

Low-Temperature Study of Bis(2-methylimidazole)(octaethylporphinato)iron(III) Perchlorate

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Abstract

The molecular structure and electron density of bis(2-methylimidazole)(octaethylporphinato)iron(III) have been determined at 120 (2) K. Crystal data are: $[\text{Fe}(\text{C}_{36}\text{H}_{44}\text{N}_4)(\text{C}_4\text{H}_6\text{N}_2)_2]\text{ClO}_4$, $M_r = 852.23$, triclinic, $P\bar{1}$, $a = 10.161(5)$, $b = 12.149(4)$, $c = 8.931(4)$ Å, $\alpha = 91.92(4)$, $\beta = 109.11(4)$, $\gamma = 89.14(3)^\circ$, $V = 1041.1$ Å³, $Z = 1$, $D_x = 1.359$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 5.5$ cm⁻¹, $F(000) = 423$. Final R factors are: for 9861 reflections with $(\sin \theta)/\lambda < 1.22$ Å⁻¹ and 395 variables (spherical-atom refinement), $R(F) = 5.32$, $wR(F) = 4.40\%$, $\text{GOF} = 1.71$ and for 6289 reflections with $(\sin \theta)/\lambda < 0.80$ Å⁻¹ (spherical-atom refinement), $R(F) = 4.03$, $wR(F) = 3.91\%$, $\text{GOF} = 1.88$ and (multipole refinement, 549 variables) $R(F) = 3.09$, $wR(F) = 2.79\%$, $\text{GOF} = 1.35$. The Fe atom is located on a center of symmetry and is axially bound to two 2-methylimidazole ligands. The porphinato core is almost planar, with the atoms $Cm1$ and $Cb4$ slightly displaced out of the least-squares plane [by 0.06 (1) and 0.07 (1) Å]. The Fe–N distances in the porphyrin ring are 2.055 (1) and 2.040 (1) Å. The two axial Fe–N distances equal 2.249 (1) Å which corresponds to a contraction of 0.026 Å relative to the room-temperature value. The distances in the 2-methylimidazole ligands are equal within experimental errors to those of the imidazole molecule [McMullan, Epstein, Ruble & Craven (1979). *Acta Cryst.* B35, 688–691], except for the angles at the methyl-substituted C atom. The angle between the plane of the imidazole ring and the closest N–Fe–N vector is 21.8°. The d -orbital populations from a multipole refinement are: $d_z^2 = 1.53(9)$, $d_{x^2-y^2} = 1.16(8)$, $d_{xz} = 1.32(8)$, $d_{yz} = 1.28(8)$, $d_{xy} = 0.90(8)$ (z is perpendicular to the porphyrin plane, x and y are in the plane pointing from the Fe towards the N atoms). The low population of d_{xy} in this high-spin complex agrees with the results of an extended Huckel calculation. The experimental electron density maps show a deviation of the Fe-atom density from fourfold symmetry which may be related to the ligand orientation.

Introduction

$\text{Fe}^{\text{III}}(2\text{-MeIm})_2\text{oepClO}_4$ [bis(2-methylimidazole)(octaethylporphinato)iron(III) perchlorate] is a six-coordinate high-spin complex, which in solution has magnetic properties consistent with a high-spin-low-spin equilibrium (Geiger, Lee & Scheidt, 1984). The corresponding tetraphenylporphyrin (tpp) compound is a low-spin complex (Scheidt, Kirner, Hoard & Reed, 1987). The difference between the magnetic properties of the two compounds has been related to the orientation of the axial ligand (Scheidt & Chipman, 1986).

This low-temperature study is part of a program to study the electron density distribution in iron porphyrins as a function of valence, coordination and spin state (Lecomte, Blessing, Coppens & Tabard, 1986). We report here on the results of the spherical-atom and multipole least-squares refinements of the title compound.

Experimental/data collection

A crystal of approximate dimensions 0.3 × 0.3 × 0.25 mm, obtained following a method described by Geiger, Lee & Scheidt (1984), was used for data collection. Data were collected in the ω - 2θ scan mode with a 6 × 6 mm scan aperture and a $(1.5 + 0.53 \tan \theta)$ scan width. CAD-4 diffractometer. 25 reflections used to measure lattice parameters. The intensity data were reduced to structure amplitudes using a procedure for analysis of the recorded profile described by Blessing (1986*a,b*). The method derives the width of the reflection profile as a function of orientation and diffraction angle from the recorded strong reflections, using the Lehmann–Larsen criteria to determine the peak boundaries (Lehmann & Larsen, 1974). The function is subsequently applied in the integration of the weak reflections, for which the Lehmann–Larsen method often does not give satisfactory results.

Numerical absorption corrections (Coppens, Leiserowitz & Rabinovich, 1965) were applied; transmission factors ranged from 0.78 to 0.83. The number of reflections for least-squares input is 9861 with

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$I > 3\sigma(I)$. * 29 977 reflections measured; h -24 – 24 , k -29 – 29 , l -19 – 19 . Five standard reflections showed no systematic decrease.

Least-squares refinements

A spherical-atom refinement, starting with the parameters obtained from the room-temperature study (Geiger, Lee & Scheidt, 1984), was performed using all observed reflections. All non-H atoms were refined anisotropically.

A high-order refinement of the data between 0.80 and 1.20 Å indicated this segment of the data to be of lower quality. As the aspherical-atom model (Hansen & Coppens, 1978) requires high-quality data, it was applied only to the 6289 observed reflections with $(\sin \theta)/\lambda < 0.80 \text{ \AA}^{-1}$. Core and valence scattering tables were taken from *International Tables for X-ray Crystallography* (1974). All atoms were described aspherically except those of the disordered perchlorate group. As described elsewhere, chemically equivalent atoms were constrained to have the same valence density parameters (Lecomte, Blessing, Coppens & Tabard, 1986). The pyrrole N atoms were assumed to have C_{2v} symmetry, while the C atoms of the porphyrin and imidazole rings were constrained to C_s symmetry. C_{3v} and C_3 symmetry was assumed for the methyl group of the imidazole and ethyl groups, respectively. The highest peak in the residual maps calculated after completion of the refinement is 0.15 e \AA^{-3} . Results are listed in Table S4.* The 9861 reflections of the spherical-atom refinement are also listed in the supplementary material. Final agreement factors are given in the *Abstract*. $w = 1/\sigma^2(F)$. Max. shift/e.s.d. = 0.1.

Crystal structure

A *PLUTO* (Motherwell, 1979) plot of the molecule illustrating the labelling scheme of the non-H atoms is given in Fig. 1(a). The atomic coordinates and B_{eq} values for both the spherical- and aspherical-atom refinements are listed in Table 1. All distances and angles discussed below are as obtained in the aspherical-atom refinement. The Fe atom is on an inversion center and is coordinated to six N atoms; the four N atoms of the porphyrin ring are at distances of 2.055 (1) and 2.040 (1) Å, and the two axial N atoms are at a distance of 2.249 (2) Å from the Fe atom, distances typical for a high-spin Fe^{III} complex. For comparison, in the low-spin compound Fe(2-

MeIm)tpp(ClO₄), the average equatorial Fe–N distance is 1.970 (4) Å and the axial distance is 2.012 (4) Å (Scheidt, Kirner, Hoard & Reed, 1987). The difference in the spin states of the Fe atom for these two similar compounds is attributed to a ligand

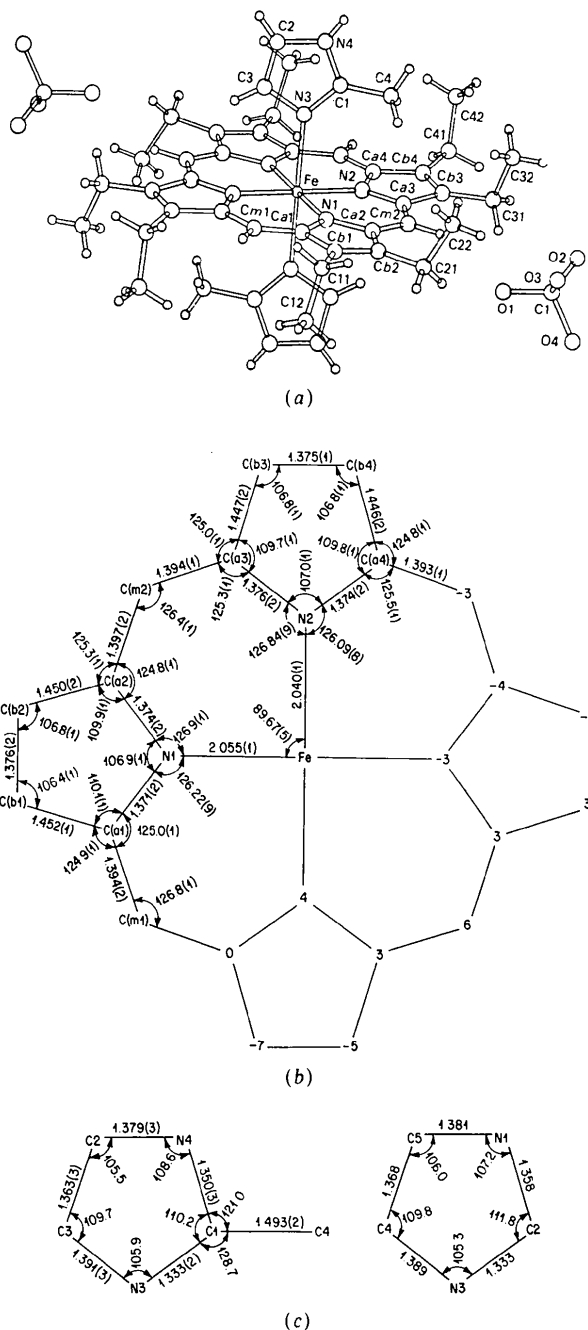


Fig. 1. (a) Perspective drawing of the molecule showing labelling of atoms. (b) Bond distances, valence angles in the porphyrin plane (top left) and deviations from the mean-square plane in units of 0.01 Å (bottom right). (c) Bond distances and valence angles in the 2-methylimidazole ligand (left) and in the imidazole molecule (right) (McMullan *et al.*, 1979).

* A list of structure factors and tables of anisotropic thermal parameters, results of the rigid-bond test, rigid-body analysis and multipole population parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43996 (69 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and their e.s.d.'s*

First line: spherical-atom refinement. Second line: multipole refinement.

	x	y	z	B* (Å ²)		x	y	z	B* (Å ²)
Fe	0.0000	0.0000	0.0000	0.857 (9)	C41	-0.0876 (1)	0.2305 (1)	-0.5630 (1)	1.56 (2)
	0.0000	0.0000	0.0000	0.837 (9)		-0.0873 (1)	0.2304 (1)	-0.5632 (1)	1.61 (2)
Cl	0.5000	0.5000	0.0000	2.42 (1)	C42	-0.2227 (2)	0.2925 (1)	-0.5779 (2)	2.77 (3)
	0.5000	0.5000	0.0000	2.43 (1)		-0.2229 (2)	0.2927 (1)	-0.5780 (2)	2.76 (3)
N1	0.1390 (1)	0.09173 (8)	0.1771 (1)	1.01 (2)	HN4	-0.390 (2)	0.267 (2)	0.028 (2)	0.063 (6)
	0.1393 (1)	0.0920 (1)	0.1775 (2)	1.05 (2)		-0.388 (3)	0.269 (2)	0.025 (2)	0.061 (8)
N2	0.02037 (8)	0.10646 (9)	-0.1621 (1)	0.98 (2)	H111	0.292 (2)	0.136 (2)	0.653 (2)	0.058 (5)
	0.02055 (8)	0.1067 (1)	-0.1625 (2)	1.02 (2)		0.291 (2)	0.133 (1)	0.653 (2)	0.063 (5)
N3	-0.1831 (2)	0.0937 (2)	0.0291 (1)	1.09 (3)	H112	0.375 (2)	0.231 (2)	0.636 (2)	0.062 (5)
	-0.1831 (2)	0.0937 (2)	0.0290 (1)	1.12 (3)		0.378 (2)	0.234 (2)	0.633 (2)	0.063 (5)
N4	-0.3479 (2)	0.2109 (2)	0.0348 (2)	1.62 (3)	H121	0.528 (2)	0.089 (2)	0.774 (3)	0.089 (7)
	-0.3483 (2)	0.2115 (2)	0.0347 (2)	1.64 (3)		0.527 (2)	0.096 (2)	0.770 (3)	0.087 (6)
O1	0.4650 (2)	0.3940 (1)	0.0207 (2)	2.15 (4)	H122	0.469 (2)	0.011 (2)	0.619 (3)	0.081 (7)
	0.4650 (2)	0.3940 (1)	0.0207 (2)	2.17 (4)		0.465 (2)	0.011 (2)	0.620 (2)	0.082 (6)
O2	0.4113 (2)	0.5557 (2)	-0.1216 (3)	4.78 (7)	H123	0.563 (2)	0.116 (2)	0.607 (3)	0.083 (7)
	0.4113 (2)	0.5558 (2)	-0.1214 (3)	4.79 (7)		0.555 (2)	0.113 (2)	0.605 (2)	0.082 (6)
O3	0.5115 (2)	0.5668 (2)	0.1530 (4)	5.26 (8)	H211	0.435 (2)	0.327 (1)	0.265 (2)	0.045 (4)
	0.5112 (2)	0.5668 (2)	0.1526 (4)	5.21 (8)		0.433 (2)	0.325 (1)	0.259 (2)	0.062 (5)
O4	0.6439 (2)	0.5024 (1)	-0.0048 (2)	2.22 (4)	H212	0.466 (2)	0.316 (1)	0.446 (2)	0.055 (5)
	0.6439 (2)	0.5025 (1)	-0.0047 (2)	2.27 (4)		0.465 (2)	0.314 (1)	0.446 (2)	0.059 (5)
Ca1	0.1848 (1)	0.06983 (9)	0.3360 (1)	1.03 (2)	H221	0.375 (2)	0.492 (2)	0.361 (3)	0.088 (7)
	0.1848 (1)	0.06987 (8)	0.3359 (1)	1.08 (2)		0.375 (2)	0.488 (2)	0.366 (2)	0.085 (6)
Ca2	0.2090 (1)	0.18437 (8)	0.1603 (1)	1.10 (2)	H222	0.236 (2)	0.436 (2)	0.248 (3)	0.072 (6)
	0.2088 (1)	0.18428 (8)	0.1602 (1)	1.14 (2)		0.241 (2)	0.436 (1)	0.253 (2)	0.070 (5)
Ca3	0.1025 (1)	0.19950 (8)	-0.1326 (1)	1.06 (2)	H223	0.281 (2)	0.432 (2)	0.436 (3)	0.083 (7)
	0.1024 (1)	0.19938 (8)	-0.1324 (1)	1.09 (2)		0.279 (2)	0.428 (2)	0.432 (3)	0.078 (6)
Ca4	-0.0517 (1)	0.10300 (9)	-0.3223 (1)	1.03 (2)	H311	0.130 (2)	0.372 (2)	-0.406 (2)	0.071 (6)
	-0.0517 (1)	0.10291 (8)	-0.3222 (1)	1.07 (2)		0.130 (2)	0.373 (2)	-0.405 (3)	0.074 (6)
Cb1	0.2848 (1)	0.15274 (9)	0.4236 (1)	1.14 (2)	H312	0.237 (2)	0.369 (1)	-0.232 (2)	0.052 (5)
	0.2846 (1)	0.15247 (9)	0.4237 (1)	1.19 (2)		0.238 (2)	0.366 (1)	-0.224 (2)	0.062 (5)
Cb2	0.3007 (1)	0.22277 (9)	0.3140 (1)	1.16 (2)	H321	0.104 (2)	0.531 (2)	-0.250 (3)	0.078 (6)
	0.3007 (1)	0.22295 (9)	0.3136 (2)	1.22 (2)		0.109 (2)	0.528 (2)	-0.250 (2)	0.083 (6)
Cb3	0.0786 (1)	0.25758 (9)	-0.2779 (2)	1.15 (2)	H322	-0.027 (3)	0.465 (2)	-0.315 (3)	0.100 (8)
	0.0788 (1)	0.25759 (9)	-0.2776 (2)	1.20 (2)		-0.025 (3)	0.461 (2)	-0.314 (3)	0.097 (7)
Cb4	-0.0174 (1)	0.19793 (9)	-0.3953 (1)	1.16 (2)	H323	0.071 (3)	0.458 (2)	-0.128 (3)	0.105 (9)
	-0.0175 (1)	0.19777 (9)	-0.3955 (1)	1.20 (2)		0.070 (2)	0.455 (2)	-0.132 (3)	0.098 (7)
Cm1	0.1441 (1)	-0.02035 (8)	0.4016 (2)	1.12 (2)	H411	-0.105 (2)	0.169 (2)	-0.636 (2)	0.055 (5)
	0.1442 (1)	-0.02044 (8)	0.4024 (2)	1.17 (2)		-0.108 (2)	0.166 (2)	-0.638 (2)	0.058 (5)
Cm2	0.1920 (1)	0.2332 (1)	0.0160 (1)	1.23 (3)	H412	-0.027 (2)	0.277 (1)	-0.597 (2)	0.054 (5)
	0.1921 (1)	0.2336 (1)	0.0160 (1)	1.26 (3)		-0.023 (2)	0.276 (1)	-0.595 (2)	0.050 (5)
C1	-0.2298 (2)	0.1964 (1)	-0.0007 (1)	1.32 (3)	H421	-0.262 (2)	0.322 (2)	-0.682 (3)	0.076 (6)
	-0.2298 (2)	0.1963 (1)	-0.0007 (1)	1.38 (3)		-0.259 (2)	0.323 (2)	-0.681 (3)	0.079 (6)
C2	-0.3797 (2)	0.1145 (2)	0.0902 (2)	1.66 (3)	H422	-0.292 (2)	0.248 (2)	-0.552 (3)	0.088 (7)
	-0.3802 (2)	0.1147 (2)	0.0903 (2)	1.67 (3)		-0.289 (2)	0.245 (2)	-0.553 (2)	0.089 (6)
C3	-0.2782 (2)	0.0427 (1)	0.0852 (1)	1.39 (3)	H423	-0.203 (2)	0.354 (2)	-0.499 (3)	0.073 (6)
	-0.2779 (2)	0.0422 (1)	0.0853 (1)	1.44 (3)		-0.203 (2)	0.351 (2)	-0.450 (2)	0.076 (6)
C4	-0.1689 (2)	0.2871 (1)	-0.0636 (2)	2.31 (4)	HCm1	0.183 (2)	-0.026 (1)	0.511 (2)	0.046 (4)
	-0.1688 (2)	0.2874 (1)	-0.0638 (2)	2.33 (4)		0.185 (2)	-0.028 (1)	0.516 (3)	0.052 (5)
C11	0.3565 (1)	0.1572 (1)	0.5992 (1)	1.50 (2)	HCm2	0.244 (2)	0.295 (1)	0.017 (2)	0.053 (5)
	0.3564 (1)	0.1574 (1)	0.5995 (1)	1.53 (2)		0.248 (2)	0.297 (2)	0.019 (2)	0.059 (5)
C12	0.4880 (2)	0.0873 (1)	0.6550 (2)	2.47 (3)	HC2	-0.457 (2)	0.107 (1)	0.119 (2)	0.055 (5)
	0.4882 (2)	0.0873 (1)	0.6551 (2)	2.46 (3)		-0.456 (2)	0.105 (2)	0.120 (2)	0.064 (7)
C21	0.3921 (1)	0.3226 (1)	0.3432 (1)	1.55 (2)	HC3	-0.270 (2)	-0.031 (2)	0.110 (2)	0.060 (5)
	0.3923 (1)	0.3224 (1)	0.3432 (2)	1.59 (2)		-0.267 (3)	-0.031 (2)	0.112 (2)	0.072 (8)
C22	0.3145 (2)	0.4302 (1)	0.3486 (2)	2.33 (3)	HC41	-0.220 (2)	0.350 (2)	-0.063 (3)	0.080 (6)
	0.3144 (2)	0.4303 (1)	0.3486 (2)	2.34 (3)		-0.224 (2)	0.350 (2)	-0.064 (2)	0.077 (6)
C31	0.1411 (1)	0.3661 (1)	-0.2911 (2)	1.67 (2)	HC42	-0.077 (2)	0.302 (2)	0.005 (3)	0.075 (6)
	0.1412 (1)	0.3661 (1)	-0.2912 (2)	1.71 (3)		-0.075 (2)	0.300 (2)	0.008 (2)	0.080 (7)
C32	0.0667 (2)	0.4630 (1)	-0.2403 (2)	3.04 (4)	HC43	-0.171 (2)	0.267 (2)	-0.168 (3)	0.071 (6)
	0.0666 (2)	0.4632 (1)	-0.2401 (2)	3.03 (4)		-0.172 (2)	0.266 (2)	-0.171 (3)	0.071 (6)

* Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

orientation effect (Scheidt & Chipman, 1986): in Fe(2-MeIm)₂oep(ClO₄) the angle φ between the N2-Fe-N3 and imidazole planes is 21.8 (1)° compared with the value of 32° in Fe(2-MeIm)₂tpp(ClO₄).

Fig. 1(b) shows the bond distances and valence angles in the porphyrin plane and the deviations from the average plane. There are small but significant variations in the bond distances to Fe as a function of temperature. The axial Fe-N distance is 0.026 Å shorter at low temperature; the difference is statistically significant (12σ). A similar but larger effect was

observed on cooling of Fe^{II}(thf)₂tpp (Lecomte, Blessing, Coppens & Tabard, 1986). Both equatorial distances are longer at low temperature by 0.006 and 0.007 Å; the differences are just significant (4-5σ). Interestingly, the pattern of small rhombic distortion in the equatorial Fe-N distances remains. Although the geometry of the ligand is in agreement with the room-temperature study, all differences (none are statistically significant) are in the direction expected for longer Fe-N equatorial distances at low temperature.

Table 2. Fe-atom valence and orbital populations

Definition of coordinate system: *z* axis perpendicular to the porphyrin plane, *x* and *y* axes along Fe–N(porphyrin) vectors.

	Experiment		Extended Huckel		Neutral spherical atom	
d_{z^2}	1.53 (9)	24.8%	1.576	23.3%	1.2	20%
$d_{x^2-y^2}$	1.16 (8)	16.7%	1.582	23.3%	1.2	20%
d_{xz}	1.32 (8)	21.3%	1.251	18.5%	1.2	20%
d_{yz}	1.28 (8)	20.7%	1.303	19.3%	1.2	20%
d_{xy}	0.90 (8)	14.5%	1.054	15.6%	1.2	20%
Total <i>d</i>	6.17 (10)		6.766			
4 <i>s</i>	1.37 (28)		0.377		2.0	
4 <i>p_x</i>	—		0.176		—	
4 <i>p_y</i>	—		0.158		—	
4 <i>p_z</i>	—		0.240		—	
Total	1.37		0.951			

The distances and angles in the 2-methylimidazole ligand (with distances corrected for a libration of 4.4° around the Fe–N3 axis) and in imidazole (McMullan, Epstein, Ruble & Craven, 1979) are shown in Fig. 1(c). No significant differences are found, except those due to substitution at the C1 atom: the N3–C1–N4 angle, which is 111.8° in imidazole is 110.2° in the present determination. A hydrogen bond between O1 (or O2) of the disordered perchlorate ion and N4 of the imidazole is observed, with a distance N4–O1 of 2.875 (3) Å (N4–O2 3.02 Å).

The rigid-bond test (Hirshfeld, 1976) was applied to the Fe–N bonds in order to check the deconvolution of the thermal parameters from the population parameters. Results shown in Table S2 (deposited) indicate that all bonds have $|\Delta u^2| \leq 0.0012 \text{ \AA}^2$. A rigid-body refinement of the temperature parameters (Shomaker & Trueblood, 1968; Dunitz & White, 1973) of the porphinato core gave an agreement factor of 9% [Table S3 (deposited)].

Discussion of the multipole refinement results

We will limit our discussion mainly to the features on the Fe atom. The κ -parameter value of 0.93 (1) indicates a considerable expansion of the valence shell. The *d*-electron population of 6.17 (10) electrons corresponds to that of a neutral atom, as observed in other porphyrins. The 4*s* population of 1.4 (3) has a large standard deviation but is significantly different from zero. The *d*-orbital populations derived from the multipole parameters are listed in Table 2. They are in reasonable agreement with values obtained in a parallel extended Huckel calculation. In particular, the depletion of the d_{xy} orbital is well reproduced. But the population parameters [Table S4 (deposited)] also indicate a significant deviation of the Fe-atom density from 4/*mmm* symmetry, which has not been found in other charge density studies of porphyrin compounds. The deviation is illustrated in the deformation density map (Fig. 2*a*) and could be related to a metal–ligand π -electron interaction. The orientation of the ligand plane, indicated in Fig. 2(*a*), is

such that the imidazole π lobes point in the direction of the asymmetric feature on the Fe atom. This observation requires further confirmation in studies on related complexes.

The deformation density in the imidazole ring (Fig. 2*b*) shows no unusual features and a low background away from the atoms, thus attesting to the quality of the data. Average standard deviations in the maps are estimated to be 0.035 e \AA^{-3} when the standard

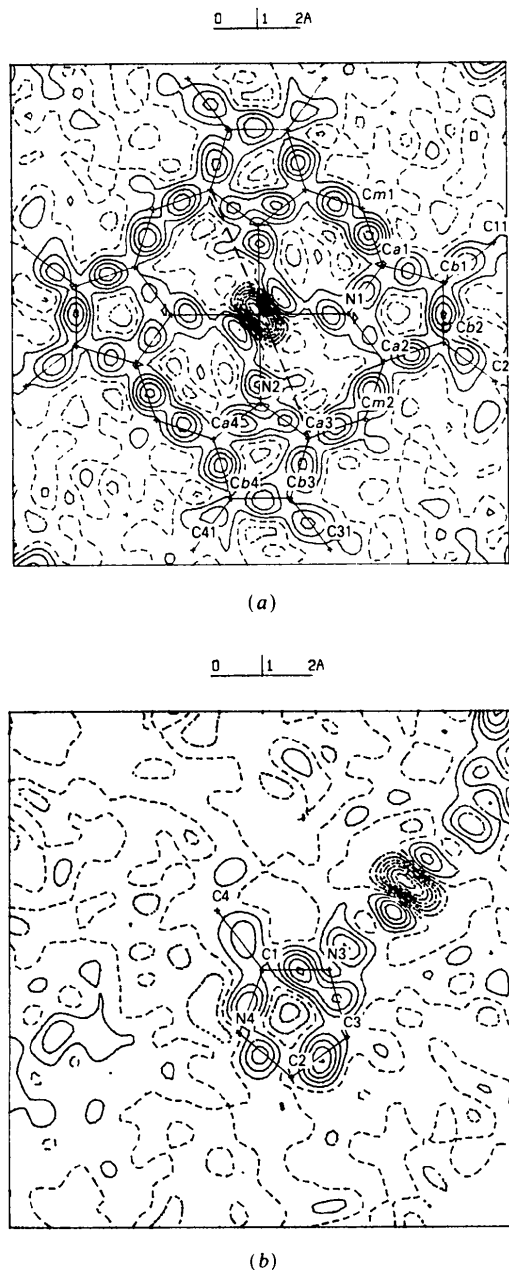


Fig. 2. (a) Deformation density in the plane of the porphyrin ring. Contours at 0.1 e \AA^{-3} . Negative contours broken. The straight line through the Fe atom indicates the direction of the imidazole plane. (b) Deformation density in the plane of the methyl-imidazole ligand. Negative contours broken.

formula $\sigma^2 = (1/V)^2 \sum \sigma^2(F_o)$ is used (Cruickshank, 1949). When the estimate is based on variations between chemically equivalent regions in the molecule, a slightly larger value of $0.05 \text{ e } \text{Å}^{-3}$ is obtained.

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Electron Density in Potassium Bis(dithiooxalato-*S,S'*)nickelate(II)

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Abstract

At room temperature, $\text{K}_2[\text{Ni}(\text{C}_2\text{O}_2\text{S}_2)_2]$ is: monoclinic, $P2_1/c$, $M_r = 377.2$, $a = 11.044$ (2), $b = 4.1949$ (7), $c = 13.404$ (2) Å, $\beta = 118.13$ (1)°, $V = 547.6$ (2) Å³, $Z = 2$, $D_x = 2.29 \text{ Mg m}^{-3}$, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 3.34 \text{ mm}^{-1}$, $F(000) = 372$, $T = 298 \text{ K}$, $R = 0.053$ and $wR = 0.027$ for 3943 reflections. The nickel coordinates with sulfur rather than oxygen in a structure which may be regarded either as square planar or as strongly distorted octahedral. To assist in understanding the structural behaviour of the system, the electron density has been analysed. For these metal-sulfur bonds, the electron density polarizes far less than it does in metal-fluorine or metal-oxygen bonds. The extent of the depletion of the nickel 3d subshell is related to the electronegativity of the ligand atom. The overlap of atomic densities is expected to result in only moderate electron movement for sulfur ligands, which are weakly electronegative. There is a net transfer of electrons towards the nickel, and the negative charge associated with the $[\text{Ni}(\text{S}_2\text{C}_2\text{O}_2)_2]$ anion resides predominantly on that atom.

Introduction

The change in atomic polarizability through the first-transition-metal series has been observed experimentally in difference density maps. In the compounds $\text{KM}F_3$, where $M = \text{Mn, Fe, Co}$ and Ni with octahedral coordination (Kijima, Tanaka & Marumo, 1981, 1983; Miyata, Tanaka & Marumo, 1983), the depletion of the sum of the atomic densities along the $M-F$ bonds rises steadily through the series. The increase in population of the valence subshell of the central atom results in greater spin conflict with the electrons in the valence subshell of the strongly electronegative F atoms.

As a consequence of the Pauli (1925) principle there is a transfer of density away from the overlap region. The effect would maximize for KCuF_3 except that the system becomes unstable, changing to structures which are elongated octahedra, or even square planar. This effect for Cu^{II} compounds is understood in terms of the Jahn-Teller theorem. For transition metals lighter than nickel, square-planar complexes are formed only when strong steric constraints are imposed on the ligands. For Ni^{II} compounds, on the