Synthesis and X-ray structure of the $[{Fe_3(CO)_9(\mu_3-O)}_2H]^{3-}$ trianion: dimerization of a metal carbonyl cluster *via* formation of an exceptionally short hydrogen bond[†]

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The synthesis, structure and characterization of the $[{Fe_3(CO)_9(\mu_3-O)}_2H]^{3-}$ trianion in its $[Cs(THF)_{0.33}]^+$ and $[NEt_4]^+$ salt are reported. The title dimeric cluster has been obtained by protonation in water or in organic solvent of the $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ dianion to the hydroxo $[Fe_3(CO)_9(\mu_3-OH)]^{-}$ derivative and crystallization. The solid state structure of $[Cs(THF)_{0.33}]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$ is based on ionic packing of $[Cs(THF)_{0,33}]^+$ cations and $[{Fe_3(CO)_9(\mu_3-O)}_2H]^{3-}$ trianions. The fractional formula is due to the particular packing of Cs⁺ cations, which are at the vertices of fused cuboctahedral and trigonal antiprismatic polyhedrons. Each cuboctahedron encapsulates a $[{Fe_3(CO)_9(\mu_3-O)}_2H]^{3-1}$ trianion, whereas each trigonal antiprism encapsulates a THF molecule. The possibility that the structure of the $[{Fe_3(CO)_9(\mu_3-O)}_2H]^{3-}$ trianion could be affected by its confinement in the cuboctahedral cage of Cs⁺ ions and the heavy disorder of the THF molecule urged a further structural determination of the trianion with a completely different cation. The corresponding $[NEt_4]_3[Fe_3(CO)_9(\mu_3-O)]_2H]$ salt has been, therefore, prepared and structurally characterized. The $[{Fe_3(CO)_9(\mu_3-O)}_2H]^{3-}$ trianion displays an identical structure and almost coincident molecular parameters in both salts. Its most notable feature is represented by the unique hydrogen atom symmetrically bridging the μ_3 -O atoms of two different [Fe₃(CO)₉(μ_3 -O)]²⁻ molecules and displaying one of shortest O ... H ... O interaction so far reported in organic, inorganic and organometallic literature. The structure of $[Cs(THF)]_2[Fe_4(CO)_{13}]$, which has been obtained as a by-product of the synthesis of $[Cs(THF)_{0.33}]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$, is also briefly reported.

Introduction

Several organometallic oxides and hydroxides of transition metal are known.¹⁻³ Most of them are derivatives of early transition metals, though notable examples are also known for late transition metals such as group 8–10 elements in low oxidation state. Focusing the attention on late transition metals containing carbonyl groups as ancillary ligands, stable species are mainly found in group 8. The species so far structurally characterized, we are aware of, are collected in Table 1.

Several years ago, we reported the synthesis and structure of the $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ dianion, which was obtained by deliberate contact with dry air of solutions of $[Fe_3(CO)_{11}]^{2-}$.⁵ Preliminary studies indicated that its reactivity was significantly different from that of the $[Fe_3(CO)_9(\mu_3-S)]^{2-}$ congener.²⁹⁻³¹ As an example, protonation of $[Fe_3(CO)_9(\mu_3-S)]^{2-}$ sequentially leads to $[Fe_3(CO)_9(\mu_3-S)(\mu-H)]^-$ and $Fe_3(CO)_9(\mu_3-S)(\mu-H)_2$ hydride derivatives,²⁶⁻²⁸ and reaction with an Au(PPh_3)⁺ moiety (isolobal with H⁺) accordingly gives rise to $[Fe_3(CO)_9(\mu_3-S)\{\mu-Au(PPh_3)\}]^{-}$.³¹ In contrast, spectroscopic evidence suggested that protonation of $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ was occurring onto the oxygen atom,⁵ whereas reaction with Au(PPh_3)⁺ was shown to give $[Fe_3(CO)_6(\mu-CO)_3(\mu_3-O)\{\mu_3-Au(PPh_3)\}]^-$,

through a $[Fe_3(CO)_9\{\mu_3\text{-}O\text{-}Au(PPh_3)\}]^-$ intermediate,¹⁰ and Fe_3(CO)_9(\mu_3\text{-}O)\{\mu_3\text{-}Au(PPh_3)\}\{\mu\text{-}Au(PPh_3)\}.^{12} Unfortunately all attempts made at that time to isolate and structurally characterize the purported $[Fe_3(CO)_9(\mu_3\text{-}OH)]^-$, as well as $[Fe_3(CO)_9(\mu_3\text{-}OR)]^-$ (R = Me, SiMe_3, $\sigma\text{-}allyl)$ species, have been unsuccessful. Systematically, only crystals of the $[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$ starting material were isolated, owing to back shift of equilibrium (1) during crystallization.

$$\begin{split} & [Fe_3(CO)_9(\mu_3\text{-}O)]^{2-} + RX \rightleftarrows [Fe_3(CO)_9(\mu_3\text{-}OR)]^- + X^- \\ & (R = H, X = BF_4; R = Me, SiMe_3; X = Cl, Br, I) \end{split}$$

However, a $[Fe_3(CO)_9(\mu_3-O-CMe_3)]^-$ species has been isolated and structurally characterized some years later.¹¹ The occurrence in solution of equilibrium (1) points out the reluctance of oxygen to share all its valence electrons in low-valent carbonyl compounds, which is also in keeping with the non-existence of metal carbonyl clusters containing oxygen as an interstitial atom and the reported failures in encapsulating the O atom of $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ even in bimetallic clusters containing more oxophilic metals. These latter attempts only led to isolation of $[Fe_3Rh_3(CO)_{15}(\mu_3-O)]^{-1}$ $[Fe_3Au_2(CO)_9(\mu_3-O)(PPh_3)_2]$,¹² $[Fe_3M(CO)_{12}(\mu_4-O)]^-$ (M = Mn, Re)¹³ and $[Fe_2Ru_3 (CO)_{14}(\mu_4-O)]^{2-14}$ clusters displaying exposed either μ_3 - or μ_4 -O atoms.

Our interest in water-soluble metal carbonyl clusters and the paucity of hydroxo-derivatives of iron led us to re-investigate the behaviour of $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ in water. As a first result, we report the synthesis and structural characterization of the

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 Table 1
 Structurally characterized oxides and hydroxides of group 8 transition metals

Compound	Ref.
[Fe ₃ (CO) ₉ (µ ₃ -O)] ²⁻	4
$Ru_3(CO)_6(dpAsm)_3(\mu_3-O)$	5
$Ru_3(CO)_4(dppm)_3(\mu_3-O)$	6
$Os_4(CO)_{12}(\mu_3-O)_4$	7
$Os_6(CO)_{19}(\mu_3-O)$	8
$Os_6(CO)_{16}(\mu-H)(\mu_3-O)(C_5H_5N)(\mu-\eta^2-NC_5H_4)$	9
$[Fe_{3}(CO)_{9}(\mu_{3}-O)(\mu_{3}-AuPPh_{3})]^{-}$	10
$[Fe_{3}(CO)_{9}(\mu_{3}-O-CMe_{3})]^{-}$	11
$Fe_3(CO)_9(\mu_3-O-CMe_3)(\mu-AuPPh_3)$	11
$Fe_3(CO)_9(\mu_3-O)(\mu_3-AuPPh_3)(\mu-AuPPh_3)$	12
$[Fe_3Rh_3(CO)_{12}(\mu_3-O)]^-$	12
$[Fe_3Mn(CO)_{12}(\mu_4-O)]^-$	13
$[Fe_{3}Re(CO)_{12}(\mu_{4}-O)]^{-}$	13
$[Fe_2Ru_3(CO)_{14}(\mu_4-O)]^{2-}$	14
$Fe_2(CO)_6(\mu$ -OH)(μ -P(p -Tol) ₂)	15
$Fe_2(CO)_6(\mu$ -OH)(μ -PH(CH(SiMe_3)_2)	16
$[Ru_{3}(CO)_{4}(dppm)_{3}(\mu_{3}-OH)]^{+}$	6
$Ru_4(CO)_8(\mu_3-OH)_2(COEt)_4(CF_3SO_3)_2$	17
$Ru_4(CO)_{10}(\mu_3-OH)(CCH-iPr)(\mu-PPh_2)$	18
$Ru_6Cl_6(CO)_{12}(COEt)_4(\mu_3-OH)_2$	19
$Ru_6(CO)_{18}(\mu-OH)_2(\mu_4-S)$	20
$Os_3(CO)_8(NMe_3)(\mu-OH)(\mu-H)(\mu_3-S)$	21
$Os_3(CO)_9(L)(\mu-OH)(\mu-H)$	22
$Os_3(CO)_9(\mu_3-C_2CPh_2)(\mu-OH)(\mu-H)$	23
$Os_3(CO)_{10}(\mu$ -OH)(μ -NCMe ₂)	24
$Os_4(CO)_{12}(\mu$ -OH)H ₃	25
$[Os_4(CO)_{12}(\mu-OH)H_4]^+$	26
$Os_6(CO)_{18}(\mu_4-O)(\mu-OH)_2$	27
$Os_6(CO)_{18}(\mu-OH)(\mu-H)(\mu_4-S)(\mu_3-S)$	21
$FeRu_2(CO)_8(PPh_3)_2(\mu-OH)_2$	28

 $[Cs(THF)_{0.33}]_{3}[{Fe_{3}(CO)_{9}(\mu_{3}-O)}_{2}(\mu-H)]$ and $[NEt_{4}]_{3}[{Fe_{3}(CO)_{9}(\mu_{3}-O)}_{2}(\mu-H)]$ salts, which both contain the notable dimeric $[{Fe_{3}(CO)_{9}(\mu_{3}-O)}_{2}(\mu-H)]^{3-}$ trianion, in which two $[Fe_{3}(CO)_{9}(\mu_{3}-O)]^{2-}$ moieties are held together by a linear and symmetric O–H–O hydrogen bond, ranging among the shortest interactions reported for organic, inorganic and organometallic compounds.

Results and discussion

1. Reinvestigation of the chemical behaviour of $[Fe_3(CO)_9-(\mu_3-O)]^{2-}$ in water : synthesis and characterization of the $[\{Fe_3(CO)_9(\mu_3-O)\}_2H]^{3-}$ trianion

Tetrasubstituted ammonium salts of the $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ dianion have originally been prepared by reaction of the corresponding $[Fe_3(CO)_{11}]^{2-}$ salts with dry air in THF,⁵ and are insoluble in water. The alkali salts of several anionic metal carbonyl clusters, *e.g.* $[Co_6(CO)_{15}]^{2-32}$ and $[Ni_{12}(CO)_{21}]^{4-}$,³³ are fairly soluble in water. In general, the solubility in water of alkali salts of anionic metal carbonyl clusters increases upon increasing the charge of the anion and is tuneable as a function of the size and concentration of the alkali cations. Differential solubility due to the above factors has been systematically exploited by Chini and Martinengo for their successful separation of complex mixtures of anionic carbonyl rhodium clusters, obtained by reduction of Rh₄(CO)₁₂ with sodium hydroxide in alcohol.^{34,35}

In order to obtain the $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ dianion as alkali salt, the Na⁺ and K⁺ salts of the $[Fe_3(CO)_{11}]^{2-}$ dianion have been synthesized by deprotonation of $[NEt_3H][HFe_3(CO)_{11}]^{36,37}$ in methanol with the corresponding hydroxide, as previously

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reported.³⁸ The resulting cloudy solution was filtered and a slow stream of dry air was directly bubbled through the solution. The solvent was, then, removed in vacuum yielding an oily residue of the alkali salts of $[Fe_3(CO)_9(\mu_3-O)]^{2-}$. These are soluble in water, THF, acetone and acetonitrile. Drop-wise addition of a 20% aqueous solution of H₂SO₄ to their water solutions led to separation of a mixture of some Fe₃(CO)₁₂, [M(H₂O)_x][HFe₃- $(CO)_{11}$ and $[M(H_2O)_x][Fe_3(CO)_9(\mu_3-OH)]$ and greater amounts of $[M(H_2O)_x][HFe_4(CO)_{13}]$, as a dark microcrystalline precipitate. It seems reasonable to speculate that [HFe₃(CO)₁₁]⁻ and [HFe₄- $(CO)_{13}$ ⁻ result from further protonation of $[Fe_3(CO)_9(\mu_3-OH)]^-$, followed by elimination of water and generation of a $\{Fe_3(CO)_9\}$ species (any eventually coordinated solvent is omitted), according to eqn (2). The carbonyl-unsaturated $\{Fe_3(CO)_9\}$ species readily disproportionates according to reactions (3) and (4) to tri- and tetra-nuclear dianions, which are readily protonated to their corresponding mono-hydride derivatives in the acid conditions of the reaction. A somehow related disproportionation of $Fe_2(CO)_9$ in THF has been reported to give Fe(THF)₄[HFe₃(CO)₁₁]₂.³⁹

$$\begin{split} [Fe_3(CO)_9(\mu_3\text{-}OH)]^- + H^+ &\rightleftharpoons \{HFe_3(CO)_9(\mu_3\text{-}OH)\} \\ &\to \{Fe_3(CO)_9\} + H_2O \end{split} \tag{2}$$

$$4\{Fe_3(CO)_9\} \to 3Fe^{2+} + 3[Fe_3(CO)_{11}]^{2-} + 3CO$$
(3)

$$5{Fe_3(CO)_9} \to 3Fe^{2+} + 3[Fe_4(CO)_{13}]^{2-} + 6CO$$
(4)

 $Fe_3(CO)_{12}$ likely derives from concomitant reaction of $\{Fe_3(CO)_9\}$ with the CO set free by reactions (3) and (4). Alternately, it might result from protonation of $[HFe_3(CO)_{11}]^-$ and decomposition of the resulting $HFe_3(CO)_{10}(CO-H)$.⁴⁰

A similar sequence of reactions also occurs in organic solvents such as MeOH, and THF. IR and ¹H NMR monitoring of the reaction failed to give any spectroscopic evidence of the purported {HFe₃(CO)₉(μ_3 -OH)} and {Fe₃(CO)₉} intermediate species, probably being too unstable to build up to a detectable concentration.

It was speculated that the above failed attempt to isolate $[Fe_3(CO)_9(\mu_3-OH)]^-$ from protonation of water solutions of $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ might be due to a relatively high solubility of the Na⁺ and K⁺ salts of $[Fe_3(CO)_9(\mu_3-OH)]^-$, which was not enabling stabilization by precipitation. Therefore, the reaction was repeated using a water solution saturated with CsCl. In these conditions, a mixture of species in their Cs⁺ salts readily separates out as a microcrystalline precipitate already from the beginning of the progressive addition of a water solution of H₂SO₄ (20% in volume). The $[Fe_3(CO)_9(\mu_3-OH)]^-$ hydroxoderivative is by far the most abundant product. The precipitate is first extracted with toluene to eliminate trace amounts of $Fe_3(CO)_{12}$ and then with dichloromethane to eliminate some [HFe₃(CO)₁₁]⁻ and a yet uncharacterized red-violet species. Subsequent extraction in THF yields a red solution which shows major infrared carbonyl absorptions at 2000(m) and 1960(s) cm⁻¹, respectively due to [HFe₄(CO)₁₃]⁻ and [Fe₃(CO)₉(µ₃-OH)]⁻. Layering of n-hexane gives rise to separation of few black crystals of [Cs(THF)]₂[Fe₄(CO)₁₃] and well shaped orange-red crystals of $[C_{s}(THF)_{0,33}]_{3}[\{Fe_{3}(CO)_{9}(\mu_{3}-O)\}_{2}H]$. Isolation of the latter trianion is prompted by the occurrence in solution of equilibria (5) and (6), and favoured by the low solubility of its cesium salt in THF.

$$[Fe_3(CO)_9(\mu_3\text{-}OH)]^- \rightleftharpoons [Fe_3(CO)_9(\mu_3\text{-}O)]^{2-} + H^+$$
(5)

$$\begin{split} [Fe_{3}(CO)_{9}(\mu_{3}\text{-}O)]^{2^{-}} + [Fe_{3}(CO)_{9}(\mu_{3}\text{-}OH)]^{-} \\ \rightleftharpoons [\{Fe_{3}(CO)_{9}(\mu_{3}\text{-}O)\}_{2}H]^{3^{-}} \end{split} \tag{6}$$

The crystals of $[Cs(THF)_{0.33}]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$ have been mechanically separated from those of $[Cs(THF)]_2[Fe_4(CO)_{13}]$, on the basis of their different colour and morphology and both salts have been characterized by X-ray crystal diffraction. The overall yield based on starting $[NEt_3H][HFe_3(CO)_{11}]$ is about 20%. The heavy disorder of the THF molecule solvating the cesium cation, though completely unravelled, and the particular packing of the ions urged a further structure determination on a different ordered salt to improve reliability of individual molecular parameters and dismiss the possibility that the presence of $[{Fe_3(CO)_9(\mu_3-O)}_2H]^{3-}$ ions could be an artefact of the confinement of the cluster in a cuboctahedral cage of Cs⁺ ions (see next section).

Tetrasubstituted ammonium and phosphonium salts of $[Fe_3(CO)_9(\mu_3-OH)]^-$ are readily available by protonation in methanol with one equivalent of diluted H₂SO₄ of the corresponding $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ salts, via the reverse reaction of equilibrium (5), and precipitation with water. As in the past, a series of attempted crystallizations in miscellaneous solvents (acetone-isopropyl alcohol, acetonitrile-di-isopropyl ether, THFtoluene) of $[Fe_3(CO)_9(\mu_3-OH)]^-$, in its $[NMe_4]^+$, $[NMe_3CH_2Ph]^+$ and [PPh₄]⁺ salt, only gave rise to separation of crystals of the starting $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ dianion. Only in the case of $[NEt_4][Fe_3(CO)_9(\mu_3-OH)]$, crystallization from a THF-toluene mixture yielded a mixture of crystals, predominantly constituted by crystals of $[NEt_4]_2[Fe_3(CO)_9(\mu_3-O)]$, accompanied by few crystals of $[NEt_4]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$. Though their amount was rather meagre (probably ca. 5-10%, as inferred by IR monitoring of a nujol mull of the mixture), they could be identified and mechanically separated on the basis of their different colour and morphology.

Spectroscopic characterization in solution (IR, NMR, ESI-MS) of the [{Fe₃(CO)₉(μ_3 -O)}₂H]³⁻ trianion has been hampered by its ready splitting in solution, according to the back reaction of equilibrium (6). Therefore, only solid state characterization such as nujol mull IR and X-ray single crystal studies (see next section) could be carried out. Significantly, the nujol mull IR spectrum of [{Fe₃(CO)₉(μ_3 -O)}₂H]³⁻ shows IR carbonyl absorptions at 1951(vs), 1920(s) and 1896(m) cm⁻¹, which are fairly close to the baricentre of those of crude [NEt₄][Fe₃(CO)₉(μ_3 -O)] (ν_{CO} at 1963(vs), 1933(s), 1910(m) cm⁻¹) and [NEt₄]₂[Fe₃(CO)₉(μ_3 -O)] (ν_{CO} 1931(vs), 1903(s), 1874(m) cm⁻¹), in perfect agreement with its intermediate charge per carbonyl groups. That points out that the negative charge is equally delocalized over both Fe₃(CO)₉(μ_3 -O) moieties.

2. Crystal structure of $[Cs(THF)_{0.33}]_3[Fe_3(CO)_9(\mu_3-O)]_2H]$ and $[NEt_4]_3[Fe_3(CO)_9(\mu_3-O)]_2H]$ salts

Both title salts contain the $[{Fe_3(CO)_9(\mu_3-O)}_2(\mu-H)]^{3-}$ trianion displaying almost coincident individual molecular parameters in both cases.

The $[{Fe_3(CO)_9(\mu_3-O)}_2(\mu-H)]^{3-}$ trianion. A first view of the trianion with the numbering scheme is given in Fig. 1. A comparison of the individual molecular parameters with those



Fig. 1 The $[\{Fe_3(CO)_9(\mu_3-O)\}_2H]^{3-}$ dimer present in the solid state structure of both $[NEt_4]_3[\{Fe_3(CO)_9(\mu_3-O)\}_2H]$ and $[Cs(THF)_{0,33}]_3-[\{Fe_3(CO)_9(\mu_3-O)\}_2H]$ (the labeling refers to Table 2; iron and hydrogen atoms are shown as hatched spheres).

of the related $[Fe_3(CO)_9(\mu_3-O-CMe_3)]^-$ monoanion is reported in Table 2. As shown in Fig. 1, the trianion is generated by formal condensation of a $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ dianion with a $[Fe_3(CO)_9(\mu_3-OH)]^-$ monoanion in a staggered conformation (see Fig. 2), *via* formation of a symmetric and linear hydrogen bond. By far the most notable feature is represented by the extremely short $O \cdots O$ separation [2.386(7) and 2.383(9) Å] and O-H bond contacts [1.193(5) and 1.191(5) Å, respectively, for the $[NEt_4]^+$ and $[Cs(THF)_{0.33}]^+$ salt]. Homonuclear hydrogen bonds displayed by organic, organometallic and inorganic compounds in the solid state have been critically discussed and classified few years ago by Gilli *et al.*⁴¹ The title trianion falls in the chemical class A, displaying the shortest $O \cdots O$ intermolecular separations, *viz.*, for

Table 2 Comparison between the bond distances (Å) in $[NEt_4]_{3-}[{Fe_3(CO)_9(\mu_3-O)}_2H]$ (A), $[Cs(THF)_{0.33}]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$ (B), and $[N(PPh_3)_2][Fe_3(CO)_9(\mu_3-O-CMe_3)]$ (C)¹¹

	(A)	(B)	$(C)^a$
Fe(1)–C(1)	1.776(5)	1.756(4)	1.768 (av)
Fe(1)-C(2)	1.743(5)	1.788(3)	
Fe(1) - C(3)	1.776(5)	b	
Fe(1)-O(4)	1.896(3)	1.890(3)	1.940 (av)
$Fe(1)-Fe(1')^c$	2.4976(11)	2.4896(10)	2.482 (av)
$Fe(1) - Fe(1'')^d$	2.4976(11)	2.4896(10)	
C(1)–O(1)	1.151(5)	1.152(5)	1.146 (av)
C(2) - O(2)	1.166(6)	1.140(4)	
C(3) - O(3)	1.156(6)	Ь	
$O(4) - O(4')^d$	2.386(7)	2.383(9)	
H(4)–O(4)	1.193(5)	1.191(5)	1.474 (O-CMe ₃)
$H(4) - O(4')^{e}$	1.193(5)	1.191(5)	

^{*a*} See ref. 11. ^{*b*} Due to the crystal symmetry, only two CO ligands per Fe atom are independent. ^{*c*} Symmetry transformations used to generate equivalent atoms: y, z, x for (A), -y + 1, x - y - 1, z for (B). ^{*d*} Symmetry transformations used to generate equivalent atoms: z, x, y for (A), -x + y + 2, -x + 1, z for (B). ^{*e*} Symmetry transformations used to generate equivalent atoms: 0.5 - x, 0.5 - z for (A), -x + 2, -y, -z for (B).



Fig. 2 View of the $[{Fe_3(CO)_9(\mu_3-O)}_2H]^{3-}$ dimer along the C_3 axis.

instance, intermolecular alcohol–alcoholate (2.39–2.43 Å) adducts and inorganic acid salts (2.36–2.43 Å).

The symmetric nature of the O–H–O bond might appear to be a consequence of the crystallographic symmetry of the unit cell of both salts. However the presence of a delocalized 3c-4e O–H–O bond seems perfectly in keeping with the equivalence of the two Fe₃(CO)₉(μ_3 -O) moieties and the observation of perfect delocalization of the negative charge, inferable from the solid state infrared spectrum. Indeed, its IR carbonyl absorptions are intermediate between those of the [Fe₃(CO)₉(μ_3 -O)]^{2–} dianion and the [Fe₃(CO)₉(μ_3 -OH)][–] monoanion. Therefore, it seems reasonable rather to suggest that the symmetric nature of the O– H–O bond might be at the origin of the high crystallographic symmetry.

In agreement with this interpretation, DFT calculations on a KH_2PO_4 phase, in which the H position is varied along the O– O axis, reveal that at the short O···O distance of 2.405 Å there is a single energy-minimum at the mid-point, whereas as the O– O distance is elongated to 2.469 and 2.51 Å the energy curve develops a well defined double well with minima separated by 0.34 and 0.41 Å, respectively.⁴²

The fact that the O–O distance is invariant with the cation points out that it represents an intrinsic feature of the [{Fe₃(CO)₉(μ_3 -O)}₂H]³⁻ trianion.



Fig. 3 The packing of Cs⁺ ions (blackened Cs⁺ spheres individuate the cuboctahedron).

A strength–length relationship is expected to hold for linear or nearly linear O–H–O bonds⁴¹ and would suggest the presence in the trianion of a relatively strong hydrogen bond. The increasing strength of O–H–O bonds with O···O distances in the 2.432– 2.554 Å range has been experimentally substantiated by progressive lowering of their IR O–H stretching frequencies and downfield shifts of their proton resonances.⁴³ Unfortunately, the fact that the title trianion is not stable in polar solvents and its salts involve the presence of tetraethylammonium cations or THF molecules solvating the Cs⁺ ions, respectively, makes unsafe any conclusion based on their IR and ¹H NMR.

The packing of Cs⁺ cations. It is worth to briefly comment the packing of Cs⁺ ions, in order to clarify the formula of the [Cs(THF)_{0.33}]₃[{Fe₃(CO)₉(μ_3 -O)}₂H] salt. As shown in Fig. 3, the Cs⁺ ions individuate the vertices of two (non-bonded) polyhedral arrangements: the non-centred cuboctahedron and the distorted octahedron. Fusion of cuboctahedrons and octahedrons gives rise to a 3D space-filling net, as predicted by Andreini.^{44,45} The slightly distorted non-bonded cuboctahedron (Cs⁺ ··· Cs⁺ 6.55 and 7.25 Å) encapsulates the [{Fe₃(CO)₉(μ_3 -O)}₂(μ -H)]³⁻ trianion (Fig. 4(a)) by interactions of all oxygen atoms of the 18 carbonyl



Fig. 4 The cuboctahedron of Cs^+ ions encapsulating the [{Fe₃(CO)₉(μ_3 -O)}₂H]³⁻ trianion (a), the distorted octahedron of Cs^+ ions encapsulating the unique rattling around THF molecules, disordered over 12 positions (b) and the coordination of each Cs^+ ion (c) (Cs^+ ions are shown as blackened spheres, iron atoms in (a) and oxygen atoms in (b) and (c) are shown as hatched spheres).

groups with the surrounding twelve Cs^+ ions. The unique bridging hydrogen atom is located in the centre of the cuboctahedron.

The slightly distorted non-bonded octahedron ($Cs^+ \cdots Cs^+ 6.55$ and 7.25 Å) encapsulates a THF molecule, which rattles around in 12 positions, probably in the attempt to saturate the coordination of all Cs^+ ions. As a result, each Cs^+ ion is coordinated to eight oxygen atoms of the carbonyl groups belonging to different [$\{Fe_3(CO)_9(\mu_3-O)\}_2(\mu-H)\}^{3-}$ cluster ions. These Cs^+-O contacts are divided in two sets averaging 3.144 Å (Cs^+-O contacts) and 3.396 Å (Cs^+-O-Cs^+ bridging contacts), respectively. Finally, the coordination sphere of each Cs^+ ion displays four coordination sites partially occupied by a disordered THF molecule [average Cs-O contact 3.725 Å; the occupancy factor for each site is 0.08333] giving an overall count of 0.33 THF molecules per Cs^+ ion.

3. Crystal structure of $[Cs(THF)]_2[Fe_4(CO)_{12}(\mu_3-CO)]$

The structure of $[Fe_4(CO)_{12}(\mu_3\text{-}CO)]^{2-}$ has been already determined two times in its $[FePy_6]^{2+46}$ and $[N(PPh_3)_2]^+$ salt.⁴⁷ Being our interest mainly confined to the coordination and packing of Cs⁺ ions, only a very brief description of the $[Fe_4(CO)_{13}]^{2-}$ dianion is given. Two views of the latter, corresponding to those originally given by Dahl⁴⁶ in its seminal paper regarding the structure of $[FePy_6][Fe_4(CO)_{13}]$, are shown in Fig. 5. The iron atoms describe a tetrahedron, one face of which is capped by a μ_3 -CO group. All other CO groups are essentially linear. The individual molecular parameters (Table 3) are very similar to those found in the corresponding $[N(PPh_3)_2]$ [Fe₄(CO)₁₂(μ_3 -CO)] salt.

In contrast to $[Cs(THF)_{0.33}]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$, the Cs⁺ ions of $[Cs(THF)]_2[Fe_4(CO)_{13}]$ do not individuate a simple polyhedral net. Indeed, the Cs⁺ ions can be divided in two sets: the first set consists of a zigzag chain of Cs⁺ ions. A fragment of this chain is shown in Fig. 6(a). Each Cs⁺ displays a coordination number of 9, achieved by interaction with a unique terminally-bonded THF molecule and eight oxygen atoms belonging to the carbonyl groups of three distinct $[Fe_4(CO)_{13}]^{2-}$ dianions. Notably, two oxygen atoms of each $[Fe_4(CO)_{13}]^{2-}$ unit behave as a bridging ligands for two consecutive pairs of Cs⁺ ions.

The second set of Cs⁺ ions are arranged in distinct pairs of ions. One incomplete pair is shown in Fig. 6(b). The coordination number of Cs⁺ is yet 9, owing to the presence of two bridging THF molecules, two bridging oxygen atoms of the carbonyl groups of two distinct $[Fe_4(CO)_{13}]^{2-}$ ions, and five oxygen atoms belonging to other two yet different $[Fe_4(CO)_{13}]^{2-}$ units. In their turn, these



Fig. 5 Two views of the $[Fe_4(CO)_{12}(\mu_3-CO)]^{2-}$ dianion.



Fig. 6 A representation of the two different motives generated by the coordination of the two independent Cs^+ ions: a fragment of the zigzag chain (a) and the pair (b) of Cs^+ ions described in the text (only the $[Fe_4(CO)_{13}]^{2-}$ ions interacting with one Cs^+ of the pair are shown for sake of clarity).

 $[Fe_4(CO)_{13}]^{2-}$ ions interact trough their remaining carbonyl groups with the Cs^+ ions of the first set.

The notable invariance of all bond distances of both $[\{Fe_3(CO)_9(\mu_3\text{-}O)\}_2H]^3\text{-}$ and $[Fe_4(CO)_{13}]^2\text{-}$ in their respective Cs⁺– $[NEt_4]^+$ and Cs⁺– $[N(PPh_3)_2]^+$ salts points out that the Cs–O interactions do not effect significantly the bonding within the metal carbonyl clusters.

Experimental

All reactions and sample manipulations were carried out using standard Schlenk techniques under nitrogen and in dried solvents.

Table 3 Bond distances (Å) of [Cs(THF)]₂[Fe₄(CO)₁₃]

Fe(1)–Fe(3)	2.5958(8)	Fe(4)-C(10)	1.762(4)
Fe(1)-Fe(2)	2.6008(8)	Fe(4) - C(12)	1.764(4)
Fe(1)– $Fe(4)$	2.6079(8)	Fe(4) - C(11)	1.774(4)
Fe(3)-Fe(4)	2.5404(8)	Fe(4) - C(13)	2.002(4)
Fe(2)-Fe(4)	2.5431(8)	C(1)–O(1)	1.152(5)
Fe(2)-Fe(3)	2.5596(8)	C(2)–O(2)	1.166(5)
Fe(1)-C(2)	1.758(4)	C(3)–O(3)	1.147(5)
Fe(1)-C(1)	1.781(4)	C(4) - O(4)	1.162(5)
Fe(1)-C(3)	1.788(4)	C(5)–O(5)	1.160(5)
Fe(2)-C(4)	1.764(4)	C(6)–O(6)	1.143(5)
Fe(2) - C(6)	1.766(5)	C(7) - O(7)	1.169(5)
Fe(2) - C(5)	1.782(4)	C(8)–O(8)	1.150(5)
Fe(2)-C(13)	2.006(4)	C(9)–O(9)	1.153(5)
Fe(3) - C(7)	1.756(4)	C(10)–O(10)	1.165(5)
Fe(3)-C(8)	1.764(4)	C(11)–O(11)	1.150(5)
Fe(3) - C(9)	1.780(4)	C(12)–O(12)	1.167(5)
Fe(3) - C(13)	2.117(4)	C(13)–O(13)	1.197(5)

The [NEt₃H][HFe₃(CO)₁₁] and [Fe₃(CO)₁₁]²⁻ and [Fe₃(CO)₉(μ_3 -O)]²⁻ salts have been prepared according to the literature.^{48,38,4} Analysis of Fe was performed by atomic absorption on a Pye-Unicam instrument. Analyses of C, H and N were obtained with a ThermoQuest FlashEA 1112NC instrument. IR spectra were recorded on a Perkin Elmer SpectrumOne interferometer. The figures were drawn with SCHAKAL99.⁴⁹

Synthesis of $[Cs(THF)_{0.33}]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$

Solid [NEt₃H][HFe₃(CO)₁₁] (2.08 g, 2.60 mmol) was dissolved in an alkaline methanol solution (30 mL) containing KOH (2.20 g, 39.3 mmol) and stirred overnight. Complete deprotonation to give the dianion $[Fe_3(CO)_{11}]^{2-}$ was confirmed by IR spectroscopy. This was completely converted into $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ by bubbling through the solution a slow stream of dry air. An oily residue of $[K(MeOH)_x]_2$ [Fe₃(CO)₉(μ_3 -O)] was, then, obtained after removing the solvent under reduced pressure. This was dissolved in water (20 mL). The solution was saturated with CsCl up to incipient precipitation and diluted H₂SO₄ (20% in water) was drop-wise added to the solution resulting in the immediate formation of a dark microcrystalline precipitate. The solid was first extracted with toluene to eliminate trace amounts of $Fe_3(CO)_{12}$, and then with CH_2Cl_2 to eliminate some $[HFe_3(CO)_{11}]^-$ and a yet uncharacterised red-violet species. Subsequent extraction in THF yielded a red solution containing [HFe₄(CO)₁₃]⁻ and [Fe₃(CO)₉(μ_3 -OH)]⁻. Layering of n-hexane resulted in the separation of few black crystals of [Cs(THF)x]2[Fe4(CO)13] and well-shaped orangered crystals of $[Cs(THF)_{0.33}]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$, which were mechanically separated to give 0.69 g of the latter compound

 $\textbf{Table 4} \quad Crystal data and experimental details for [NEt_4]_3[{Fe_3(CO)_9(\mu_3-O)}_2H], [Cs(THF)_{0.33}]_3[{Fe_3(CO)_9(\mu_3-O)}_2H] and [Cs(THF)]_2[Fe_4(CO)_{13}]_3[Cs(THF)_{0.33}]_3[{Fe_3(CO)_9(\mu_3-O)}_2H] and [Cs(THF)]_2[Fe_4(CO)_{13}]_3[Cs(THF)_{0.33}]_3[{Fe_3(CO)_9(\mu_3-O)}_2H] and [Cs(THF)]_2[Fe_4(CO)_{13}]_3[Cs(THF)_{0.33}]_3[$

$[NEt_4]_3[\{Fe_3(CO)_9(\mu_3\text{-}O)\}_2H]$	$[Cs(THF)_{0.33}]_3[\{Fe_3(CO)_9(\mu_3\text{-}O)\}_2H]$	$[\mathrm{Cs}(\mathrm{THF})]_2[\mathrm{Fe}_4(\mathrm{CO})_{13}]$
$\begin{array}{c} C_{42}H_{61}Fe_6N_3O_{20}\\ 1263.04 \end{array}$	$C_{22}H_9Cs_3Fe_6O_{21}$ 1343.12	$\begin{array}{c} C_{21}H_{16}Cs_{2}Fe_{4}O_{15}\\ 997.56 \end{array}$
295(2)	295(2)	100(2)
0.71073	0.71073	0.71073
Cubic	Rhombohedral	Triclinic
Ia3	$R\bar{3}m$	$P\overline{1}$
22.1927(17)	13.0952(3)	9.3755(11)
22.1927(17)	13.0952(3)	9.4461(11)
22.1927(17)	18.5660(10)	17.669(2)
90	90	90.984(2)
90	90	96.280(2)
90	120	101.695(2)
10931.3(15)	2757.23(17)	1521.9(3)
8	3	2
1.535	2.427	2.177
1.623	5.312	4.292
5200	1890	952
$0.21 \times 0.18 \times 0.15$	$0.19 \times 0.16 \times 0.11$	$0.19 \times 0.15 \times 0.12$
1.84-25.03	2.84–27.98	2.20-27.00
$-26 \le h \le 26$	$-16 \le h \le 17$	$-11 \le h \le 11$
$-26 \le k \le 26$	$-16 \le k \le 16$	$-12 \le k \le 12$
$-24 \le l \le 24$	$-24 \le l \le 24$	$-22 \le l \le 22$
44478	10703	16581
$1626 [R_{int} = 0.2068]$	$837 [R_{int} = 0.0194]$	$6562 [R_{int} = 0.0351]$
1626/0/110	837/31/64	6562/108/379
1.012	1.108	1.020
0.0505	0.0225	0.0293
0.1010	0.0591	0.0722
0.370/-0.311	0.457/-0.576	1.353/-0.954
	$[NEt_4]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$ $C_{42}H_{61}Fe_6N_3O_{20}$ 1263.04 295(2) 0.71073 Cubic Ia3 22.1927(17) 22.1927(17) 22.1927(17) 22.1927(17) 90 90 90 10931.3(15) 8 1.535 1.623 5200 0.21 × 0.18 × 0.15 1.84-25.03 -26 ≤ h ≤ 26 -26 ≤ h ≤ 26 -26 ≤ k ≤ 26 -24 ≤ l ≤ 24 44478 1626 [$R_{int} = 0.2068$] 1626/0/110 1.012 0.0505 0.1010 0.370/-0.311	$\begin{array}{llllllllllllllllllllllllllllllllllll$

(yield 20% based on [NEt₃H][HFe₃(CO)₁₁]). Anal. Found (Calcd.): C 19.91 (19.67), H 0.45 (0.68), Cs 29.41 (29.69), Fe 25.09 (24.95).

Synthesis of $[NEt_4]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$

Solid $[NEt_4]_2[Fe_3(CO)_9(\mu_3-O)]$ (1.72 g) was suspended in THF (30 mL). The suspension was treated drop-wise with diluted H₂SO₄ (20% in water) up to complete disappearance of the IR absorptions of the $[Fe_3(CO)_9(\mu_3-O)]^{2-}$ dianion. The resulting orange-red solution (showing IR absorptions at 2025(w), 1963(vs), 1933(s), 1910(m) cm⁻¹) was filtered and precipitated by layering toluene (50 mL). The resulting red-orange crystalline precipitate was mainly constituted by crystals of the $[NEt_4]_2[Fe_3(CO)_9(\mu_3-O)]$ starting material. Only a few crystals exhibiting a slightly different colour and morphology could be noticed, and have been hand separated. These showed a nujol mull spectrum related to that of the $[Fe_3(CO)_9(\mu_3-O)]_2H]^{3-}$ trianion and have been kept apart for further characterization. Anal. Found (Calcd.): C 39.67 (39.94), H 4.78 (4.87), N 3.21 (3.33), Fe 26.35 (26.53).

X-Ray crystallographic study

Crystal data and collection details for $[NEt_4]_3[{Fe_3(CO)_9(\mu_3 - \mu_3)}]$ O) $_{2}$ H], [Cs(THF)_{0.33}]₃[{Fe₃(CO)₉(μ_{3} -O)}₂H] and [Cs(THF)]₂- $[Fe_4(CO)_{13}]$ are reported in Table 4. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo-Ka radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).⁵⁰ Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^{2.51} Hydrogen atoms bonded to C-atoms were fixed at calculated positions and refined by a riding model. Oxygen bonded hydrogen atoms were located in the Fourier map and found to be on an inversion centre for both structures, they were, then, refined isotropically using the 1.5 fold U_{iso} value of the parent O-atom. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated. The cation in the structure of $[NEt_4]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$ has imposed two-fold symmetry and the anion has -3 symmetry. In the case of $[Cs(THF)_{0,33}]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$ the anion has imposed -3 symmetry and the THF molecule is disordered over 12 symmetry-related positions, therefore, the unique THF molecule was refined isotropically with a fixed occupancy factor of 0.08333. Restraints were applied on the C-O and C-C distances of the THF molecules of both $[Cs(THF)_{0.33}]_3[{Fe_3(CO)_9(\mu_3-O)}_2H]$ and $[Cs(THF)]_2[Fe_4(CO)_{13}]$, as well as similar U restraints on all oxygen and carbon atoms, in order to obtain satisfactory models.

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Notes and references

- 1 H. W. Roesky, I. Haiduc and N. S. Hosmane, *Chem. Rev.*, 2003, **103**, 2579.
- 2 J. W. Gilje and H. W. Roesky, Chem. Rev., 1994, 94, 895.

- 3 H. W. Roesky, S. Singh, K. K. M. Yusuff, J. A. Maguire and N. S. Hosmane, *Chem. Rev.*, 2006, **106**, 3813 and ref. therein.
- 4 A. Ceriotti, L. Resconi, F. Demartin, G. Longoni, M. Manassero and M. Sansoni, J. Organomet. Chem., 1983, 249, C35.
- 5 G. Lavigne, N. Lugan and J.-S. Bonnet, Nouv. J. Chim., 1981, 5, 42.
- 6 H. A. Mirza, J. J. Vittal and R. J. Puddephatt, *Inorg. Chem.*, 1995, **34**, 4239.
- 7 F. Bottomley, D. E. Paez, L. Sutin and P. S. White, *J. Chem. Soc., Chem. Commun.*, 1985, 597.
- 8 R. S. Goudsmith, B. F. G. Johnson, J. Lewis, P. R. Raithby and K. M. Whitemire, J. Chem. Soc., Chem. Commun., 1983, 246.
- 9 K. S.-Y. Leung and W.-T. Wong, J. Chem. Soc., Dalton Trans., 1997, 4537.
- 10 V. G. Albano, C. Castellari, C. Femoni, M. C. Iapalucci, G. Longoni, M. Monari, M. Rauccio and S. Zacchini, *Inorg. Chim. Acta*, 1999, **291**, 372.
- 11 S. P. Gubin, L. A. Polyakova, A. V. Chukarov and L. G. Kuz'mina, *Russ. Chem. Bull.*, 1999, 48, 1757.
- 12 L. A. Polyakova, S. P. Gubin, O. A. Belyakova, Ya. V. Zubavichus and Yu. L. Slovokhotov, *Organometallics*, 1997, 16, 4527.
- 13 C. K. Schauer and D. F. Shriver, Angew. Chem., Int. Ed. Engl., 1987, 26, 255.
- 14 C. K. Schauer, E. J. Voss, M. Sabat and D. F. Shriver, J. Am. Chem. Soc., 1989, 111, 7662.
- 15 P. M. Treichel, W. K. Dean and J. C. Calabrese, *Inorg. Chem.*, 1973, 13, 2908.
- 16 A. M. Arif, A. H. Cowley, M. Pakulski, M.-A. Pearsall, W. Clegg, N. C. Norman and A. G. Orpen, J. Chem. Soc., Dalton Trans., 1988, 2713.
- 17 T. Funaioli, C. Cavazza, F. Marchetti and G. Facchinetti, *Inorg. Chem.*, 1999, 38, 3361.
- 18 A. J. Carty, S. A. MacLaughlin and N. J. Taylor, J. Chem. Soc., Chem. Commun., 1981, 476.
- 19 S. Merlino, G. Montagnoli, G. Braca and G. Sbrana, *Inorg. Chim. Acta*, 1978, 27, 233.
- 20 R. D. Adams, J. E. Babin and M. Tasi, Inorg. Chem., 1987, 26, 2561.
- 21 R. D. Adams, J. E. Babin and H. S. Kim, *Inorg. Chem.*, 1986, 25, 1122.
- 22 A. J. Deeming, P. J. Manning, I. P. Rothwell, M. B. Hursthouse and N. P. C. Walker, J. Chem. Soc., Dalton Trans., 1984, 2039.
- 23 S. Aime, A. J. Deeming, M. B. Hursthouse and J. D. J. Backer-Dirks, J. Chem. Soc., Dalton Trans., 1982, 1625.
- 24 A. J. Deeming, D. W. Owen and N. I. Powell, J. Organomet. Chem., 1990, 398, 299.
- 25 B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. Puga, K. Henrick and M. McPartlin, J. Chem. Soc., Dalton Trans., 1983, 1203.
- 26 J. S.-Y. Wong, Z.-Y. Lin and W.-T. Wong, Organometallics, 2003, 22, 4798.
- 27 B. F. G. Johnson, J. Lewis, P. R. Raithby and C. Zuccaro, J. Chem. Soc., Dalton Trans., 1980, 716.
- 28 D. F. Jones, P. H. Dixneuf, A. Benoit and J.-Y. LeMarouille, *Inorg. Chem.*, 1983, 22, 29.
- 29 L. Markò, J. Takacs, S. Papp and B. Markò-Monostory, *Inorg. Chim. Acta*, 1980, **45**, L189.
- 30 J.-J. Cherng, Y.-C. Tsai, C.-H. Ueng, G.-H. Lee, S.-M. Peng and M. Shieh, *Organometallics*, 1998, 17, 255 and ref. therein.
- 31 J. Willem van Hal and K. H. Whitmire, Organometallics, 1998, 17, 5197.
- 32 V. G. Albano, P. Chini and V. Scatturin, J. Organomet. Chem., 1968, 15, 423.
- 33 A. Ceriotti, P. Chini, R. Della Pergola and G. Longoni, *Inorg. Chem.*, 1983, 22, 1595.
- 34 P. Chini and S. Martinengo, J. Chem. Soc. D, 1969, 1092.
- 35 S. Martinengo, G. Ciani and A. Sironi, J. Am. Chem. Soc., 1980, 102, 7564.
- 36 W. Hieber and G. Brendal, Z. Anorg. Allg. Chem., 1957, 289, 332.
- 37 J. F. Blount and L. F. Dahl, Inorg. Chem., 1987, 4, 1373.
- 38 F. Y. K. Lo, G. Longoni, P. Chini, L. Lower and L. F. Dahl, J. Am. Chem. Soc., 1980, 102, 7691.
- 39 D. J. R. Brook, V. Lynch and T. H. Koch, *Inorg. Chem.*, 1995, 34, 5691.
- 40 H. A. Hodali, D. F. Shriver and C. A. Ammlung, J. Am. Chem. Soc., 1978, 100, 5239.
- 41 P. Gilli, V. Bertolasi, V. Ferretti and G. Gilli, J. Am. Chem. Soc., 1994, 116, 909.

- 42 Q. Zhang, N. Kioussis, S. G. Demos and H. B. Radousky, J. Phys.: Condens. Matter, 2002, 14, L89.
- 43 V. Bertolasi, P. Gilli, V. Ferretti and G. Gilli, J. Am. Chem. Soc., 1991, 113, 4917.
- 44 A. Andreini, Mem. Soc. Ital. Sci., 1907, 14, 75.
- 45 A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley, New York, 1977.
- 46 R. J. Doedens and L. F. Dahl, J. Am. Chem. Soc., 1966, 88, 4847.
- 47 G. van Buskirk, C. B. Knobler and H. D. Kaesz, *Organometallics*, 1985, 4, 149.
- 48 K. Farmery, M. Kilner, R. Greatrex and N. N. Greenwood, J. Chem. Soc. A, 1969, 2339.
- 49 E. Keller, SCHAKAL99, University of Freiburg, Germany, 1999.
- 50 G. M. Sheldrick, SADABS, University of Göttingen, Germany, 1996.
 51 G. M. Sheldrick, SHELX97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.