

1988). The three characteristic broad bands (one in the near-IR region, $27\,700\text{ cm}^{-1}$, and the other two in the visible region, at $17\,700$ and $10\,500\text{ cm}^{-1}$, respectively) support a distorted octahedral geometry in solution, owing to a d^8 ion in a nearly octahedral field. A spin forbidden band (${}^3A_{2g} \rightarrow {}^1E_g$) is observable as a shoulder near $12\,800\text{ cm}^{-1}$. Finally the broad character of the bands indicates the presence of low-symmetry components in the ligand field (Lever, 1982).

In conclusion, the X-ray analysis demonstrates unequivocally that the structure of the present compound in the solid state must really be formulated as $[\text{Ni}(\text{tren})(\text{H}_2\text{O})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$, whereas in aqueous solution, although the *cis* conformation is maintained (Marzotto *et al.*, 1993), it should be represented as $[\text{Ni}(\text{tren})(\text{H}_2\text{O})_2]\text{Cl}_2$.

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A New Tetranuclear Iron(III) Complex with an $[\text{Fe}_4\text{O}_2]$ Core: Synthesis, Structure and Mössbauer Studies of $[\text{Fe}_4(\mu_3\text{-O})_2(\mu\text{-O}_2\text{CCH}_3)_6\text{Cl}_2(3\text{-Mepy})_4]\cdot\text{CH}_3\text{C}\equiv\text{N}$ (3-Mepy = 3-Methylpyridine)

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Abstract. Hexakis(μ -acetato)bischlorotetrakis(3-methylpyridine)bis(μ_3 -oxo)tetrairon(III) acetonitrile, $[\text{Fe}_4\text{Cl}_2(\text{C}_2\text{H}_3\text{O}_2)_6\text{O}_2(\text{C}_6\text{H}_7\text{N})_4]\cdot\text{C}_2\text{H}_3\text{N}$, $M_r = 1094.1$, triclinic, $P\bar{1}$, $a = 11.236(2)$, $b = 11.709(3)$, $c = 19.897(4)\text{ \AA}$, $\alpha = 75.55(2)$, $\beta = 81.02(1)$, $\gamma = 78.92(2)^\circ$, $V = 2471(1)\text{ \AA}^3$, $Z = 2$, $D_x = 1.471\text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073\text{ \AA}$, $\mu = 13.2\text{ cm}^{-1}$, $F(000) = 1124$, room temperature, $R = 0.045$ for 6551 reflections with $I > 3\sigma(I)$. The title compound contains a

tetrairon core linked by bridging oxygen and acetate ions. Each of the octahedrally coordinated iron(III) atoms is bonded to 3-methylpyridine, three μ -acetates and at least one μ_3 -oxygen. Two Fe atoms are also coordinated by chlorides while the other two are additionally coordinated by another μ_3 -oxygen. Mössbauer results indicate two quadrupole splittings in accordance with the two types of iron coordination spheres. The quadrupole splittings of 1.04 and 0.67 mm s^{-1} are assigned to the chloride- and non-chloride-bonded Fe atoms, respectively.

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Molecules of acetonitrile are incorporated in the crystal.

Introduction. In a variety of proteins, oxo-bridged binuclear and polynuclear iron(III) centers have been found to perform important biological functions such as oxygen storage and transport. Compounds containing a planar or bent tetranuclear [Fe₄O₂] core are a newly emerging class of oxo-bridged poly-iron aggregates. In addition to those found in minerals, [Fe₂(SO₄)₂O].7H₂O (Susse, 1968) and K₂[Fe₄(OH)₂(H₂O)₂(PO₄)₄].2H₂O (Moore, 1972), several synthesized compounds containing μ₃-oxo bridges have been reported, such as [Fe₄O₂(CF₃CO₂)₈(H₂O)₆].2H₂O (Ponomarev, Atovmyan, Bobkova & Turte, 1984); {[Fe₈(μ₃-O)₂(μ₂-OH)₁₂(C₆H₁₅N₃)₆]-Br₇(H₂O)}[Br(H₂O)]₈ (Wieghardt, Pohl, Jibril & Huttner, 1984); [Et₄N][Fe₄O₂(O₂CPh)₇(H₂B(pz)₂)] (Armstrong, Roth & Lippard, 1987) where H₂B(pz)₂⁻ is the dihydrobis(1-pyrazolyl)borate anion; [Fe₄O₂(BICOH)₂(BICO)₂(O₂CPh)₄]Cl₂ (Gorum & Lippard, 1988), where BICOH is bis(*N*-methylimidazol-2-yl)-carbinol.

In our attempt to synthesize a trinuclear mixed-valence iron compound, [Fe₃(μ₃-O)(μ-O₂CCH₃)₆(3-Mepy)₃](CH₃CN) (Oh, Wilson, Hendrickson, Woehler, Wittebort, Inniss & Strouse, 1987), a new tetranuclear iron(III) compound was found. Here we report the synthesis, structure and Mössbauer spectra of the tetranuclear iron(III) complex and discuss the relationship to other μ₃-oxo-bridged complexes.

Experimental. 20 g [FeCl₂].4H₂O (Baker), 20 g sodium acetate (Fisher) and 60 g glacial acetic acid were dissolved in 100 ml water. The reaction mixture was heated at 343–358 K under reflux for 2 h with vigorous bubbling by a stream of air. {Slightly lower temperatures and moderate bubbling gives [Fe₃(μ₃-O)(μ-O₂CCH₃)₆].3H₂O (Oh *et al.*, 1987).} The reaction mixture was cooled to room temperature and the brown precipitate was filtered, washed with ethanol and ether and dried on the frit under suction. The yield was 8 g of light brown solid (1).

The remainder of the synthesis was carried out in a nitrogen atmosphere in a glove box. 5 g of (1) was dissolved in 30 ml of 3-methylpyridine (Aldrich). The mixture was stirred for 1 h at 323–328 K and evaporated over 3 d under constant nitrogen purge leaving a brown solid. The solid was redissolved in 25 ml of 3-methylpyridine under nitrogen and stirred for 1 h at 333–343 K. The mixture was evaporated over 2 d leaving a dark brown solid (2). Crystals of the title compound were prepared by recrystallizing (2) from acetonitrile.

A well formed black crystal with approximate dimensions 0.2 × 0.3 × 0.4 mm was sealed in a glass

capillary under nitrogen atmosphere. Unit-cell dimensions were determined by least-squares refinement of the setting angles of 25 reflections (10 < 2θ < 25°). The choice of the space group *P* $\bar{1}$ was supported by the intensity statistics and by the successful solution and refinement of the structure. Room-temperature data were collected on a MicroVAX-controlled CAD-4 diffractometer with the ω/2θ scan technique, 2θ range 2–50°. Two standard reflections monitored throughout the data collection showed less than 2% change in intensity.

Data reduction was carried out as described by Blessing (1987). The absorption correction applied was calculated by numerical integration; the transmission factor ranged from 0.74 to 0.63. Fe atom positions were determined by direct methods using *MULTAN*11/82 (Main *et al.*, 1982) in the *SDP* package (Enraf-Nonius, 1985). All remaining non-H atoms were located from difference Fourier maps. The methyl H atoms and H atoms on the pyridine rings were constrained with a C—H distance of 0.95 Å and idealized *sp*³ and *sp*² geometry, respectively. 6651 unique reflections with *I* > 3σ(*I*) were used in the final full-matrix refinement, 554 variables, using the program *LINEX*84 (1984). The function Σw(|*F*_o| - *k*|*F*_c|)² was minimized, where *w* = 1/σ²(*F*); σ(*F*) = σ(*F*²)/2*F*; σ(*F*²) = [σ_{counting}² + (0.02|*F*|²)²]^{1/2}. The initial refinement converged at *R* = 5.9, *wR* = 9.1%. The highest residual peaks in the final difference map of 2.581, 2.130 and 1.841 e Å⁻³ suggested the presence of solvent molecules, and were identified as representing the C and N atoms of acetonitrile (CH₃CN). Final *R* factors are *R* = 4.5, *wR* = 6.1, *S* = 3.3%. The largest shift/e.s.d. ratio in the final cycle was 0.05. Scattering factors and the anomalous contributions were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final positional parameters for all non-H atoms are listed in Table 1.*

All Mössbauer measurements were performed at room temperature in transmission geometry using a 2 mCi ⁵⁷Co (Rh) source (1 Ci = 3.7 × 10¹⁰ Bq) with equipment used in previous work (DeMarco, Qi, Wang, Chaparala & Naughton, 1991). Powdered single-crystal absorber samples of the compound were prepared with natural iron which contained 0.2 mg cm⁻² of ⁵⁷Fe.

Discussion. The title compound crystallizes in space group *P* $\bar{1}$ with two molecules in the unit cell. Fig. 1 shows a perspective view of the molecular structure.

* Lists of structure factors and thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55952 (74 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1024]

Table 1. Atomic parameters and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses
$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq} (Å ²)
Fe(1)	-0.26642 (5)	0.37538 (5)	0.28476 (3)	3.21 (1)
Fe(2)	0.18939 (5)	0.11913 (5)	0.15050 (3)	3.28 (1)
Fe(3)	0.02670 (5)	0.21693 (5)	0.28633 (3)	3.17 (1)
Fe(4)	-0.12255 (4)	0.18585 (5)	0.18790 (3)	3.01 (1)
Cl(1)	-0.3642 (1)	0.2731 (1)	0.38737 (7)	5.43 (3)
Cl(2)	0.2066 (1)	-0.0859 (1)	0.15744 (7)	4.69 (3)
O(A)	-0.1445 (2)	0.2496 (2)	0.2700 (1)	3.83 (6)
O(B)	0.0460 (2)	0.1401 (2)	0.2095 (1)	3.79 (6)
O(1)	-0.1675 (2)	0.4473 (2)	0.3352 (1)	4.96 (6)
O(2)	-0.0061 (2)	0.3076 (3)	0.3639 (1)	4.89 (7)
O(3)	0.2024 (2)	0.1649 (3)	0.3121 (2)	5.26 (7)
O(4)	0.3027 (3)	0.0820 (3)	0.2267 (2)	5.77 (7)
O(5)	0.1108 (2)	0.1628 (2)	0.0596 (1)	4.61 (6)
O(6)	-0.0785 (2)	0.1270 (2)	0.0985 (1)	4.29 (6)
O(7)	-0.3008 (2)	0.2183 (3)	0.1695 (2)	5.27 (7)
O(8)	-0.3941 (2)	0.3499 (3)	0.2305 (2)	5.93 (7)
O(9)	0.0854 (2)	0.3661 (2)	0.2232 (1)	4.70 (6)
O(10)	0.2039 (2)	0.2980 (2)	0.1353 (2)	5.02 (7)
O(11)	-0.2063 (3)	0.4806 (3)	0.1894 (1)	5.15 (7)
O(12)	-0.1102 (3)	0.3514 (2)	0.1247 (1)	4.57 (6)
N(1)	-0.4000 (3)	0.5428 (3)	0.2919 (2)	4.77 (8)
N(2)	0.3649 (3)	0.1213 (3)	0.0815 (2)	4.61 (8)
N(3)	-0.0050 (3)	0.0538 (3)	0.3618 (2)	5.09 (9)
N(4)	-0.1649 (3)	0.0115 (3)	0.2428 (2)	4.42 (8)
Cl(1)	-0.0773 (4)	0.4017 (4)	0.3689 (2)	4.4 (1)
C(1)	-0.0558 (5)	0.4660 (5)	0.4206 (3)	8.1 (1)
C(2)	0.2960 (4)	0.1129 (4)	0.2827 (2)	4.5 (1)
C(3)	0.4099 (4)	0.0836 (5)	0.3179 (3)	7.0 (1)
C(4)	0.0057 (3)	0.1511 (3)	0.0508 (2)	3.73 (9)
C(5)	-0.0224 (4)	0.1681 (5)	-0.0224 (2)	5.5 (1)
C(6)	-0.3884 (3)	0.2931 (4)	0.1849 (2)	4.11 (9)
C(7)	-0.4971 (4)	0.3174 (5)	0.1465 (3)	6.9 (1)
C(8)	0.1542 (3)	0.3777 (4)	0.1664 (2)	4.14 (9)
C(9)	0.1820 (5)	0.5004 (4)	0.1344 (3)	6.3 (1)
C(10)	-0.1518 (3)	0.4546 (4)	0.1345 (2)	3.97 (9)
C(11)	-0.1381 (7)	0.5532 (5)	0.0725 (3)	7.9 (2)
C(12)	-0.4488 (4)	0.6116 (4)	0.2370 (2)	5.7 (1)
C(13)	-0.5380 (5)	0.7088 (5)	0.2400 (3)	6.7 (1)
C(14)	-0.5760 (5)	0.7376 (5)	0.3024 (3)	7.1 (1)
C(15)	-0.5252 (5)	0.6685 (4)	0.3618 (3)	5.9 (1)
C(16)	-0.4387 (4)	0.5728 (4)	0.3531 (2)	5.0 (1)
C(17)	-0.5639 (7)	0.6950 (6)	0.4312 (3)	9.6 (2)
C(18)	0.3766 (4)	0.2028 (4)	0.0221 (2)	5.3 (1)
C(19)	0.4856 (5)	0.2113 (5)	-0.0185 (3)	6.8 (1)
C(20)	0.5864 (4)	0.1362 (5)	0.0018 (3)	7.2 (1)
C(21)	0.5791 (4)	0.0489 (4)	0.0641 (3)	5.8 (1)
C(22)	0.4660 (4)	0.0457 (4)	0.1009 (2)	4.8 (1)
C(23)	0.6879 (4)	-0.0340 (5)	0.0899 (3)	8.1 (1)
C(24)	0.0556 (4)	-0.0518 (4)	0.3534 (3)	6.0 (1)
C(25)	0.0336 (6)	-0.1550 (5)	0.3992 (4)	8.1 (2)
C(26)	-0.0572 (6)	-0.1507 (5)	0.4556 (3)	8.5 (2)
C(27)	-0.1216 (5)	-0.0443 (6)	0.4629 (3)	7.5 (2)
C(28)	-0.0912 (4)	0.0569 (4)	0.4157 (3)	5.7 (1)
C(29)	-0.2193 (8)	-0.038 (1)	0.5145 (4)	13.1 (3)
C(30)	-0.2502 (4)	-0.0010 (4)	0.2972 (3)	5.3 (1)
C(31)	-0.2790 (4)	-0.1111 (5)	0.3313 (3)	6.7 (1)
C(32)	-0.2170 (5)	-0.2118 (4)	0.3097 (3)	6.6 (1)
C(33)	-0.1268 (4)	-0.1996 (4)	0.2538 (3)	5.5 (1)
C(34)	-0.1058 (4)	-0.0857 (4)	0.2221 (2)	4.7 (1)
C(35)	-0.0547 (7)	-0.3020 (5)	0.2293 (4)	9.5 (2)
C(36)	0.3095 (8)	0.4112 (8)	0.3401 (5)	21.3 (4)*
C(37)	0.2943 (9)	0.4005 (8)	0.4092 (5)	22.7 (5)*
N(5)	0.284 (1)	0.382 (1)	0.4713 (6)	32.9 (6)*

* Refined isotropically.

The packing diagram is shown in Fig. 2. Selected bond distances and angles are given in Table 2. The complex contains the $(\mu\text{-acetato})_6(\mu_3\text{-oxo})_2$ tetra-iron(III) core. The dihedral angle between the planes of the two Fe triangles [Fe(1)Fe(3)Fe(4) and Fe(2)Fe(3)Fe(4)] is 157.6°. The O(A) atom is displaced by 0.337 Å from the Fe(1)Fe(3)Fe(4) plane, the corresponding displacement of O(B) from the

Fe(2)Fe(3)Fe(4) plane is 0.327 Å. There are three types of independent Fe—O(oxo) distances, ranging from 1.854 to 1.951 Å. The closest iron-iron separation is 2.897 Å for Fe(3)⋯Fe(4) which falls in the range 2.829 to 3.108 Å observed in other [Fe₄O₂]-containing compounds. Other intramolecular Fe⋯Fe distances range from 3.32–3.46 Å. There are six bridging acetate ligands in the complex. Each iron is in a distorted octahedral coordination environment. The large temperature factors for the atoms of the solvent molecule indicate a considerable amount of disorder. The occupancy of the acetonitrile molecule consistently refined to a value close to 1 [0.92 (2)].

Mössbauer measurements at different maximum speeds yielded equivalent spectra. One such spectrum

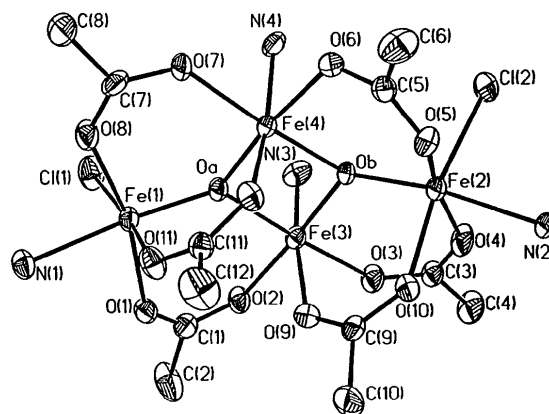


Fig. 1. Perspective view of the molecular structure. Thermal ellipsoids are drawn at the 30% probability level. All but the N atoms of the 3-methylpyridine ligands have been omitted for clarity.

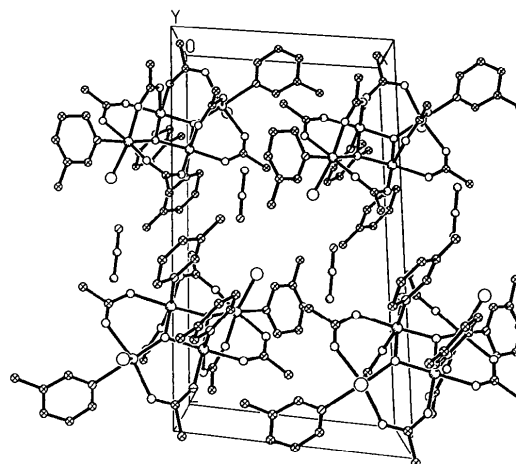


Fig. 2. Packing diagram. Elements differentiated by symbol: shaded circles Fe; large open circles Cl; dotted circles O; circles with one line N; circles with two crossed lines C.

Table 2. Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses

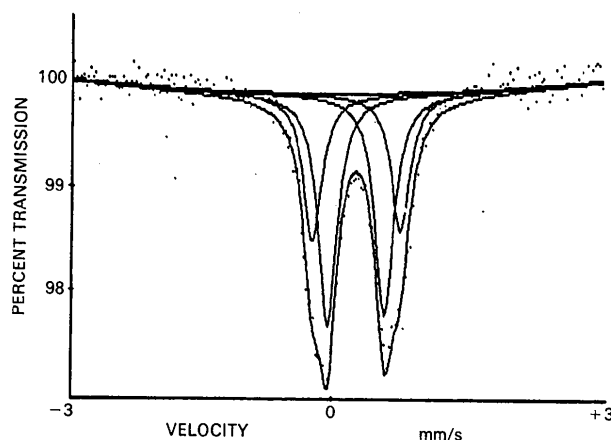
Fe(1)—Cl(1)	2.323 (1)	Fe(2)—N(2)	2.220 (2)
Fe(1)—O(A)	1.856 (1)	Fe(3)—O(A)	1.950 (1)
Fe(1)—O(1)	2.020 (2)	Fe(3)—O(B)	1.924 (1)
Fe(1)—O(8)	2.031 (2)	Fe(3)—O(2)	2.033 (2)
Fe(1)—O(11)	2.081 (2)	Fe(3)—O(3)	2.056 (2)
Fe(1)—N(1)	2.249 (2)	Fe(3)—O(9)	2.038 (2)
Fe(2)—Cl(2)	2.342 (1)	Fe(4)—O(A)	1.924 (1)
Fe(2)—O(B)	1.854 (1)	Fe(4)—O(B)	1.951 (1)
Fe(2)—O(4)	2.042 (2)	Fe(4)—O(6)	2.023 (2)
Fe(2)—O(5)	2.043 (2)	Fe(4)—O(7)	2.039 (2)
Fe(2)—O(10)	2.075 (2)	Fe(4)—O(12)	2.047 (2)
Fe(3)—Fe(4)	2.897 (1)		
Cl(1)—Fe(1)—O(A)	96.9 (1)	O(4)—Fe(2)—O(10)	88.1 (1)
Cl(1)—Fe(1)—O(1)	93.7 (1)	O(4)—Fe(2)—N(2)	82.2 (1)
Cl(1)—Fe(1)—O(8)	89.8 (1)	O(5)—Fe(2)—O(10)	88.0 (1)
Cl(1)—Fe(1)—O(11)	171.0 (1)	O(5)—Fe(2)—N(2)	85.1 (1)
Cl(1)—Fe(1)—N(1)	90.2 (1)	O(10)—Fe(2)—N(2)	80.8 (1)
O(A)—Fe(1)—O(1)	95.7 (1)	O(A)—Fe(3)—O(B)	83.0 (1)
O(A)—Fe(1)—O(8)	99.6 (1)	O(A)—Fe(3)—O(2)	92.7 (1)
O(A)—Fe(1)—O(11)	90.4 (1)	O(A)—Fe(3)—O(3)	173.3 (1)
O(A)—Fe(1)—N(1)	172.7 (1)	O(A)—Fe(3)—O(9)	100.3 (1)
O(1)—Fe(1)—O(8)	163.8 (1)	O(B)—Fe(3)—O(2)	175.1 (1)
O(1)—Fe(1)—O(11)	90.8 (1)	O(B)—Fe(3)—O(3)	97.4 (1)
O(1)—Fe(1)—N(1)	82.3 (1)	O(B)—Fe(3)—O(9)	92.0 (1)
O(8)—Fe(1)—O(11)	83.8 (1)	O(2)—Fe(3)—O(3)	87.1 (1)
O(8)—Fe(1)—N(1)	81.9 (1)	O(2)—Fe(3)—O(9)	86.5 (1)
O(11)—Fe(1)—N(1)	82.6 (1)	O(3)—Fe(3)—O(9)	86.4 (1)
Cl(2)—Fe(2)—O(B)	99.0 (1)	O(A)—Fe(4)—O(B)	83.0 (1)
Cl(2)—Fe(2)—O(4)	89.4 (1)	O(A)—Fe(4)—O(6)	172.6 (1)
Cl(2)—Fe(2)—O(5)	92.3 (1)	O(A)—Fe(4)—O(7)	97.9 (1)
Cl(2)—Fe(2)—O(10)	170.2 (1)	O(A)—Fe(4)—O(12)	91.1 (1)
Cl(2)—Fe(2)—N(2)	89.5 (1)	O(B)—Fe(4)—O(6)	91.3 (1)
O(B)—Fe(2)—O(4)	95.5 (1)	O(B)—Fe(4)—O(7)	174.9 (1)
O(B)—Fe(2)—O(5)	96.7 (1)	O(B)—Fe(4)—O(12)	98.8 (1)
O(B)—Fe(2)—O(10)	90.6 (1)	O(6)—Fe(4)—O(7)	88.3 (1)
O(B)—Fe(2)—N(2)	171.2 (1)	O(6)—Fe(4)—O(12)	85.1 (1)
O(4)—Fe(2)—O(5)	167.2 (1)	O(7)—Fe(4)—O(12)	86.3 (1)
Fe(1)—O(A)—Fe(3)	130.5 (1)	Fe(2)—O(B)—Fe(3)	124.3 (1)
Fe(1)—O(A)—Fe(4)	123.0 (1)	Fe(2)—O(B)—Fe(4)	129.8 (1)
Fe(3)—O(A)—Fe(4)	96.8 (1)	Fe(3)—O(B)—Fe(4)	96.8 (1)

Table 3. Results of Mössbauer experiments

	Area (%)	EQ* (mm s ⁻¹)	FWHM (mm s ⁻¹)	IS† (mm s ⁻¹)
Site 1	38.6 (10)	1.04 (3)	0.130 (15)	0.36 (3)
Site 2	61.4 (10)	0.67 (3)	0.130 (15)	0.36 (3)

* EQ is the electrical quadrupole.

† IS is the isomer shift relative to the iron foil.

Fig. 3. Room-temperature Mössbauer spectrum of ⁵⁷Co(Rh) versus [Fe₄(μ₃-O)₂(μ-O₂CCH₃)₆Cl₂(3-Mepy)₄] with relative percent transmission versus drive velocity. The best fit line to the data (dots) is a superposition of the subspectra.

is shown in Fig. 3. These experimental spectra are best fit by multiple doublets; the line width and the shape of the experimental data spectrum is too broad for a satisfactory fit by a single doublet. The results shown in Table 3 were obtained with a computer program prepared by Ranger Scientific (DeMarco, Wang, Trbovich, Naughton & Chaparala, 1990). The two different sets of doublets indicate two different quadrupole splittings (QS) (Table 3), which in turn implies two Fe sites with different coordination spheres, in agreement with the molecular structure. Both sites have equivalent isomer shifts of a magnitude consistent with Fe^{III}.

The somewhat smaller thermal parameters of Fe(3) and Fe(4), relative to Fe(1) and Fe(2), respectively, indicate smaller vibrational displacements, which in turn are expected to lead to a larger recoil-free fraction in the Mössbauer experiment. Since the larger absorption is associated with the smaller splitting, this suggests that the QS of 1.04 and 0.67 mm s⁻¹ may be due to the Fe(1), Fe(2) and Fe(3), Fe(4) atoms, respectively.

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