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Compounds with Intermediate Spin.
II*. The Crystal Structure of Tris(1,10-phenanthroline)iron(II) Iodide Dihydrate

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The crystal structure of tris(1,10-phenanthroline)-iron(II) iodide dihydrate, $Fe(C_{12}N_2H_8)_3I_2 \cdot 2H_2O$, has been determined from X-ray intensity data collected on a four circle diffractometer. The space group is $P2_1/a$ *with four formula units in the cell. The cell dimensions are* a = *10.623(2),* b = *16.402(2),* c = *20.375(4) Å, and* β = *104.48(1)°. The structure was refined by least-squares methods to a conventional* R *factor of 7.2%. Each Fe is pseudo-octahedrally coordinated by three phenanthroline molecules with Fe–N distances in the range 1.96–1.99 Å. The coordination polyhedra are packed in layers parallel to the ab-plane with Fe close to z = 0.25 and 0.75. The water molecules and the iodide ions form hydrogen bond chains between the layers of the metal complexes. The Fe–O distances are in the range 4.90–5.45 Å, and the Fe–I distances 6.06–6.43 Å.*

Introduction

Compounds with the formula $Fe(phen)_3X_2 \cdot nH_2O$, where phen = 1,10-phenanthroline and X = halide or pseudohalide, are low spin compounds [1]. By either splitting off one of the phenanthroline molecules [1] or disrupting the geometry of the coordination sphere by introducing a large substituent in the 2-position of the phenanthroline molecule [2] it is possible to form compounds with a strongly temperature dependent magnetic moment. One of the research projects at this Institute aims at correlating the anomalous temperature dependent magnetic moment of various iron complexes with their geometrical features: (i) bond distances and bond angles in the coordination sphere and (ii) the symmetry of the coordination sphere [3]. A crystal structure determination of $Fe(phen)_3I_2 \cdot 2H_2O$ would give the structural parameters for a typical iron(II) low spin compound.

Another interest in $Fe(phen)_3^{2+}$ and related complexes stems from their ability to form outer-sphere complexes [4], $Fe(phen)_3L_n$, where L is an anion [5–6] or a neutral molecule [7]. Due to the rigid planar structure of the phenanthroline molecule the $Fe(phen)_3$ complex cannot be spherical in shape, but has three major pockets between the phenanthroline molecules and two minor pockets along the three-fold axis. It is thus possible for outer-sphere ligands of suitable sizes to intrude into these pockets and bind, *e.g.* by electrostatic or dipole–dipole interaction,to the $Fe(phen)_3$ specimen. Important factors are the hydrophobic character of the pockets and the ability of the phenanthroline ligands to attract other molecules with π electron systems.

The ability of forming outer-sphere complexes must have a profound influence on properties such as solubility in various solvents and the mode of packing in the solid state of $Fe(phen)_3$ and related compounds.

In aqueous solution the complexes $Fe(phen)_3I_n$, n = 1–4, have been established [5]. A crystal structure determination of $Fe(phen)_3I_2 \cdot 2H_2O$ should give important information about geometrical features related to the formation of outer-sphere complexes.

Experimental

The compound was prepared as described previously [5]. It was dissolved in hot water and dark red plate-like crystals were obtained by slowly cooling the solution. Weissenberg photograms revealed the Laue class $2/m$ and the systematic absences $0k0; k \neq 2n$, and $h0l; h \neq 2n$, which exclusively determines the space group as $P2_1/a$.

Table I gives information concerning the crystal data, the collection and reduction of the intensity data, and the refinement based on them.

The unit cell dimensions were improved by a least-squares treatment of powder spectra obtained with a Guinier–Hägg focusing camera ($CuK\alpha_1$- radiation, λ = 1.54056 Å, 23 °C). Aluminium (cubic, a = 4.04934 Å) was used as internal standard. A four circle single crystal diffractometer (CAD-4) was used for the intensity data collection. The ω–2θ scan technique was employed and the scan interval, $\Delta\omega$,

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*For Part I in this series, see ref. [3].

TABLE I. Crystal Data, Collection of the Intensity Data, and the Least-squares Refinement.

$Fe(C_{12}N_2H_8)_3I_2 \cdot 2H_2O$
F.W. = 886.3
Monoclinic, $P2_1/a$
a = 10.623(2) Å
b = 16.402(2) Å
c = 20.375(4) Å
β = 104.48(1)°
V = 3437 $Å^3$
Z = 4
Crystal size:
0.350 × 0.050 × 0.188 mm^3
λ = 0.7107 Å (graphite monochromated MoKα)

Take off angle: 3°
μ = 22.5 cm^{-1}
Range of transmission factor: 0.65–0.90
θ interval: 3–25°
ω–2θ scan with $\Delta\omega = 1.0 + 1.0 \tan\theta$
Minimum number of counts in a scan: 3000
Maximum recording time: 3 min
Number of measured reflexions: 6610
Number of reflexions with zero weight
$(I \leq 3\sigma(I))$: 3493
Number of parameters refined: 247
$R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.072$
$R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma |F_o|^2]^{1/2} = 0.086$
$S = [\Sigma w(|F_o| - |F_c|)^2 / (m - n)]^{1/2} = 2.4$
C (weighting function): 0.015

TABLE II. Atomic Coordinates × 10^4 with Estimated Standard Deviations.

	x	y	z
Fe	731(2)[a]	4819(1)	7430(1)
I(1)	-3579(1)	6648(1)	5476(1)
I(2)	667(1)	1972(1)	9364(1)
O(1)	397(14)	3507(9)	4947(8)
O(2)	2706(13)	3745(8)	9687(6)
Ligand 1			
N(1)	1696(10)	4960(6)	6715(5)
N(10)	2383(9)	5176(7)	8041(5)
C(2)	1308(14)	4857(9)	6056(7)
C(3)	2141(15)	5023(9)	5623(7)
C(4)	3407(14)	5249(9)	5892(7)
C(5)	5160(15)	5538(10)	6932(8)
C(6)	5528(15)	5615(10)	7615(8)
C(7)	4916(15)	5620(10)	8726(8)
C(8)	3931(16)	5529(10)	9067(8)
C(9)	2665(14)	5301(9)	8698(7)
C(11)	3335(13)	5287(8)	7700(7)
C(12)	4633(14)	5504(9)	8038(7)
C(13)	2980(12)	5178(8)	7003(6)
C(14)	3845(13)	5336(8)	6590(7)
Ligand 2			
N(1)	-813(10)	4364(7)	6802(6)
N(10)	1242(9)	3657(6)	7554(5)
C(2)	-1870(14)	4737(9)	6408(7)
C(3)	-2864(16)	4306(10)	5983(8)
C(4)	-2809(15)	3467(10)	5930(7)
C(5)	-1594(16)	2183(10)	6335(8)
C(6)	-536(16)	1803(10)	6732(8)
C(7)	1607(16)	1950(10)	7606(8)
C(8)	2507(15)	2463(10)	7969(7)
C(9)	2295(14)	3327(10)	7940(7)
C(11)	320(13)	3158(8)	7156(7)
C(12)	489(16)	2306(10)	7158(7)
C(13)	-767(14)	3519(9)	6752(7)
C(14)	-1733(15)	3056(9)	6343(7)
Ligand 3			
N(1)	73(9)	5944(6)	7309(5)
N(10)	-139(10)	4821(7)	8177(5)
C(2)	179(15)	6491(9)	6838(7)
C(3)	-354(16)	7288(10)	6818(8)
C(4)	-1015(16)	7516(10)	7316(8)
C(5)	-1731(15)	7116(9)	8368(8)
C(6)	-1794(15)	6545(10)	8831(8)
C(7)	-1372(15)	5089(9)	9227(8)
C(8)	-874(15)	4328(9)	9134(7)
C(9)	-234(14)	4228(9)	8608(7)
C(11)	-690(13)	5565(8)	8260(7)
C(12)	-1297(14)	5724(9)	8797(7)
C(13)	-560(13)	6164(9)	7799(7)
C(14)	-1106(14)	6954(9)	7825(7)

[a] Numbers in parentheses represent estimated standard deviations.

was extended 25% at both ends for the background measurement. After every 100 measurements three standard reflexions were checked. No systematic variation in their intensities was observed. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization, and absorption effects ($\sigma_c(I)$ is based on counting statistics). The expression $p = (\cos^2 2\theta + \cos^2 2\theta_M)/(1 + \cos^2 2\theta_M)$ was used in the correction of the polarization effects. θ_M (8.06°) is the Bragg angle for the monochromator.

TABLE III.

A. Thermal Parameters $\beta_{ij} \times 10^4$ with Estimated Standard Deviations. The expression used is $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	34(2)	15(1)	13(1)	−4(1)	8(1)	−1(1)
I(1)	103(1)	49(1)	33(1)	18(1)	28(1)	11(1)
I(2)	94(2)	63(1)	43(1)	−12(1)	7(1)	20(1)
O(1)	146(19)	73(9)	74(7)	−28(10)	30(9)	−27(6)
O(2)	162(18)	65(7)	26(4)	12(9)	33(7)	−2(4)
Ligand 1						
N(1)	58(12)	18(5)	17(3)	2(6)	15(5)	−3(3)
N(10)	37(10)	24(5)	16(3)	−8(6)	10(5)	−4(3)
Ligand 2						
N(1)	36(11)	27(6)	24(4)	6(6)	15(5)	9(3)
N(10)	32(10)	17(5)	17(3)	10(5)	6(5)	0(3)
Ligand 3						
N(1)	16(9)	17(5)	16(3)	−5(5)	−0(4)	−2(3)
N(10)	58(11)	25(5)	13(3)	−6(6)	10(5)	4(3)

B. Isotropic thermal parameters $B/\text{Å}$

	Ligand 1	Ligand 2	Ligand 3
C(2)	2.7(3)	3.0(3)	3.2(3)
C(3)	3.2(3)	3.5(3)	4.1(4)
C(4)	2.8(3)	3.1(3)	3.6(3)
C(5)	3.2(3)	3.6(3)	3.3(3)
C(6)	3.3(3)	4.1(4)	3.4(3)
C(7)	3.2(3)	3.6(3)	3.1(3)
C(8)	3.5(3)	3.3(3)	3.0(3)
C(9)	2.9(3)	3.0(3)	2.7(3)
C(11)	2.2(3)	2.0(3)	2.1(3)
C(12)	2.5(3)	3.5(3)	2.6(3)
C(13)	1.9(2)	2.3(3)	2.2(3)
C(14)	2.1(3)	3.0(3)	2.7(3)

Structure Determination and Refinement

The positions of the iodide ions were deduced from a vector map. The remaining non-H atoms were located from a difference synthesis. The atomic parameters were refined with full-matrix least-squares technique, minimizing $\Sigma w(|F_o|-|F_c|)^2$ with weights $w^{-1} = \sigma_c^2/4|F_o|^2 + C|F_o|^2$. C was adjusted so that constant values of $\langle w(|F_o|-|F_c|)^2\rangle$ were obtained in different $|F_o|$ and $\sin\theta$ intervals. Anisotropic temperature factors for Fe, N, I and O were introduced in the last cycles of refinement. In the final cycle the shifts in the parameters were less than 5% of the estimated standard deviations. The atomic scattering factors were taken from International Tables for X-ray Crystallography [8]. Tables II and III give the positional and thermal parameters, respectively. A final difference synthesis was featureless. A list of observed and calculated structure factors may be obtained from the authors.

Description of the Structure

Crystal Packing

The structure is composed of mononuclear Fe(phen)_3^{2+} complexes (Fig. 1) stacked into layers parallel to the *ab*-plane, with Fe close to $z = 0.25$ and 0.75 (Fig. 2 and 3). The iodide ions and the water molecules are located between the layers. Each complex is surrounded by four other complexes and the phenanthroline ligands of one complex intrude into the pockets of the neighbouring complexes. Within the layers there are zig-zag formed chains running along *a* in which the intruding phenanthroline ligands are almost parallel. This zipper shaped structure gives a large contact surface between the ligands in neighbouring complexes. The tilt angle between these phenanthroline ligands is 8.5° and the shortest distance between them 4.2 Å. The shortest Fe–Fe distance within a layer is 9.28 Å and between the layers 9.65 Å.

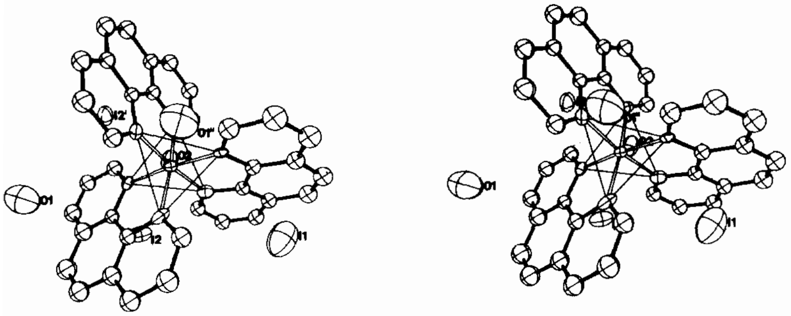

Figure 1. The coordination polyhedron with the water molecules located closer than 6.5 Å to Fe. The view is along the pseudo-threefold axis. The superscripts (i)–(iii) used in Fig. 1 and in Table VII give the transformation applied to the x, y, z values given in Table II: (i) $1/2 + x, 1/2 - y, z$; (ii) $-x, 1 - y, 1 - z$; (iii) $-1/2 - x, -1/2 + y, 1 - z$.

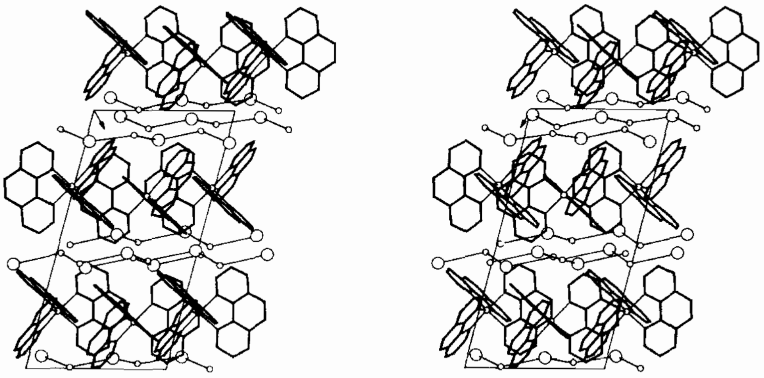

Figure 2. The packing viewed along **b**. Coordination bonds and possible hydrogen bonds are denoted with thin lines.

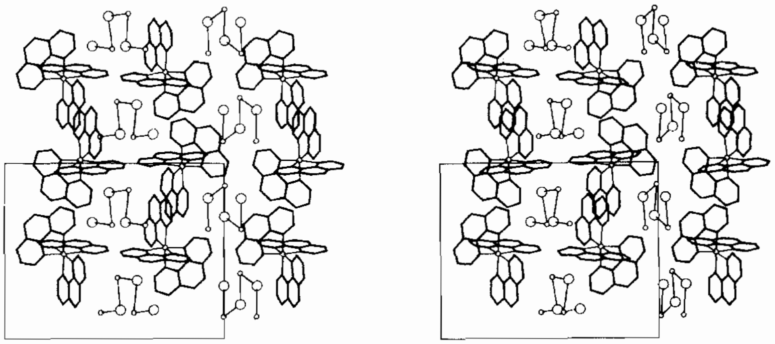

Figure 3. The packing viewed along **a**.

The iodide ions and water O atoms located closer than 6.5 Å to Fe are depicted in Fig. 1. The water oxygen atom O(1) is situated exactly between the layers of the $Fe(phen)_3^{2+}$ complexes with a distance of 5.43(2) Å to Fe in the adjacent layers. The water molecule O(2) is located in one of the minor pockets of the $Fe(phen)_3^{2+}$ complex along the pseudo-threefold axis with an Fe–O(2) distance of 4.88(1) Å. Since the distance from O(2) to the next Fe is longer than 8 Å, O(2) is clearly associated with one specific complex. In Fig. 1 it is seen that the water molecules are located in or very close to the pockets of the complex, while the iodide ions are situated further away from the pockets.

The Coordination Polyhedron

Six nitrogen atoms form a distorted octahedron around the iron atom. The mean Fe–N distance is 1.973(5) Å. Fig. 1 shows the complex viewed along the pseudo-threefold axis. The almost equilateral triangles are twisted 53° relative to each other (calculated by method 1 of Dymock and Palenik [9]), and the tilt angle between them is 1.7°. The height of the polyhedron measured as the distance between the centroids of the triangular faces is 7% less than required for a true octahedron. This compression along the pseudo-threefold axis as well as the twist distortion from O_h geometry is probably caused by the small ligand bite, which is only 92% of the mean

TABLE IV. Selected Bond Distances (A) within the Coordination Polyhedron. The ligands 2 and 3 are denoted ' and ", respectively.

Fe–N(1)	1.994(10)	N(1)–N(1)'	2.886(15)
Fe–N(10)	1.969(10)	N(1)–N(1)"	2.844(14)
Fe–N(1)'	1.958(11)	N(1)'–N(1)"	2.861(15)
Fe–N(10)'	1.980(10)	N(10)–N(10)'	2.839(15)
Fe–N(1)"	1.967(10)	N(10)–N(10)"	2.822(14)
Fe–N(10)"	1.968(10)	N(10)'–N(10)"	2.888(14)

TABLE V. Selected Distances (A) and Angles (°) within the Phenanthroline Molecules.

Ligand 1			
N(1)•••N(10)	2.640(14)	C(2)–N(1)–C(13)	119(1)
N(1)–C(2)	1.313(17)	N(1)–C(2)–C(3)	122(1)
C(2)–C(3)	1.424(20)	C(2)–C(3)–C(4)	120(1)
C(3)–C(4)	1.371(20)	C(3)–C(4)–C(14)	119(1)
C(4)–C(14)	1.389(19)	C(4)–C(14)–C(13)	119(1)
C(14)–C(13)	1.416(18)	C(4)–C(14)–C(5)	124(1)
N(1)–C(13)	1.390(16)	N(1)–C(13)–C(14)	121(1)
C(13)–C(11)	1.387(18)	N(1)–C(13)–C(11)	117(1)
C(11)–C(12)	1.424(19)	C(14)–C(13)–C(11)	122(1)
C(12)–C(6)	1.446(21)	C(13)–C(11)–C(12)	121(1)
C(6)–C(5)	1.355(21)	C(11)–C(12)–C(6)	116(1)
C(14)–C(5)	1.435(20)	C(6)–C(12)–C(7)	126(1)
C(12)–C(7)	1.371(21)	C(12)–C(6)–C(5)	123(1)
C(7)–C(8)	1.403(22)	C(14)–C(5)–C(6)	121(1)
C(8)–C(9)	1.417(21)	C(13)–C(14)–C(5)	117(1)
N(10)–C(9)	1.313(17)	C(11)–C(12)–C(7)	118(1)
N(10)–C(11)	1.375(16)	C(12)–C(7)–C(8)	119(1)
		C(7)–C(8)–C(9)	119(1)
		C(11)–N(10)–C(9)	119(1)
		N(10)–C(11)–C(13)	117(1)
		N(10)–C(11)–C(12)	122(1)
		N(10)–C(9)–C(8)	122(1)
Ligand			
N(1)•••N(10)	2.605(14)	C(2)–N(1)–C(13)	116(1)
N(1)–C(2)	1.353(18)	N(1)–C(2)–C(3)	122(1)
C(2)–C(3)	1.382(22)	C(2)–C(3)–C(4)	121(1)
C(3)–C(4)	1.382(22)	C(3)–C(4)–C(14)	118(1)
C(4)–C(14)	1.411(21)	C(4)–C(14)–C(13)	118(1)
C(14)–C(13)	1.376(20)	C(4)–C(14)–C(5)	123(1)
N(1)–C(13)	1.391(18)	N(1)–C(13)–C(14)	124(1)
C(13)–C(11)	1.373(19)	N(1)–C(13)–C(11)	115(1)
C(11)–C(12)	1.409(21)	C(14)–C(13)–C(11)	121(1)
C(12)–C(6)	1.465(23)	C(13)–C(11)–C(12)	121(1)
C(6)–C(5)	1.361(23)	C(11)–C(12)–C(6)	119(1)
C(14)–C(5)	1.440(22)	C(6)–C(12)–C(7)	122(1)
C(12)–C(7)	1.429(23)	C(12)–C(6)–C(5)	118(2)
C(7)–C(8)	1.348(22)	C(14)–C(5)–C(6)	121(1)
C(8)–C(9)	1.433(23)	C(13)–C(14)–C(5)	120(1)
N(10)–C(9)	1.312(18)	C(11)–C(12)–C(7)	120(1)
N(10)–C(14)	1.375(16)	C(12)–C(7)–C(8)	117(1)
		C(7)–C(8)–C(9)	121(1)
		C(11)–N(10)–C(9)	119(1)
		N(10)–C(11)–C(13)	118(1)
		N(10)–C(11)–C(12)	121(1)
		N(10)–C(9)–C(8)	122(1)

TABLE V.
(continued)

Ligand 3			
N(1)•••N(10)	2.602(14)	C(2)–N(1)–C(13)	119(1)
N(1)–C(2)	1.339(18)	N(1)–C(2)–C(3)	122(1)
C(2)–C(3)	1.422(23)	C(2)–C(3)–C(4)	119(1)
C(3)–C(4)	1.420(22)	C(3)–C(4)–C(14)	119(1)
C(4)–C(14)	1.409(21)	C(4)–C(14)–C(13)	118(1)
C(14)–C(13)	1.427(29)	C(4)–C(14)–C(5)	125(1)
N(1)–C(13)	1.383(17)	N(1)–C(13)–C(14)	123(1)
C(13)–C(11)	1.389(19)	N(1)–C(13)–C(11)	117(1)
C(11)–C(12)	1.426(19)	C(14)–C(13)–C(11)	120(1)
C(12)–C(6)	1.454(22)	C(13)–C(11)–C(12)	122(1)
C(6)–C(5)	1.342(22)	C(11)–C(12)–C(6)	116(1)
C(14)–C(5)	1.451(21)	C(6)–C(12)–C(7)	126(1)
C(12)–C(7)	1.378(21)	C(12)–C(6)–C(5)	122(1)
C(7)–C(8)	1.387(22)	C(14)–C(5)–C(6)	121(1)
C(8)–C(9)	1.415(21)	C(13)–C(14)–C(5)	118(1)
N(10)–C(9)	1.331(18)	C(11)–C(12)–C(7)	117(1)
N(10)–C(11)	1.381(17)	C(12)–C(7)–C(8)	121(1)
		C(7)–C(8)–C(9)	119(1)
		C(11)–N(10)–C(9)	117(1)
		N(10)–C(11)–C(13)	115(1)
		N(10)–C(11)–C(12)	123(1)
		N(10)–C(9)–C(8)	123(1)

TABLE VI. Deviations (A) from the Least-squares Planes through the Phenanthroline Ligands. The distances of Fe to these planes are also calculated.

Ligand 1			
N(1)	–.048	C(8)	0.063
N(10)	–.009	C(9)	0.052
C(2)	–.047	C(11)	–.034
C(3)	0.055	C(12)	–.043
C(4)	0.075	C(13)	–.047
C(5)	–.006	C(14)	0.033
C(6)	–.044	Fe	–.107
C(7)	0.00		
Ligand 2			
N(1)	–.017	C(8)	0.010
N(10)	0.003	C(9)	0.018
C(2)	–.012	C(11)	0.005
C(3)	–.006	C(12)	0.016

(continued overleaf)

TABLE VI. *(continued)*

C(4)	0.025	C(13)	0.004
C(5)	0.004	C(14)	–.004
C(6)	–.007	Fe	0.005
C(7)	–.039		
Ligand 3			
N(1)	–.041	C(8)	0.056
N(10)	–.014	C(9)	0.009
C(2)	–.019	C(11)	0.000
C(3)	0.036	C(12)	–.017
C(4)	0.060	C(13)	–.030
C(5)	–.007	C(14)	0.002
C(6)	–.046	Fe	–.116
C(7)	0.010		

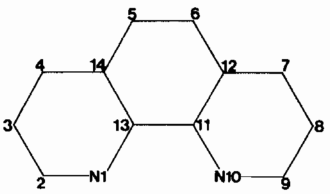

Figure 4. Designation of the atoms in the phenanthroline molecule.

N···N distance of the triangular faces. The metal ion is located only 0.01 Å from the centroid of the coordinating N atoms. The geometrical parameters of the coordination polyhedron are very close to those found in L-tris-(1,10-phenanthroline)iron(II) bis antimony(III) D-tartrate octahydrate [10] and in the iron(III) compound tris(1,10-phenanthroline)iron(III) perchlorate hydrate [11].

The Phenanthroline Ligands

The atoms of the three independent phenanthroline ligands are designated in Fig. 4. The agreement between corresponding interatomic distances and angles within the ligands as well as between them is good (Table V) and they also agree well with those observed in other compounds [10–12]. A comparison with non-coordinated phenanthroline molecules shows no significant geometrical differences [13–15]. The C–C and N–C distances are in the range 1.34–1.47 and 1.31–1.39 Å, respectively. Coulson [16] has suggested that bond lengths in conjugated molecules chiefly are dependent on (i) bond order, (ii) hybridization and (iii) formal charge distribution. The order of importance is often, though not always (i) > (ii) > (iii). The phenanthroline molecules are planar within 0.06 Å (Table VI) and the bond angles around the carbon atoms are close to 120° (Table V). All carbon atoms can therefore be described as sp^2 hybridized and factor (ii) should be of minor importance in accounting for the observed differences in the C–C bond lengths. The shortest bond, C(5)–C(6), is in the range 1.34–1.36 Å and it is also expected to have the largest bond order [17]. The bond C(11)–C(13), expected to have the smallest bond order [17], has distances in the range 1.38–1.39 Å. This small value might be caused by the fact that the heteroatom is adjacent to the bond. The N(1)–C(2) and N(10)–C(9) bond lengths are in the range 1.31–1.35 while N(1)–C(13) and N(10)–C(11) are 1.38–1.39 Å. This order is expected from bond order considerations.

TABLE VII. Possible Hydrogen Bonds (Å).

$O(1)\cdots I(1^{iii})$	3.597(15)	$O(2)\cdots I(2)$	3.587(13)
$O(1)\cdots I(1^{ii})$	3.700(14)	$O(2)\cdots I(2^{i})$	3.570(13)

The Hydrogen Bonds

The hydrogen atoms have not been located so that the hydrogen bond system must be deduced from geometrical considerations. The observed O–I distances are in the range 3.6–3.7 Å, which are characteristic hydrogen bond distances [18]. At $z \approx 0$ there most certainly are hydrogen bond chains ...I(2)...O(2)...I(2)...O(2)... and at $z \approx 0.5$ ...I(1)... O(1)...I(1)...O(1)... running along ***a***. Some geometrical features of the hydrogen bonds are given in Table VII and the hydrogen bond scheme is depicted in Figs. 2 and 3.

Discussion

The major pockets of the $Fe(phen)_3^{2+}$ complex are more or less occupied by other phenanthroline ligands. Since two of the intruding phenanthroline ligands are almost parallel with one of the phenanthroline ligands of the "host" complex it may be concluded that there are interactions between the π-electron systems in these ligands. Structures with π-electron interaction between planar aromatic moieties are quite common [19–22]. The fact that $Fe(phen)_3^{2+}$ in the present structure evidently prefers an interaction with phenanthroline rather than with I^-, strengthens the view expressed earlier [7] that outer-sphere complexes must not necessarily be bound by electrostatic forces. Thus there is a possibility for neutral or even positively charged species to act as ligands in outer-sphere complexes. The π-electron interaction moreover explains why an anion like salicylate is bound more strongly than *e.g.* acetate [7].

In the present structure, the lamellar "zipper" chains are formed despite the charges of the $Fe(phen)_3^{2+}$ ions. Thus, one might speculate about the charge distribution within the $Fe(phen)_3^{2+}$ ion. An

ESCA study [23] of the present compound revealed that the iron atom has a rather low, positive charge (+0.26 charge units), while the six nitrogens and the 36 carbons have average charges of, respectively, −0.15 and +0.06 units. However, differences between the three phenanthroline ligands are not excluded. Indeed, differences are indicated by a significant broadening of the N and C peaks, when compared to uncomplexed phenanthroline.

The water oxygen atom O(2) is deeply embedded into one of the minor pockets. The iodides I(2) and $I(2)^{i}$ are kept in place by hydrogen-bonding to O(2) rather than interaction with the $Fe(phen)_3^{2+}$ complex. The other water oxygen atom, O(1), is displaced from the ideal position of the other minor pocket. In fact it is located at equal distances from two Fe. It is evidently more advantageous for O(1) to be placed here, where it can tie together the two complexes, and also be engaged in the hydrogen bonding.

From geometrical considerations it seems reasonable to conclude that in the solid state there are indications of outer-sphere complexes, including not I^- but rather other phenanthroline complexes and water molecules. In this respect, the present structure differs from that of tris(1,10-phenanthroline)iron(III) perchlorate hydrate [11], where perchlorate anions are located in all pockets of the $Fe(phen)_3^{3+}$ complex, more or less in direct contact (van der Waals) with the phenanthroline ligands.

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