PPN^+(=[Ph_3P)_2N]^+)$ salts). It is also the basis for the structure of the neutral $[HCoRu_3(CO)_{13}]$ [7] with the addition of a μ-H along one Ru–Ru bond. Another variant is found for the $[Fe_4(CO)_{13}]^{2-}$ ion in the $[Fe(py)_6]^{2+}$ salt [8], as shown in **1b**, where there are three unsymmetrical μ-CO ligands around the edge of the basal plane, with a μ_3-CO on the face of the basal plane. This arrangement is clearly influenced by the cation since the same $[Fe_4(CO)_{13}]^{2-}$ ion as the PPN^+ salt [9] has only the triply-bridging CO, with all the others terminal as in **1c**. Other variations are found for $[PPN][IrRu_3(CO)_{13}]$ [10] which has three independent anions in the asymmetric unit, one with four bridging CO's (three along edges to one apex and one along a basal edge (**1d**)) while the other two anions have only two bridging CO ligands and are related to the structure of $[IrOs_3(CO)_{13}]^-$ [11]. The neutral analogue, $[Co_2Ru_2(CO)_{13}]$ [12] has a structure with four μ-CO ligands arranged in a similar way to **1d**.

A full summary and analysis of these $[M_4(CO)_{13}]^{n-}$ structures in terms of the Ligand Polyhedral Model has recently appeared from Johnson's group [13]. This rationalises the structures in terms of a face-capped icosahedral array of CO ligands (the lowest energy arrangement for 13 vertices) with the M_4 tetrahedron adopting various orientations within this cage. Only for the larger cluster cores $IrRu_3$ and $IrOs_3$ does the CO ligand cage adopt the less-favoured capped cubeoctahedral arrangement.

We have now determined the structure of the anion $[CoFe_3(CO)_{13}]^-$, crystallised as the $[NEt_4]^+$ salt. The structure obtained differs markedly from that found in the PPN^+ salt previously reported [4], and from those discussed above for the other anions, and provides another clear example for the Ligand Polyhedral Model [1,13].

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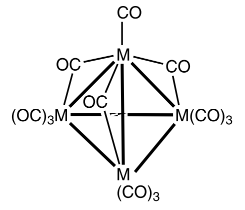
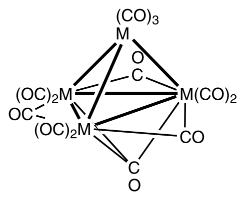


(1a)



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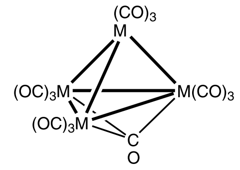
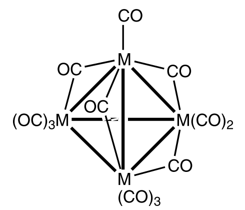
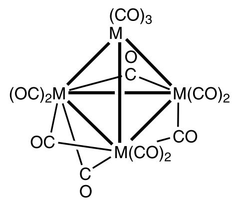


(1c)



(1d)



(1e)

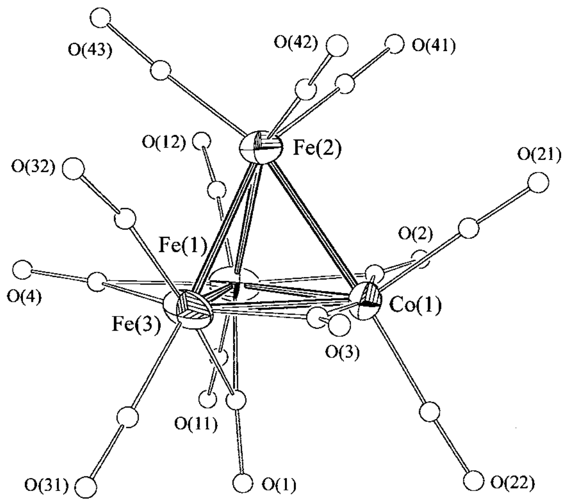


Fig. 1. The structure of the $[CoFe_3(CO)_{13}]^-$ ion.

Table 1
Selected bond lengths (Å) and angles (°) for $[Et_4N][CoFe_3(CO)_{13}]$

Bond lengths			
Fe(1)–Fe(2)	2.5749(11)	Fe(1)–Fe(3)	2.4979(11)
Fe(2)–Fe(3)	2.5688(11)	Fe(1)–Co(1)	2.5260(10)
Fe(2)–Co(1)	2.5879(9)	Fe(3)–Co(1)	2.5229(10)
Fe(1)–C(1)	1.959(8)	Co(1)–C(1)	2.396(7)
Fe(3)–C(1)	1.993(8)	Co(1)–C(2)	1.938(5)
Co(1)–C(3)	1.950(5)	Fe(3)–C(3)	2.058(5)
Fe(1)–C(2)	2.078(5)	Fe(3)–C(4)	2.088(8)
Fe(1)–C(4)	2.126(8)	C(1)–O(1)	1.216(8)
Bond angles			
Fe(3)–Co(1)–Fe(1)	59.31(3)	Fe(1)–Fe(3)–Co(1)	60.41(3)
Fe(3)–Fe(1)–Co(1)	60.28(3)	O(1)–C(1)–Fe(1)	140.2(9)
O(1)–C(1)–Fe(3)	140.1(9)	O(1)–C(1)–Co(1)	124.3(6)
Co(1)–C(2)–Fe(1)	77.8(2)	Co(1)–C(3)–Fe(3)	78.0(2)
Fe(3)–C(4)–Fe(1)	72.7(2)		

2. Results and discussion

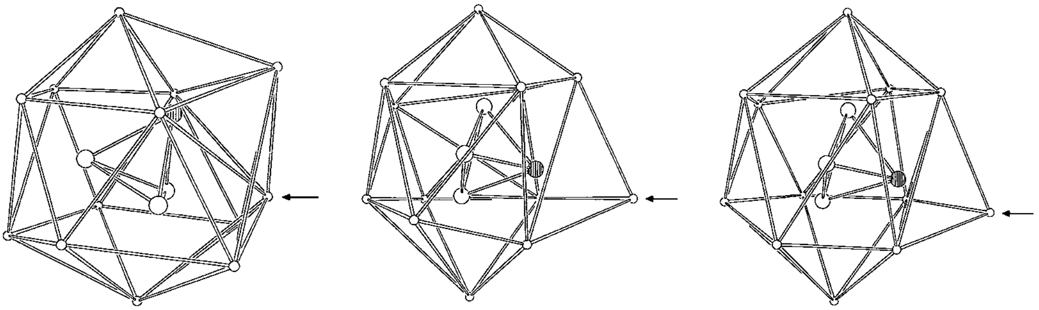
2.1. Synthesis of $[Et_4N][CoFe_3(CO)_{13}]$

The title compound was isolated from a mixture of anions (as determined by electrospray mass spectrometry) produced by reaction of $[Et_4N][Co(CO)_4]$ with $Ge[Co_2(CO)_7]_2$ and $Fe_3(CO)_{12}$; more direct syntheses are known from $[Fe_4(CO)_{13}]^{2-}$ and $Co_2(CO)_8$ [4] or from $Fe_3(CO)_{12}$ and $[Co(CO)_4]^-$ [5].

2.2. Structure of $[Et_4N][CoFe_3(CO)_{13}]$

$[Et_4N][CoFe_3(CO)_{13}]$ forms an orthorhombic lattice with well separated cations and anions. The structure of the anion is shown in Fig. 1 with relevant bond lengths and angles given in Table 1. The X-ray experiment cannot unambiguously determine the positions of the Co and Fe atoms, but the unique apex assigned to Co is based on an analysis of the U_{iso} values (see Section 3) and localised electron-counting. A comparison of the M–M and M–CO bond lengths with those in the corresponding $[Fe_4(CO)_{13}]^{2-}$ anions is inconclusive because of the small differences expected and the different arrangement of bridging carbonyls. An alternative structure with Co(1) and Fe(2) interchanged cannot be completely excluded. However, this would not invalidate the general arguments given below, since it is the orientation of the M_4 tetrahedron within the ligand polyhedron that is important, not the definite assignment of the different M's.

The metal atoms are in a tetrahedral arrangement as expected for a cluster containing 60 valence electrons. The anion has a $Fe(CO)_3$ moiety capping the $CoFe_2$ triangle. The $CoFe_2$ triangle is linked to six terminal CO ligands, with three bridging CO ligands around the basal plane. These latter are only slightly unsymmetrical. The final CO ligand adopts a position below the $CoFe_2$ triangle, as shown in **1e**. The idealised C_{3v} symmetry is broken by this last CO, which rather than being equidistant from all basal atoms is more closely associated with Fe(1) and Fe(3) than with Co(1) [Fe(1)–C(1) 1.965 Å, Fe(3)–C(1) 1.991 Å, Co(1)···C(1) 2.385 Å]. This supports the assignment of Co(1) to a position in the basal plane, since otherwise a more symmetrical μ_3-CO would be expected, as found for $[Fe_4(CO)_{13}]^{2-}$ [8]. Localised electron counting for the basal metal atoms gives each an 18-electron configuration, with the extra electron for the d^9 cobalt atom,



(a) $[CoFe_3(CO)_{13}]^-$ with $[Et_4N]^+$ (b) $[CoFe_3(CO)_{13}]^-$ with PPN^+ (c) $[CoRu_3(CO)_{13}]^-$ with $[Et_4N]^+$

Fig. 2. The polyhedra defined by the oxygen atoms of the CO ligands of the anions for: (a) $[Et_4N][CoFe_3(CO)_{13}]$; (b) $[PPN][CoFe_3(CO)_{13}]$ [4]; and (c) $[Et_4N][CoRu_3(CO)_{13}]$. The 'capping' ligands of the icosahedra are indicated by the arrow, and the shaded atom of the core is the Co atom in each case.

compared with the d^8 iron atoms, compensating for the lack of interaction with the CO(1).

This structure **1e** contrasts markedly with that reported for the same anion $[CoFe_3(CO)_{13}]^-$ as the PPN^+ salt [4] where the cobalt atom possesses three bridging carbonyl ligands and a single terminal ligand (**1a**). The structure of the $[Et_4N]^+$ salt shows more similarity with that of the $[Fe_4(CO)_{13}]^{2-}$ anion **1b** [8] except that the final CO is doubly-rather than triply-bridging. One other *formal* difference between the **1a** and **1e** forms of the $[CoFe_3(CO)_{13}]^-$ anion is that to conform to the 18-electron rule the former requires that the electron associated with the negative charge be localised on the Co atom, while in the latter it is assigned to the unique Fe atom (Fe(2)).

The average Fe–Fe and Co–Fe bond lengths in the present form **1e** (2.547 and 2.546 Å, respectively) are significantly different from those in the previously reported form **1a** (2.667 and 2.487 Å, respectively [4]), but this is expected since the pattern of CO bridging is different in the two forms.

The preferred polyhedra for 13 CO's, based on the positions of the oxygen atoms, have been calculated [1,3,13]. The two with lowest energy are the edge- and face-bridged icosahedra [1]. The present example (**1e**) corresponds to the face-bridged icosahedron, with the face-capping CO being the asymmetric μ_2 one below the $CoFe_2$ plane. The same basic polyhedron is found in the earlier form (**1a**) of the same anion, but here the unique terminal CO on the cobalt atom is the face-bridging one [4]. The two different structures are therefore related by a re-orientation of the $CoFe_3$ tetrahedron within essentially the same set of CO ligands (see Fig. 2), using the Ligand Polyhedral Model approach [13]. Ignoring the distinction between the Co and Fe atoms, this rearrangement of the core is essentially an inversion of the M_4 tetrahedron within the icosahedral ligand polyhedron. It is interesting that this can be caused by changing the cation in the crystal, so the relative orientation is clearly decided by subtle effects, and the energy difference between the two forms is presumably small. The difference between the two arrangements of the $[CoFe_3(CO)_{13}]^-$ ions is more dramatic than for the two isomers of the $[Fe_4(CO)_{13}]^{2-}$ anion, which require only a small rotation of the M_4 core around a pseudo-C_3 axis to interconvert.

The distinction between the two isomers is presumably just a solid state effect since interconversion is likely to be facile in solution. This is consistent with variable temperature NMR studies on $[M_4(CO)_{13}]^{n-}$ species, which show only one ^{13}CO signal to very low temperatures in solution. However, in the solid the isomers are locked in position, since there are no indications of disorder of the metal core within the capped-icosahedron in either form of $[CoFe_3(CO)_{13}]^-$ (nor indeed in most of the other $[M_4(CO)_{13}]^{n-}$) anions in the solid state. This contrasts with dodecacarbonyl clusters $[M_n(CO)_{12}]$ with the higher-symmetry icosahedral array of CO ligands (e.g. $[Fe_3(CO)_{12}$ or $[Co_4(CO)_{12}]$) which show disorder which can be interpreted in terms of core re-orientation within the ligand sphere even in the solid state [14].

2.3. Structure of $[Et_4N][CoRu_3(CO)_{13}]$

The crystal structure of the equivalent $[Et_4N][CoRu_3(CO)_{13}]$ was also determined for comparison with the earlier report of the PPN^+ salt [5]. In this case however the anion adopts exactly the same arrangement (**1a**) in both salts, possibly because the bridging carbonyls prefer Co–Ru to Ru–Ru edges (Fig. 3). It is of note that the structures of $[Et_4N][CoRu_3(CO)_{13}]$ and $[Et_4N][CoFe_3(CO)_{13}]$ are not isomorphous, despite the fact that the exterior surface of the ligand polyhedron is essentially the same in each case, and the crystals were grown from the same solvent. This suggests that there is a reciprocity: the small differences in the crystal packing between the PPN^+ and $[Et_4N]^+$ salts of $[CoFe_3$-

$(CO)_{13}]^-$ are sufficient to induce different isomers, while the small differences in the arrangements of the cores of $[CoFe_3(CO)_{13}]^-$ and $[CoRu_3(CO)_{13}]^-$ are sufficient to induce different crystal packing in their $[Et_4N]^+$ salts.

The Co–Ru and Ru–Ru bond parameters in $[Et_4N][CoRu_3(CO)_{13}]$ are identical to those reported previously for the PPN^+ salt [5], so detailed discussion is not warranted.

3. Experimental

3.1. General

All reactions were carried out under an inert atmosphere (either Ar or nitrogen) using standard Schlenk techniques. Dichloromethane was freshly distilled over CaH_2 under a nitrogen atmosphere. $Ge[Co_2(CO)_7]_2$ [15] and $[Et_4N][Co(CO)_4]$ [16] were prepared according to standard procedures. $Fe_3(CO)_{12}$ was purchased from Strem Chemicals and purified by Soxhlet extraction into petroleum spirits and crystallised before use.

ESMS spectra were recorded on a VG Platform II instrument in negative ion mode using 1,2 dichloroethane as the mobile phase. Samples of the reaction solution were diluted in CH_2Cl_2 prior to injection. Spectra were acquired with a 5 V potential difference across the skimmer cones. Stated m/z values correspond to the most intense peak in the isotope pattern.

3.1.1. Preparation of $[Et_4N][CoFe_3(CO)_{13}]$

A mixture containing $Ge[Co_2(CO)_7]_2$, $Fe_3(CO)_{12}$, and $[Et_4N][Co(CO)_4]$ was refluxed in dichloromethane for 3–4 h. ESMS analysis of the solution at this time revealed the formation of an anion of the form $[GeFe_3Co_3(CO)_{18}]^-$ (m/z 923) along with $[CoFe_3(CO)_{13}]^-$ (m/z 591) and $[Co_3Fe(CO)_{12}]^-$ (m/z 569). The solution was filtered, reduced in volume to ca. 2–3 ml, then cooled to −20 °C. A deep red crystalline product was formed and shown to be $[Et_4N][CoFe_3(CO)_{13}]$ by X-ray crystallography. The larger anion has yet to be isolated in a form suitable for full characterisation.

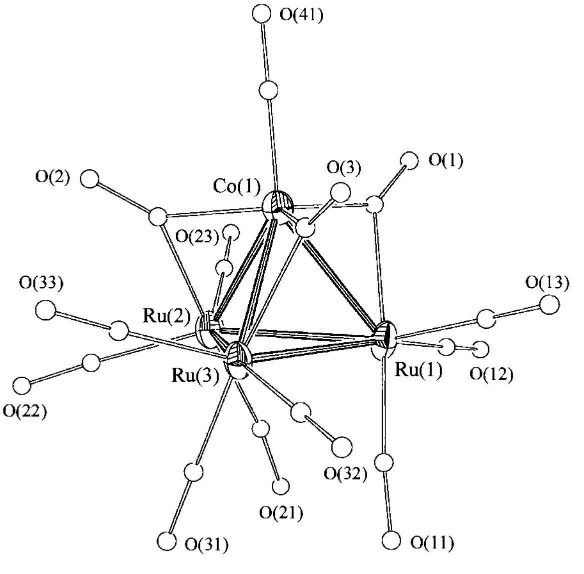


Fig. 3. The structure of the $[CoRu_3(CO)_{13}]^-$ ion.

3.1.2. Preparation of $[Et_4N][CoRu_3(CO)_{13}]$

$Ru_3(CO)_{12}$ (0.10 g, 0.16 mmol) and $[Et_4N][Co(CO)_4]$ (0.05g, 0.16 mmol) in thf (20 ml) were heated under reflux for 2 h (Ref. [5]). Infrared spectra (2017 (vs), 1997(sh), 1792(m) cm^{-1} [5]) and ESMS (negative ion, m/z 728) indicated reaction was complete. The solvent was removed under vacuum and the product recrystallised by addition of Et_2O to a CH_2Cl_2 solution of the crude product (0.067 g, 52%). Crystals for the X-ray structure determination were grown by diffusion of Et_2O into a CH_2Cl_2 solution of the compound at −20 °C.

3.2. X-ray crystallography

Unit cell dimensions, space group and intensity data were obtained with a Siemens SMART CCD diffractometer, using Mo–K_α-radiation ($\lambda = 0.71073$ Å).

3.2.1. Structure determination of $[Et_4N][CoFe_3(CO)_{13}]$

Crystal data for $[Et_4N][CoFe_3(CO)_{13}]$: $C_{21}H_{20}CoFe_3NO_{13}$, $M_r = 720.86$, orthorhombic, space group $P2_12_12_1$, $a = 12.138(3)$, $b = 12.717(3)$, $c = 17.462(5)$ Å, $V = 2695.4(12)$ Å^3, $Z = 4$, $D_{calc} = 1.776$ g cm^{-3}, μ(Mo–K_α) = 2.252 mm^{-1}, $F(000) = 1448$, $T = 163(2)$ K, crystal size = 0.70 × 0.45 × 0.25 mm.

A total of 35 463 reflections was collected to $\theta = 27.7°$, 5900 of which were unique (R_{int} 0.0267). Reflections were corrected for absorption using SADABS [17] ($T_{max} = 1.00$, $T_{min} = 0.894$). The structure was solved and refined on F^2. The Co atom cannot be reliably distinguished from the Fe atoms on X-ray grounds alone, so was assigned as illustrated in Fig. 1 based on the following considerations:

1. the U_{iso} values for the four metal atoms were 0.032, 0.040, 0.039 and 0.043 using the final model, whereas exchanging Co(1) with Fe(2) gave 0.044 (Co(1)), 0.029 (Fe(2)), 0.039, 0.043.
2. placing the Co atom in the basal plane provides a ready explanation for the CO below the plane being μ_2 rather than μ_3.

This model converged to $R_1 = 0.0407$ (for $I > 2\sigma(I)$ data), $R_1 = 0.0503$, $wR_2 = 0.1232$ for all data), with Goodness-of-Fit = 1.074, Flack absolute structure parameter = 0.00.

3.2.2. Structure determination of $[Et_4N][CoRu_3(CO)_{13}]$

Crystal data for $[Et_4N][CoRu_3(CO)_{13}]$: $C_{21}H_{20}CoNO_{13}Ru_3$, $M_r = 856.52$, monoclinic, space group $P2_1/n$, $a = 12.787(4)$, $b = 12.397(4)$, $c = 18.232(6)$ Å, $B = 94.520(4)°$, $V = 2881.2(16)$ Å^3, $Z = 4$, $D_{calc} = 1.975$ g cm^{-3}, $\mu(Mo-K_\alpha) = 2.169$ mm^{-1}, $F(000) = 1664$, $T = 168(2)$ K, crystal size $= 0.42 \times 0.21 \times 0.08$ mm.

A total of 20 501 reflections was collected, 5658 of which were unique (R_{int} 0.0459). Reflections were corrected for absorption using SADABS [17]. ($T_{max} = 1.00$, $T_{min} = 0.739$). The structure was solved and refined on F^2. The asymmetric unit consisted of one well-defined $[CoRu_3(CO)_{13}]^-$ anion and two half-$[Et_4N]^+$ cations, each disordered about a centre of symmetry. No hydrogen atoms were included in the model. Refinement converged to $R_1 = 0.0565$ (for $I > 2\sigma(I)$ data), $wR_2 = 0.1323$ for all data), with Goodness-of-Fit $= 1.107$.

All calculations used the SHELX-97 programs [18] manipulated through WinGx [19].

4. Supplementary material

Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC no. 174262 and 174263.

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