Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1376). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Oxo-Centered Trinuclear Cobalt(II)–Diiron(III) Acetate–Aqua Complex

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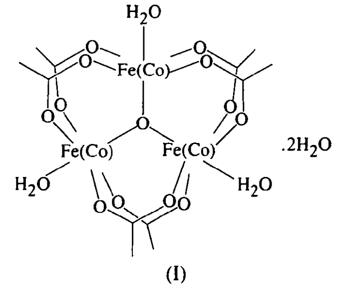
Abstract

The structure of hexakis-μ-acetato-1:2κ^4O:O';2:3κ^4-O:O';1:3κ^4O:O'-triaqua-1κO,2κO,3κO-μ_3-oxo-cobalt(II)-diiron(III) dihydrate, $[CoFe_2O(C_2H_3O_2)_6(H_2O)_3].2H_2O$, is reported. The compound is isostructural with the related mixed-valence trinuclear iron(II,III,III) acetate–aqua complex, $[Fe_3O(C_2H_3O_2)_6(H_2O)_3].2H_2O$. The coordination geometries around the three metal atoms of the cobalt–iron complex are almost identical to those of the trinuclear iron complex, and the Co and Fe atoms cannot be distinguished.

Comment

The structures of oxo-centered trinuclear metal–carboxylate complexes have been reported for various combinations of transition metal atoms (isometal mixed-valence and mixed-metal complexes) (see Cannon & White, 1988, and references therein). In many isometal mixed-valence complexes, the symmetry of the molecules is strongly related to the mixed-valence states of the metal atoms (localized or delocalized). The structures of the mixed-metal complexes of $[M^{II}M'^{III}_2O(C_2H_3O_2)_6(pyridine)_3]$.solvent ($M^{II}M'^{III}_2$ = $CoMn_2$, $CoFe_2$, $NiRu_2$, $CoRu_2$) have been reported in the same space group ($R32$) (Cannon *et al.*, 1993; Jang *et al.*, 1990; Ohta, Sasaki & Ito, 1994). These mixed-metal molecules have imposed D_{3h} symmetry and different kinds of metal atoms are indistinguishable.

We reported recently the structure of a mixed-valence trinuclear iron acetate–aqua complex, $[Fe_3O(C_2H_3O_2)_6(H_2O)_3].2H_2O$ (Sato *et al.*, 1996). ^{57}Fe Mössbauer spectroscopic data of this compound indicate that thermally induced intramolecular electron transfer takes place between the Fe atoms. The structural data are consistent with the results of ^{57}Fe Mössbauer spectroscopy. The coordination geometries around the three Fe atoms show good equivalence. The bond distances between the central O atom and the Fe atoms are 1.867 (4) (for Fe1), 1.904 (4) (for Fe2) and 1.906 (4) Å (for Fe3) at 293 K. Here, the structure of the corresponding trinuclear cobalt–iron acetate–aqua complex, (I), is reported.



(I)

The structure of a $[CoFe_2O(CH_3CO_2)_6(H_2O)_3]$ molecule is shown in Fig. 1. This compound is isostructural with the trinuclear iron acetate–aqua complex. Although ^{57}Fe Mössbauer data indicate that the Fe atoms are in an Fe^{III} state at room temperature, the three metal sites are almost equivalent in terms of geometry. Bond distances and angles in the molecule are almost identical to those found in the trinuclear iron acetate–aqua complex. The three Fe(Co) atoms form a near equilateral triangle. The central O4 atom is in the Fe(Co) triangular plane

[0.004 (5) Å] near the center of the triangle [Fe(Co)1—O4 1.882 (7), Fe(Co)2—O4 1.898 (6) and Fe(Co)3—O4 1.897 (6) Å]. The crystal water molecules are located along the *c* axis in the same manner as for the trinuclear iron acetate–aqua complex, with distances between the O21 and O22 atoms being 3.09 (4) (for O22 at x, y, z) and 4.73 (3) Å (for O22 at $x, -y, -\frac{1}{2}+z$). The O3 and O8 atoms are nearest to the O21 atom at distances of 2.87 (2) (for O3) and 3.03 (2) Å (for O8).

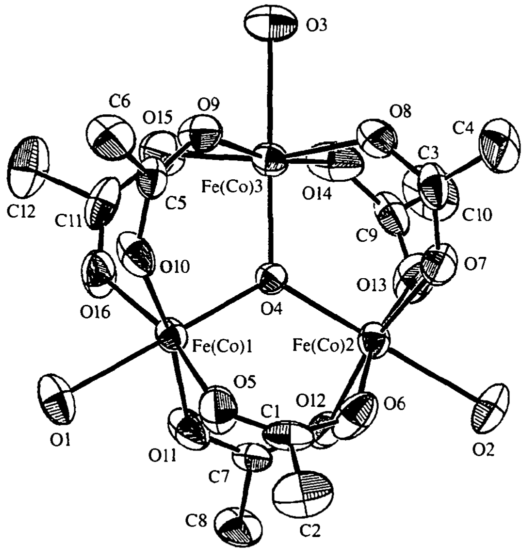


Fig. 1. *ORTEP*II (Johnson, 1976) view of the $[CoFe_2O(C_2H_3O_2)_6(H_2O)_3]$ molecule showing displacement ellipsoids at the 50% probability level. The crystal water molecules are not shown.

Experimental

Aqueous solutions of $[Fe(NO_3)_3].9H_2O$ (2.7 g in 150 ml) and $[Co(NO_3)_2].6H_2O$ (3.0 g in 150 ml) were added to a mixture of CH_3COOH (17.4 ml) and an aqueous solution of $Na(CH_3COO).3H_2O$ (14.0 g in 150 ml). The reaction solution was allowed to stand for a month. Precipitated crystals were filtered and washed with water. Analysis calculated for $C_{12}H_{28}CoFe_2O_{18}$: C 22.84, H 4.56, Co 9.34, Fe 17.70%; found: C 22.71, H 4.20, Co 7.79, Fe 18.68%.

Crystal data

$[CoFe_2O(C_2H_3O_2)_6(H_2O)_3]$.-$2H_2O$
$M_r = 630.97$
Monoclinic
$C2/c$
$a = 27.031 (1)$ Å
$b = 13.838 (1)$ Å
$c = 15.286 (1)$ Å
$\beta = 123.27 (1)°$
$V = 4780.6 (4)$ Å^3
$Z = 8$
$D_x = 1.75$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 9–18°$
$\mu = 1.96$ mm^{-1}
$T = 295$ K
Prism
0.36 × 0.13 × 0.07 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.872$, $T_{max} = 0.835$
11 822 measured reflections
5471 independent reflections

3003 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.024$
$\theta_{max} = 27.5°$
$h = -35 \rightarrow 29$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: 3.3%

Refinement

Refinement on F
$R = 0.061$
$wR = 0.085$
$S = 2.20$
3003 reflections
288 parameters
H atoms not included
$w = 1/[\sigma^2(F)]$

$(\Delta/\sigma)_{max} = 0.03$
$\Delta\rho_{max} = 1.11$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

B_{iso} for O21 and O22; $B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	B_{eq}/B_{iso}
Fe(Co)1†	0.88919 (4)	0.3974 (1)	0.71296 (8)	2.24 (3)
Fe(Co)2†	0.82479 (4)	0.4566 (1)	0.83488 (8)	2.26 (3)
Fe(Co)3†	0.84653 (5)	0.2281 (1)	0.80696 (9)	2.41 (3)
C1	0.9362 (4)	0.5543 (7)	0.8729 (7)	3.1 (2)
C2	0.9817 (4)	0.6315 (8)	0.9336 (9)	5.0 (3)
C3	0.8795 (3)	0.3162 (8)	1.0154 (6)	3.4 (2)
C4	0.9062 (5)	0.2984 (9)	1.1327 (7)	5.3 (3)
C5	0.9681 (3)	0.2321 (7)	0.8460 (6)	2.8 (2)
C6	1.0295 (4)	0.1857 (8)	0.8991 (8)	4.5 (3)
C7	0.7865 (3)	0.5392 (6)	0.6224 (6)	2.5 (2)
C8	0.7457 (4)	0.6050 (8)	0.5322 (7)	4.0 (3)
C9	0.7292 (3)	0.3071 (8)	0.7572 (6)	3.4 (2)
C10	0.6641 (3)	0.284 (1)	0.7145 (9)	5.5 (3)
C11	0.8274 (3)	0.2191 (8)	0.5940 (7)	3.4 (2)
C12	0.8071 (4)	0.1522 (9)	0.4977 (7)	5.1 (3)
O1	0.9302 (2)	0.4385 (6)	0.6319 (4)	3.7 (2)
O2	0.7923 (2)	0.5638 (5)	0.8927 (4)	3.7 (2)
O3	0.8380 (3)	0.0778 (5)	0.8343 (5)	4.3 (2)
O4	0.8535 (2)	0.3609 (4)	0.7845 (4)	2.0 (1)
O5	0.9405 (3)	0.5038 (5)	0.8120 (5)	4.2 (2)
O6	0.8957 (2)	0.5462 (5)	0.8914 (5)	4.1 (2)
O7	0.8669 (3)	0.4023 (5)	0.9822 (4)	4.1 (2)
O8	0.8713 (3)	0.2437 (5)	0.9587 (4)	3.8 (2)
O9	0.9309 (2)	0.1928 (5)	0.8575 (5)	3.6 (2)
O10	0.9603 (2)	0.3105 (5)	0.7967 (4)	3.8 (2)
O11	0.8250 (2)	0.4948 (5)	0.6172 (5)	3.8 (2)
O12	0.7790 (2)	0.5312 (5)	0.6960 (4)	3.3 (2)
O13	0.7487 (2)	0.3883 (5)	0.7895 (5)	4.4 (2)
O14	0.7596 (2)	0.2358 (5)	0.7548 (6)	4.4 (2)
O15	0.8219 (3)	0.1825 (6)	0.6624 (5)	4.8 (2)
O16	0.8475 (2)	0.2993 (5)	0.5974 (4)	3.8 (2)
O21	0.9214 (8)	0.047 (2)	1.054 (1)	22.3 (8)
O22	0.9017 (7)	0.022 (2)	1.234 (1)	20.2 (8)

† Site occupancies for Fe/Co = 0.667/0.333.

Table 2. *Selected geometric parameters (Å, °)*

Fe(Co)1—O4	1.882 (7)	Fe(Co)2—O7	2.030 (6)
Fe(Co)1—O1	2.143 (8)	Fe(Co)2—O12	2.055 (6)
Fe(Co)1—O5	2.019 (6)	Fe(Co)2—O13	2.011 (7)
Fe(Co)1—O10	2.021 (6)	Fe(Co)3—O4	1.897 (6)

Fe(Co)1—O11	2.046 (6)	Fe(Co)3—O3	2.160 (7)
Fe(Co)1—O16	2.012 (6)	Fe(Co)3—O8	2.043 (7)
Fe(Co)2—O4	1.898 (6)	Fe(Co)3—O9	2.025 (6)
Fe(Co)2—O2	2.145 (8)	Fe(Co)3—O14	2.027 (6)
Fe(Co)2—O6	2.035 (6)	Fe(Co)3—O15	2.027 (7)
Fe(Co)1—Fe(Co)2—Fe(Co)3	59.80 (4)	Fe(Co)1—O4—Fe(Co)2	120.2 (3)
Fe(Co)1—Fe(Co)3—Fe(Co)2	59.95 (4)	Fe(Co)1—O4—Fe(Co)3	119.9 (3)
Fe(Co)2—Fe(Co)1—Fe(Co)3	60.26 (4)	Fe(Co)2—O4—Fe(Co)3	119.9 (4)

Cell constants were automatically obtained and refined for the internally centered cell (*I*2/*a*) [$a = 15.286\,(1)$, $b = 13.838\,(1)$, $c = 22.605\,(1)$ Å and $\beta = 91.161\,(4)°$], and reflections were collected with the setting. For comparison of the structure with that of the corresponding trinuclear iron complex, the structure was solved after revising the cell constants and reflection data to those for *C*2/*c*. Refinements were performed for the three cases (Co1/Fe2/Fe3, Fe1/Co2/Fe3 and Fe1/Fe2/Co3) by locating one Co and two Fe atoms at the three Fe(Co) sites. In the three cases, refinement converged to $R = 0.062$ and there was no significant difference in geometry between them. The structure was therefore refined by locating an Fe atom of site occupancy 0.667 and a constrained Co atom of site occupancy 0.333 at each metal position. Peaks corresponding to H-atom positions could not be seen in difference Fourier syntheses and no theoretical calculations were performed to obtain the positions of H atoms. The five largest positive peaks in the final difference Fourier map were located near water molecules of crystallization.

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1992). Cell refinement: *SET*4 in *CAD*-4 *Express*. Data reduction: *DATA* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *DRAW* in *MolEN*. Software used to prepare material for publication: *OMEGA* in *MolEN*.

The authors are grateful to Professor Kazutoyo Endo and Dr Tadahiro Nakamoto for their help in measurements.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1083). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Di-μ-chloro-bis[(diethylenetriamine)copper(II)] Dinitrate

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Abstract

The crystal structure of the title compound, di-μ-chloro-bis{[*N*-(2-aminoethyl)-1,2-ethanediamine-*N*,*N*′,*N*″]copper(II)} dinitrate, $[Cu_2Cl_2(dien)_2](NO_3)_2$ (dien is diethylenetriamine; $C_4H_{13}N_3$), consists of chloride-bridged copper(II) dimers. Each copper ion is five-coordinate with geometry that is approximately square-pyramidal. Hydrogen bonding involving the three O atoms of the nitrate counteranions and the three H atoms of the amine groups of the organic ligand stabilizes the crystal packing.

Comment

Polynuclear copper(II) halide systems are of interest from both the inorganic and bio-inorganic viewpoints, particularly with respect to the study of the structural parameters which may have an influence on the strength and sign of magnetic coupling (Rojo, Arriortua, Ruiz, Darriet, Villeneuve & Beltrán-Porter, 1987). Cu^{II} atoms are also present in several metalloproteins and so the study of model systems is useful for the interpretation of their biological functions (Fee, 1975).

The ligands selected to block the metal have been shown to play an important role in determining the final structure and, consequently, the structural parameters. In this sense, the use of rigid aromatic amine ligands gives rise to minor variations in certain parameters, such as the bridging angles, which have a great influence on the final magnetic behaviour (Rojo, Arriortua, Mesa, Cortés, Villeneuve & Beltrán-Porter, 1987). The use of a non-rigid aliphatic ligand would lead to a wider range of