

Cl—O4	1.386 (5)	Cl—O5	1.453 (4)
N1—C1	1.471 (6)	N2—C8	1.497 (8)
O1—C7	1.360 (5)	C1—C2	1.505 (7)
C2—C3	1.390 (6)	C3—C4	1.384 (7)
C2—C7	1.399 (6)	C4—C5	1.371 (8)
C5—C6	1.387 (7)	C6—C7	1.396 (6)
C6—C8	1.484 (7)	C4—C9	1.510 (7)
N1—Cu—O1	91.0 (1)	O3—Cl—O2	108.9 (3)
O4—Cl—O2	111.2 (4)	O4—Cl—O3	113.4 (3)
O5—Cl—O2	108.0 (3)	O5—Cl—O3	107.1 (3)
O5—Cl—O4	107.9 (3)	Cu—O1—Cu	102.2 (1)
C7—O1—Cu	129.5 (3)	C1—N1—Cu	112.6 (3)
Cu—N2—C8	110.7 (4)	C2—C1—N1	112.9 (4)
C3—C2—C1	119.6 (4)	C7—C2—C1	121.6 (4)
C7—C2—C3	118.8 (4)	C4—C3—C2	122.4 (5)
C5—C4—C3	117.1 (4)	C9—C4—C3	120.4 (5)
C9—C4—C5	122.6 (5)	C6—C5—C4	123.2 (5)
C7—C6—C5	118.5 (4)	C8—C6—C5	121.1 (5)
C8—C6—C7	120.4 (4)	C2—C7—O1	121.2 (4)
C6—C7—O1	119.0 (4)	C6—C7—C2	119.8 (4)
C6—C8—N2	112.0 (4)		

The structure was solved and refined using *SHELX76* (Sheldrick, 1976). The metal-atom position was deduced from a Patterson synthesis and remaining non-H atoms were located by successive ΔF syntheses. Refinement was by full-matrix least squares. H atoms (except the methyl H atoms) were located from the difference Fourier map and refined isotropically. Molecular geometry calculations were performed using *PARST* (Nardelli, 1982).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including H-atom geometry, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71655 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE1005]

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Tetrapotassium μ -Carbonato- μ -oxo-bis[nitriilotriacetatoiron(III)] Dimethanol Dihydrate

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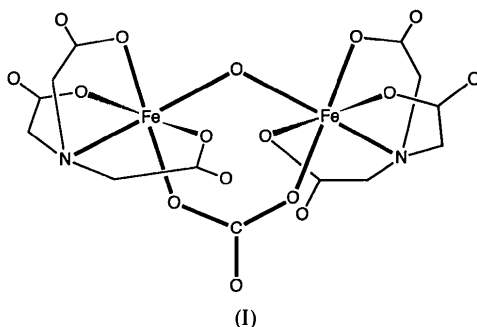
Abstract

The structure of a μ -carbonato- μ -oxo-diiron(III) complex with the tetradentate tripodal ligand nitriilotriacetate (nta), [Fe₂(nta)₂(CO₃)O]⁴⁻, has been determined by single-crystal X-ray diffraction for the potassium salt, K₄[Fe₂(C₆H₆NO₆)₂(CO₃)O].2CH₃-OH.2H₂O. The binuclear complex has crystallographic twofold symmetry and the coordination geometry around the Fe atoms is distorted octahedral. The Fe—O—Fe bridge angle is 121.1 (2)° and the Fe...Fe interatomic distance is 3.188 (1) Å. The Fe₂(CO₃)O core is not planar; the dihedral angle between the Fe₂O and CO₃ planes is 33.8 (5)°.

Comment

The Fe^{III}-nta solution, prepared by mixing an iron(III) solution and nitriilotriacetic acid, H₃nta, exhibits unique reactivity. The repeated intraperitoneal injection of the Fe^{III}-nta solution to rats and rabbits induces an iron overload similar to human hemochromatosis (Awai, Narasaki, Yamanoi & Seno, 1979). The Fe^{III}-nta solution is nephrotoxic and renal carcinoma is also induced (Okada & Midorikawa, 1982). In animals treated with the above solution, the products of lipid peroxidation increase (Goddard, Basford & Sweeney, 1986). Nishida, Yoshizawa & Akamatsu (1991) succeeded in isolating the Fe^{III} complex with the nta ligand, [Fe₂O(acetato)(nta)₂]³⁻, and concluded that the unique reactivity of the Fe^{III}-nta solution described

above is due to its dimeric structure with a μ -oxo bridge (Nishida, 1991). In this study the μ -oxo-Fe^{III}-nta complex with a carbonato bridge, (I), was isolated.



The dimensions of the μ -carbonato- μ -oxo-diron(III) core are similar to those of the tris(2-pyridylmethyl)amine (TPA) adduct in crystals of $[\text{Fe}_2\text{O}(\text{CO}_3)(\text{TPA})_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{OH}$ (Norman, Holz, Ménage, O'Connor, Zhang & Que, 1990). The structures and magnetic properties of μ -carboxylato- μ -oxo-diron(III) complexes with TPA have been reported also (Norman, Yan, Que, Backes, Ling, Sanders-Loehr, Zhang & O'Connor, 1990). The μ -oxo-diron(III) complexes show strong intramolecular antiferromagnetic coupling *via* a superexchange mechanism of two high-spin ferric ions (Drücke, Wieghardt, Nuber, Weiss, Fleischauer, Gehring & Haase, 1989). The $-J$ value (Hamiltonian, $\hat{H} = -2Js_1 \cdot s_2$) of the title compound after efflorescence was determined to be 83 cm^{-1} by measuring magnetic susceptibilities in the temperature range 80–300 K using the Faraday method.

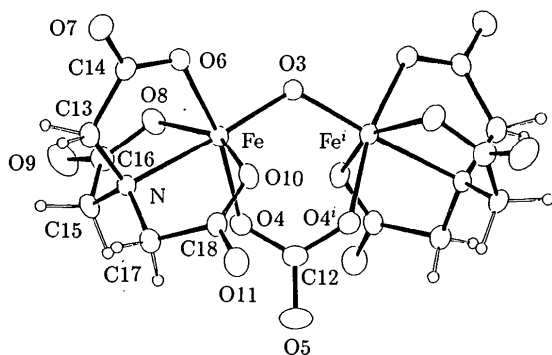


Fig. 1. ORTEP drawing (Johnson, 1965) of $[\text{Fe}_2\text{O}(\text{CO}_3)(\text{nta})_2]^{4-}$ with the displacement ellipsoids at the 25% probability level.

Experimental

By adding methanol to a solution (pH 7.2) of ferric chloride, $\text{N}(\text{CH}_2\text{COOH})_3$ and NaHCO_3 , the crude samples were obtained as brown powder, and were recrystallized from a methanol/water

(8/2) solution. Analysis found: C 21.77, H 2.90, N 3.43%. Analysis calculated for $\text{K}_4[\text{Fe}_2(\text{C}_6\text{H}_6\text{NO}_6)_2(\text{CO}_3)(\text{O})] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$: C 21.96, H 2.95, N 3.41%. The specimen was sealed in a capillary to prevent efflorescence.

Crystal data

$\text{K}_4[\text{Fe}_2(\text{C}_6\text{H}_6\text{NO}_6)_2(\text{CO}_3)(\text{O})] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$
 $M_r = 820.45$
 Monoclinic
 $C2/c$
 $a = 15.628 (2) \text{ \AA}$
 $b = 12.915 (2) \text{ \AA}$
 $c = 14.533 (2) \text{ \AA}$
 $\beta = 102.90 (1)^\circ$
 $V = 2859.4 (6) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.91 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 29 reflections
 $\theta = 10\text{--}15^\circ$
 $\mu = 1.68 \text{ mm}^{-1}$
 $T = 298 (2) \text{ K}$
 Prism
 $0.80 \times 0.40 \times 0.20 \text{ mm}$
 Dark green

Data collection

Rigaku AFC-5 diffractometer
 θ - 2θ scans
 Absorption correction: by integration from crystal shape
 $T_{\min} = 0.469$, $T_{\max} = 0.755$
 3415 measured reflections
 3287 independent reflections

2207 observed reflections
 $[|F_o| > 3\sigma(|F_o|)]$
 $R_{\text{int}} = 0.022$
 $\theta_{\max} = 27.5^\circ$
 $h = -20 \rightarrow 20$
 $k = 0 \rightarrow 16$
 $l = 0 \rightarrow 18$
 5 standard reflections monitored every 100 reflections
 intensity variation: 2.0%

Refinement

Refinement on F
 $R = 0.045$
 $wR = 0.057$
 $S = 2.32$
 2207 reflections
 194 parameters
 H-atom parameters not refined
 $w = 1/[\sigma^2(|F_o|) + (0.015|F_o|)^2]$

$(\Delta/\sigma)_{\max} = 0.18$
 $\Delta\rho_{\max} = 0.68 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.57 \text{ e \AA}^{-3}$
 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 (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Fe	-0.09580 (4)	0.32474 (5)	-0.22888 (4)	2.4 (1)
K1	-0.10859 (7)	-0.06221 (8)	0.05169 (8)	3.8 (1)
K2	0.09596 (7)	0.38284 (9)	-0.00760 (9)	4.2 (1)
O3	0	0.3944 (3)	-1/4	3.0 (1)
O4	-0.0725 (2)	0.1864 (2)	-0.2809 (2)	3.3 (1)
O5	0	0.0399 (4)	-1/4	6.2 (2)
O6	-0.1421 (2)	0.4439 (2)	-0.1636 (2)	3.5 (1)
O7	-0.2380 (2)	0.4944 (3)	-0.0808 (3)	4.5 (1)
O8	-0.1885 (2)	0.3484 (2)	-0.3482 (2)	3.5 (1)
O9	-0.3135 (3)	0.2906 (3)	-0.4381 (3)	5.5 (1)
O10	-0.0480 (2)	0.2618 (2)	-0.0954 (2)	3.1 (1)
O11	-0.0593 (2)	0.1276 (3)	-0.0039 (2)	4.5 (1)
N	-0.2142 (3)	0.2491 (3)	-0.1944 (2)	2.4 (1)
C12	0	0.1359 (5)	-1/4	3.5 (2)
C13	-0.2575 (3)	0.3282 (4)	-0.1478 (3)	3.5 (1)
C14	-0.2092 (3)	0.4297 (4)	-0.1284 (3)	2.9 (1)
C15	-0.2686 (3)	0.2169 (4)	-0.2865 (3)	3.0 (1)

C16	-0.2568 (3)	0.2913 (4)	-0.3635 (3)	3.4 (1)
C17	-0.1801 (3)	0.1617 (4)	-0.1310 (3)	3.2 (1)
C18	-0.0892 (3)	0.1858 (4)	-0.0710 (3)	3.0 (1)
O19	0.0178 (3)	0.4393 (3)	0.3928 (3)	5.4 (1)
C20	0.0857 (4)	0.3845 (6)	0.3666 (5)	6.7 (2)
O21	0.0854 (6)	0.0863 (7)	0.1578 (6)	10.2 (2)
O22	-0.032 (1)	0.157 (2)	0.308 (1)	9.0 (5)

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Table 2. Selected geometric parameters (Å, °)

Fe...Fe ⁱ	3.188 (1)	Fe—O10	2.082 (3)
Fe—O3	1.830 (2)	Fe—N	2.246 (4)
Fe—O4	2.005 (3)	O4—C12	1.298 (4)
Fe—O6	2.025 (3)	O5—C12	1.240 (8)
Fe—O8	2.020 (3)	O11...O21	2.924 (9)
O3—Fe—O4	98.7 (1)	N—Fe—O3	175.4 (1)
O3—Fe—O6	95.5 (1)	N—Fe—O4	85.6 (1)
O3—Fe—O8	103.8 (1)	N—Fe—O6	80.1 (1)
O3—Fe—O10	102.5 (1)	N—Fe—O8	77.8 (1)
O4—Fe—O6	165.5 (1)	N—Fe—O10	76.4 (1)
O4—Fe—O8	88.1 (1)	Fe—O3—Fe ⁱ	121.1 (2)
O4—Fe—O10	86.9 (1)	Fe—O4—C12	122.4 (3)
O6—Fe—O8	91.4 (1)	O4—C12—O5	120.2 (3)
O6—Fe—O10	87.2 (1)	O4—C12—O4 ⁱ	119.7 (5)
O8—Fe—O10	154.0 (1)		

Symmetry code: (i) $-x, y, -z - \frac{1}{2}$.

Laue group 2/m and systematic absences, hkl for $h + k \neq 2n$ and $h0l$ for $l \neq 2n$, indicated the space group Cc (No. 9) or $C2/c$ (No. 15). Assuming the space group to be $C2/c$, the position of the Fe atom was obtained by direct methods and the other non-H atoms were located from Fourier syntheses. All the H atoms of the complex ion were located from difference syntheses, as were the methanol and water molecules of crystallization, but their H atoms were not included in the refinement. The water molecule is disordered and the site occupation ratio of two possible positions, O20 and O21, was estimated at 7:3 from the isotropic displacement parameters. Calculations were carried out using *CRYSTAN-GM* software (MAC Science, 1992) on a SUN SPARC2 workstation at Keio University.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71620 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1044]

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Structural Characterization of Mixed-Valence 1',2',1''',2'''-Tetraethylbiferrocenium Triiodide

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Abstract

The structure determination of the title compound $\{\mu-1(\eta^5):2(\eta^5)-1,1'$ -bicyclopentadienyldiyl-bis[1,2-(η^5)-1,2-diethylcyclopentadienyl]diiron(II,III) triiodide chlorobenzene solvate, $[\text{Fe}_2(\text{C}_9\text{H}_{13})_2(\text{C}_{10}\text{H}_8)(\text{I}_3)\cdot\text{C}_6\text{H}_5\text{Cl} (10)]\}$ indicates that this mixed-valence cation has a valence-trapped electronic state.

Comment

Studies of electron transfer in mixed-valence biferrocenium complexes [(1)–(8)] have revealed that the environment around a given mixed-valence molecule is the most important factor in determining the rate of intramolecular electron transfer (Hammack, Drickamer, Lowery & Hendrickson, 1988; Sinha, Lowery, Ley, Drickamer & Hendrickson, 1988; Webb, Geib, Staley, Rheingold & Hendrickson, 1990; Dong, Kambara & Hendrickson, 1986; Dong, Hendrickson, Iwai, Cohn, Geib, Rheingold, Motoyama & Nakashima, 1985). A recent finding of interest is that there is a correlation between the dihedral angle of the Cp rings for a given ferrocenyl moiety and the rate of electron transfer, *i.e.* the larger the dihedral angle, the faster the electron transfer (Dong & Chou, 1990; Dong, Chang, Huang, Wen, Lee, Chen, Yeh & Yeh, 1992; Dong, Lee & Lin, 1992). In a previous communication (Dong *et al.*, 1992), we reported that there is a dramatic difference in electron-transfer rates between complexes (9) and (10), which were prepared by