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The Structure of the Three-Dimensional Polymer Poly[μ-hexakis(2-methylimidazolato-N,N')-triiron(II)], $[Fe_3(C_4H_5N_2)_6]_n$

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Abstract. $M_r = 218{\cdot}04$ (for 1 asymmetric unit $\equiv \frac{1}{3}$ formula unit in the *Title*), hexagonal, $P6_422$, $a = b = 8{\cdot}617$ (2), $c = 12{\cdot}907$ (4) Å, $U = 830{\cdot}0$ (3) Å^3, $Z = 3$, $D_m = 1{\cdot}315$, $D_x = 1{\cdot}309$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 13{\cdot}6$ cm^{-1}, $F(000) = 336$, $T = 295$ K, $R = 0{\cdot}057$ for 219 observed reflections $[F > \sigma(F)]$. The iron atoms are tetrahedrally coordinated by four 2-methylimidazole ligands and each ligand coordinates to two iron atoms in such a way that a three-dimensional network results.

Introduction. In recent years there has been an increasing interest in coordination compounds mimicking metalloprotein active sites (Ibers & Holm, 1980). In order to interpret EXAFS data of metalloproteins and to determine metal–ligand distances with this technique, data from crystal structure determinations of appropriate model compounds are needed.

Lipoxygenase-1 from soybeans is an enzyme which catalyses the dioxygenation of polyunsaturated fatty acids. The enzyme consists of a single polypeptide chain (M_r 98 500) and contains one mol of non-hæme iron per mol of enzyme. The functional role of the Fe atom in the catalysis of the enzymatic reaction has been demonstrated by EPR spectroscopy (for a review see Vliegenthart & Veldink, 1982). Exploratory EXAFS investigations of this protein suggested direct coordination of the iron to three–four nitrogen atoms of imidazoles of histidine residues of the polypeptide chain.

To obtain further evidence in support of this suggestion, model compounds containing similar structural elements have to be investigated.The synthesis of coordination compounds of iron(II) and several imidazoles have been described (Seel, Wende, Marcolin, Trautwein & Maeda, 1976). An X-ray study of the compound with unsubstitued imidazole showed that it is unsuitable as a model compound for EXAFS studies of metalloproteins because it contains two types of differently coordinated iron atoms (Lehnert & Seel, 1978).

This paper reports the crystal structure of the (2-methylimidazole)iron(II) compound that has been shown to contain only one type of iron atom and as such is, in principle, suitable for EXAFS studies and comparison with soybean lipoxygenase-1.

Experimental. Synthesized from ferrocene and 2-methylimidazole as described by Seel *et al.* (1976), rod-shaped white crystal, $0{\cdot}07 \times 0{\cdot}07 \times 0{\cdot}45$ mm, sealed under nitrogen in a Lindemann-glass capillary, D_m by flotation, Enraf–Nonius CAD-4F diffractometer; cell parameters from setting angles of ten reflections, each being an appropriate average for the four possible alternative reflection setting angles; $\theta = 25°$, $\omega/2\theta$ scan, Zr-filtered Mo $K\alpha$ radiation, 401 reflections scanned, h –4–0, k 0–10, l 0–15; two reference reflections ($20\bar{3}$ and $\bar{1}01$) measured every hour showed no decay, variation <3%, absorption effects neglected on the basis of a ψ scan about the close-to-axial reflection $00\bar{3}$ with a variation of up to 3·5% about the mean; correction for usual factors resulted in 339 reflections, 219 observed $[F > \sigma(F)]$; structure was solved by standard Patterson and Fourier methods and refined on F by full-matrix least squares, hydrogen atoms introduced at calculated positions; refinement in $P6_422$ gave better agreement than the enantiomorphous $P6_222$, former adopted in subsequent calculations; site symmetry of methyl moiety calls for a statistical twofold axis, disorder model chosen, no attempts made to study an order model in the lower-symmetry space group $P6_4$ in view of the relatively poor quality of the crystal; $wR = 0{\cdot}059$ $\{w^{-1} = [\sigma^2(F) + 0{\cdot}003F^2]/0{\cdot}70$, max. shift/error = 1, $S = 1{\cdot}37\}$; refined parameters included all positional parameters and anisotropic temperature factors for non-hydrogen atoms, hydrogen atoms refined in riding mode with overall isotropic temperature factor, residual density in final difference Fourier was –0·36 to 0·45 e Å^{-3}; scattering factors from Cromer & Mann (1968), anomalous dispersion corrections from Cromer

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& Liberman (1970),* calculations carried out on either the CDC-Cyber175 of the University of Utrecht with programs of the *APOLLO* (data reduction and correction by ALS) and *EUCLID* (calculation of geometrical data and preparation of illustrations including an extended version of the program *PLUTO*; Spek, 1982) packages or on the in-house DG-Eclipse S/230 minicomputer using the programs of the *ILIAS* package [an adaptation and extension (by ALS) of the *SHELX76* package (Sheldrick, 1976)].

Discussion. The final parameter values are given in Table 1.

The iron atoms and the 2-methylimidazole moieties join to form a three-dimensional network as shown in Fig. 1. The iron atoms are pseudotetrahedrally coordinated by four equivalent ligands, conforming with the crystallographic site symmetry 222 (Fig. 2). Relevant data on the geometry are given in Table 2. The imidazole ring is strictly planar, as expected, and the iron atom is 0·26 (4) Å out of this plane. The Fe—N = 2·03 (1) Å bond distance lies in the range (2·01–2·06 Å) that is observed for the four-coordinated iron in the iron compound with unsubstituted imidazole ligands (Lehnert & Seel, 1978).

Thanks are due to Drs P. H. M. Budzelaar and J. Boersma for their help in the synthesis and to Professor J. F. G. Vliegenthart for stimulating discussions. The

Table 1. *Final coordinates and equivalent isotropic thermal parameters*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
Fe	0	0·5	0·3333	0·036 (1)
N(1)	–0·124 (1)	0·292 (1)	0·2330 (6)	0·052 (3)
C(1)	–0·257 (1)	0·257 (1)	0·1667	0·055 (4)
C(2)	–0·072 (2)	0·173 (2)	0·2062 (9)	0·065 (4)
C(3)	–0·360 (1)	0·360 (1)	0·1667	0·108 (5)

Table 2. *Relevant geometrical data*

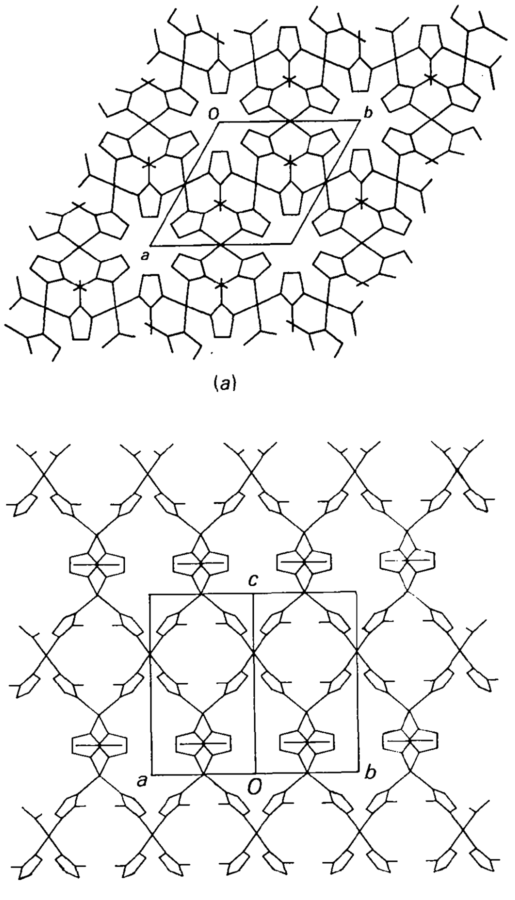
(*a*) Bond distances (Å)

Fe—N(1)	2·03 (1)	N(1)—C(1)	1·34 (1)	N(1)—C(2)	1·35 (2)
C(1)—C(3)	1·53 (2)	C(2)—C($2^{\rm iv}$)	1·34 (2)		

(*b*) Bond angles (°)

N(1)—Fe—N($1^{\rm i}$)	100·8 (4)	C(1)—N(1)—C(2)	104 (1)
N(1)—Fe—N($1^{\rm ii}$)	125·6 (4)	N(1)—C(1)—N($1^{\rm iv}$)	113 (1)
N(1)—Fe—N($1^{\rm iii}$)	103·3 (5)	N(1)—C(2)—C($2^{\rm iv}$)	109 (1)
Fe—N(1)—C(1)	128·2 (9)	N(1)—C(1)—C(3)	123 (1)
Fe—N(1)—C(2)	127·2 (8)		

Symmetry code: (i) $-x$, $1-y$, z; (ii) x, $1+x-y$, $\frac{2}{3}-z$; (iii) $-x$, $y-x$, $\frac{2}{3}-z$; (iv) $-y$, $-x$, $\frac{1}{3}-z$.



(*a*)

(*b*)

Fig. 1. (*a*) Projection of the structure down [001] and (*b*) projection of the structure down [110] illustrating the three-dimensional network structure of poly[μ-hexakis(2-methylimidazolato-*N*,*N*′)-triiron(II).

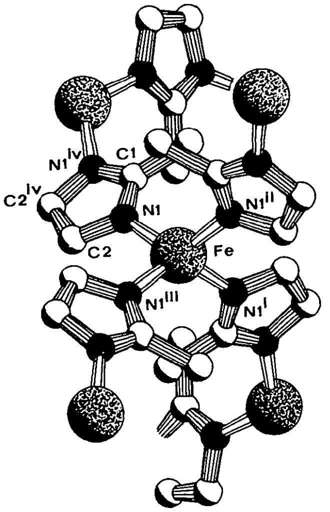


Fig. 2. *PLUTO* (Spek, 1982) drawing of part of the structure illustrating the tetrahedral coordination of the iron(II) atom along with the adopted numbering scheme.

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* A list of structure factors, anisotropic temperature factors and bond distances and angles for the hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38630 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of [1,3-Dimethyl-2,4,5,6(1*H*, 3*H*)-pyrimidinetetrone 5-oximato][1,3-dimethyl-2,4,5,6(1*H*, 3*H*)-pyrimidinetetrone 5-oxime]silver(I), $[Ag(C_6H_6N_3O_4)(C_6H_7N_3O_4)]$

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Abstract. $M_r = 477\cdot14$, orthorhombic, $P2_12_12_1$, $a = 6\cdot345\ (5)$, $b = 14\cdot01\ (2)$, $c = 17\cdot92\ (2)$ Å, $V = 1593\ (3)$ Å^3, $Z = 4$, $D_x = 1\cdot99$ Mg m^{-3}, $\mu(\text{Mo}\ K\alpha) = 1\cdot31$ mm^{-1}, $\lambda(\text{Mo}\ K\alpha) = 0\cdot71069$ Å, $F(000) = 952$, $T = 291$ K, $R = 0\cdot06$ for 1667 observed reflexions. The Ag atom is coordinated with two organic bidentate ligands, of the same asymmetric unit, and with one O atom of a neighbouring molecule, forming a chain structure. No Ag—Ag interaction occurs.

Introduction. This investigation has been undertaken because of the increasing interest in the coordination of the Ag^+ ion with organic bidentate ligands. In this work we report the crystal structure of the title compound, prepared by J. D. López-González and co-workers, at the Department of Inorganic Chemistry of the University of Granada (Spain).

Experimental. Fibrous red needle-like crystal, $0\cdot5 \times 0\cdot2 \times 0\cdot2$ mm. Nonius CAD-4F automatic diffractometer. Cell dimensions refined by least-squares fitting of the θ values of 25 reflexions. 3336 unique reflexions, $1° < \theta < 33°$, h,k,l range from 0,0,0 to 9,21,26, monochromatic Mo $K\alpha$ radiation, $\omega/2\theta$ scans. Due to radiation damage a progressive decrease in intensities occurred. To account for this effect, three standard reflexions were monitored periodically and the time limit for a final scan was 45 s. Intensities scaled from the variations of the three standard reflexions whose intensities fell to 50% at the end of the data collection. Intensities corrected for Lorentz and polarization effects, 1667 considered observed $[I > 2\sigma(I)]$. No absorption corrections ($\mu R = 0\cdot65$). Scattering factors for neutral atoms and anomalous-dispersions corrections for Ag from *International Tables for X-ray Crystallography* (1974). Structure solved by three-dimensional Patterson and Fourier syntheses allowing the location of all non-hydrogen atoms. Anisotropic full-matrix least-squares refinement using F's and unit weights led to $R = 0\cdot69$ with 244 parameters refined. H atoms of the methyl groups fixed at calculated positions. The oxime H(21) was located on a difference synthesis calculated with reflexions having $\sin\theta/\lambda < 0\cdot5$ Å^{-1} as the highest peak of the map. In order to prevent bias on ΔF *vs* F_o or $\sin\theta/\lambda$, the last steps of the refinement were carried out with weights $w = 1/(a + b|F_o|)^2$ where $a = 4\cdot33$, $b = 0\cdot15$ if $|F_o| < 20$ and $a = 0\cdot76$, $b = 0\cdot03$ if $|F_o| > 20$, calculated by *PESOS* (Martinez-Ripoll & Cano, 1975). Final refinement with fixed isotropic temperature factors and coordinates for H atoms gave $R = 0\cdot060$, and $R_w = 0\cdot067$.[*] Maximum and average shift/error: 0·3386 and 0·0610 respectively. A final difference synthesis had no electron density $>0\cdot56$ e Å^{-3}, and $<-0\cdot40$ e Å^{-3}. Most of the calculations were carried out with XRAY70 (Stewart, Kundell & Baldwin, 1970).

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[*] Lists of structure amplitudes, anisotropic thermal parameters and H atom parameters (six half-atoms per methyl group) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38588 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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