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The Crystal and Molecular Structure of *Cis*-dichlorobis(2,2′-biimidazole)-iron(III) Chloride Monohydrate

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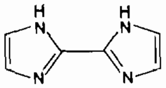
Possible cis–trans *isomerism in octahedral dihalobis(2,2′-biimidazole)metal complexes has been investigated by determination of the crystal structure of the title compound, which crystallises with* cis-*octahedral coordination stereochemistry: Fe–N = 2.112(2), 2.209(2), 2.152(2), 2.108(2); Fe–Cl = 2.290(1), 2.326(1). The two NH hydrogen atoms on each biimidazole ligand are hydrogen bonded to chloride and water in the crystal. Apparently related to this hydrogen-bonding is the fact that,* within *each imidazole ring, the C–N bond distances to the iron-coordinated nitrogen atom are not significantly different from the C–N distances to the hydrogen-bonded NH group. Crystal data:* a = *7.625(1),* b = *11.682(2),* c = *21.533(3) Å, β = 113.72(2)°;* $P2_1/c$; *Z = 4 × $FeC_{12}H_{14}N_8Cl_3O$; 2749 observed reflections, anisotropic refinement, R = 0.027.*

Introduction

We have previously described [1] complexes formed by 2,2′-biimidazole, biim, *1*.



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For octahedral complexes $[M(biim)_2Cl_2]$, M = Co, Ni, and $[Fe(biim)_2Cl_2]^+$ the question of *cis–trans* isomerism could not be resolved with the spectroscopic data available. The electronic spectrum of $[Ni(biim)_2Cl_2]$ favoured *cis* octahedral stereochemistry [1], but the structure of $[Ni(biim)_2(OH_2)_2]^{2+}$ in the crystal phase has been shown to be *trans* [2]. Steric conflict of hydrogen atoms in the 6 and 6′ positions of the comparable ligand 2,2′-bipyridine (bipy) prevents the formation of complexes containing two coplanar ligands, but the volume of biim is smaller than that of bipy, permitting the coordination of coplanar biim ligands [3].

Since both *cis* and *trans* stereochemistry are feasible for $[Fe(biim)_2Cl_2]^+$, and the spectroscopic data on $[Fe(biim)_2Cl_2]Cl$ previously reported are not conclusive, the crystal structure of $[Fe(biim)_2Cl_2]Cl\cdot OH_2$ (the only compound to yield suitable crystals) has been determined. The complex cation is closely related to that in $[Fe(phen)_2Cl_2][FeCl_4]$ which has been shown to have *cis*-octahedral stereochemistry [4].

Experimental

Crystallisation of Cis-dichlorobis(2,2′-biimidazole)-iron(III) Chloride Monohydrate

To 2,2′-biimidazole (1.0 g) suspended in methanol (100 ml) was added anhydrous ferric chloride (0.6 g) dissolved in methanol. The mixture was heated and stirred for 0.5 hr, then filtered, and the volume of the filtrate reduced to about 50 ml by boiling. Acetonitrile (50 ml) was added to the hot solution, which on cooling and evaporation during three days deposited the product as dark red-brown needles. Found: C, 32.55; H, 3.01; N, 24.92; Fe, 12.54%. Calcd. for $C_{12}H_{14}N_8OCl_3Fe$: C, 32.14; H, 3.15; N, 24.98; Fe, 12.45%. IR: 2500–3300 cm^{-1}, broad, hydrogen bonding; 315 cm^{-1}, Fe–Cl str. Magnetic moment: μ = 5.88 BM (303 K), θ = 8 K. Mössbauer: quadrupole splitting (ΔE_q) = 0.29 (±0.03) mm s^{-1}; isomer shift ($\delta_{i.s.}$) = 0.80 (±0.02) mm sec^{-1} (measured at 90 K).

Physical measurements were made as previously described [1].

Crystallography

X-ray crystallographic facilities and methods have been described [5]. Solution and refinement of the structure proceeded without difficulty: the details are set out in Table I. Neutral atom scattering factors, and real and imaginary corrections for anomalous scattering by iron and chloride, were from standard sources [6]. An isotropic extinction correction [7] was included and refined. Anisotropic temperature factors were refined for all non-hydrogen

TABLE I. Crystallographic Details for $[Fe(biim)_2Cl_2]Cl1OH_2$.

Crystal habit and form	monoclinic needles, {011}, {001}, {100}, {111}
Space-group	$P2_1/c$
a (A)	7.625(1)
b (A)	11.682(2)
c (A)	21.533(3)
β (°)	113.72(2)
V (A^3)	1756.0
Radiation	CuK_α, 1.5418 A
T (K)	293
d_{obsd} ($g\ cm^{-3}$)	1.66(2)
d_{calcd} ($g\ cm^{-3}$)	1.70
Cell contents	4 × ($FeC_{12}H_{14}N_8OCl_3$)
μ (cm^{-1})	114.2
Min, max transmission factor	0.038, 0.384
No. of intensity measurements	3425
No. of independent observed reflections (m)	2749
No. of parameters refined (n)	283
$R = \frac{\sum^m \lvert\Delta F\rvert}{\sum^m \lvert F_o\rvert}$	0.027
$Rw = \left[\frac{\sum^m \lvert\Delta F\rvert^2}{\sum^m w\lvert F_o\rvert^2}\right]^{1/2}$	0.034
$[\Sigma w\lvert\Delta F\rvert^2/(m-n)]^{1/2}$	1.24
Larson's extinction parameter, g	99(18) × 10^{-6}

TABLE II. Atomic Coordinates for $[Fe(biim)_2Cl_2]^+Cl^-\cdot OH_2$. Estimated standard deviations (in parentheses) refer to the least significant digit(s) quoted.

Atom	x	y	z
Fe	0.51139(5)	0.94151(3)	0.82280(2)
Cl1	0.77535(9)	0.85381(5)	0.90196(3)
Cl2	0.3239(1)	0.77692(6)	0.79441(3)
Cl3	−0.24535(9)	0.97336(6)	0.50405(3)
O	−0.4471(3)	1.2148(2)	0.5468(1)
N11	0.3680(3)	0.9935(2)	0.8840(1)
N12	0.6479(3)	1.1066(2)	0.8656(1)
C11	0.4377(3)	1.0864(2)	0.9216(1)
C12	0.5925(3)	1.1449(2)	0.9132(1)
N13	0.3428(3)	1.1084(2)	0.9606(1)
C13	0.2201(4)	0.9562(2)	0.9001(1)
C14	0.2044(4)	1.0262(2)	0.9474(1)
N14	0.7016(3)	1.2334(2)	0.9468(1)
C15	0.7966(4)	1.1749(2)	0.8693(1)
C16	0.8315(4)	1.2540(2)	0.9194(1)
N21	0.2994(3)	1.0338(2)	0.7401(1)
N22	0.6149(3)	0.9309(2)	0.7458(1)
C21	0.3243(3)	1.0260(2)	0.6827(1)
C22	0.4976(3)	0.9723(2)	0.6861(1)
N23	0.1725(3)	1.0676(2)	0.6305(1)
C23	0.1234(4)	1.0839(2)	0.7232(1)
C24	0.0442(4)	1.1052(2)	0.6556(1)
N24	0.5642(3)	0.9516(2)	0.6384(1)
C25	0.7648(4)	0.8813(2)	0.7350(1)
C26	0.7338(4)	0.8934(3)	0.6689(1)
H1	−0.4314(50)	1.2311(30)	0.5881(19)
H2	−0.5318(54)	1.1559(35)	0.5337(19)
HN13	0.3687(42)	1.1664(27)	0.9870(15)
HN14	0.6880(43)	1.2670(27)	0.9762(16)
HN23	0.1606(56)	1.0727(34)	0.5940(20)
HN24	0.5079(43)	0.9626(26)	0.5985(16)
HC13	0.1477(38)	0.8896(24)	0.8807(13)
HC14	0.1197(43)	1.0303(26)	0.9684(15)
HC15	0.8512(41)	1.1675(28)	0.8404(14)
HC16	0.9191(44)	1.3078(28)	0.9345(15)
HC23	0.0802(42)	1.1021(26)	0.7557(15)
HC24	−0.0701(43)	1.1347(26)	0.6289(15)
HC25	0.8610(38)	0.8444(23)	0.7701(14)
HC26	0.8123(47)	0.8668(29)	0.6465(16)

TABLE III. Root-mean-square Vibrational Amplitudes (A) for $[Fe(biim)_2Cl_2]^+Cl^-(OH_2)$.

Atom	Minimum		Maximum
Fe	0.149		0.199
Cl1	0.181		0.225
Cl2	0.173		0.276
Ligand 1	0.169[a]		0.212[a]
Ligand	0.170[a]		0.216[a]
Cl3	0.175		0.253
O	0.196		0.273
H1		0.281[b]	
H2		0.303[b]	
Ligand Hydrogens		0.239[b,c]	

[a] Averaged over all non-hydrogen atoms of the ligand. [b] Isotropic vibration. [c] Averaged over all hydrogen atoms of both ligands.

atoms, while isotropic temperature factors as well as positions were refined for all hydrogen atoms. The final least squares cycle involved two blocks, one for all atomic coordinates and the other for all other parameters: all position parameter correlation has therefore been included in the estimated standard deviations of atomic coordinates.

Atomic coordinates and their calculated e.s.d's are listed in Table II, while Table III provides a summary of vibrational amplitudes. No anomalous anisotropics of vibration were found. A complete listing of refined

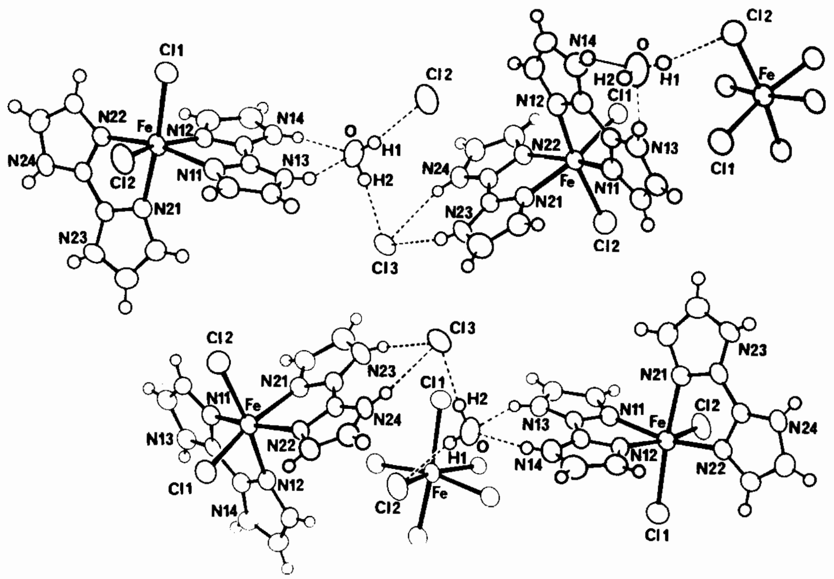


Fig. 1. A non-axial projection of part of crystalline *cis*-$[Fe(biim)_2Cl_2]Cl{\cdot}OH_2$, showing the hydrogen bonds which link the *cis*-$[Fe(biim)_2Cl_2]^+$ complexes, chloride ions (Cl3) and water molecules (O, H1, H2). The thermal ellipsoid outlines are drawn to enclose 50% probability.

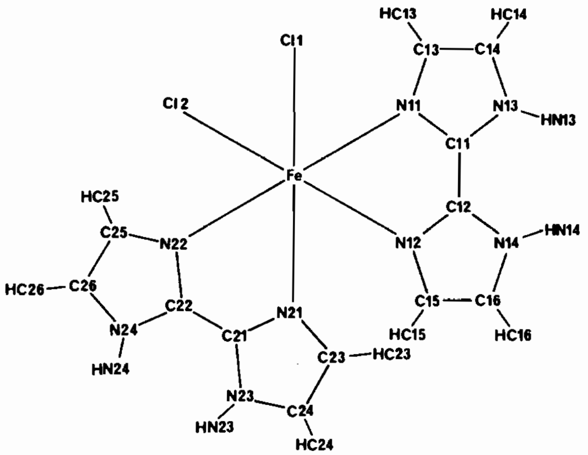


Fig. 2. The atom labelling scheme.

TABLE IV. Selected Distances (Å) and Angles (degrees) in $[Fe(biim)_2Cl_2]^+Cl^-(OH_2)$. Estimated standard deviations (in parentheses) refer to the least significant digit(s) quoted.

A. Coordination sphere

Bond		Angle	
Fe–N11	2.112(2)	N11–Fe–N12	76.37(7)
Fe–N12	2.209(2)	N21–Fe–N22	76.91(8)
Fe–N21	2.152(2)	Cl1–Fe–Cl2	95.11(3)
Fe–N22	2.108(2)	N11–Fe–N22	163.69(8)
Fe–Cl1	2.290(1)	Cl1–Fe–N21	169.34(6)
Fe–Cl2	2.326(1)	Cl2–Fe–N12	165.45(5)
		N11–Fe–N21	88.09(7)
		N12–Fe–N22	96.69(7)
		Cl1–Fe–N11	100.66(5)
		Cl1–Fe–N12	87.40(5)
		Cl2–Fe–N21	91.09(6)
		Cl2–Fe–N22	97.44(6)
		Cl1–Fe–N22	93.66(6)
		Cl2–Fe–N11	89.09(6)
		N12–Fe–N21	88.77(7)
		Fe–N11–C11	115.7(2)
		Fe–N12–C12	111.8(2)
		Fe–N21–C21	113.2(2)
		Fe–N22–C22	114.9(2)
		Fe–N11–C13	138.4(2)
		Fe–N12–C15	141.1(2)
		Fe–N21–C23	139.7(2)
		Fe–N22–C25	139.0(2)

B. Water molecule

O–H1	0.87(4)	H1–O–H2	106(3)
O–H2	0.91(4)		

(continued overleaf)

parameters and their e.s.d's, together with a complete listing of final calculated and observed structure factors, have been deposited with the Editor.

Results and Discussion

Needles of the monohydrate $[Fe(biim)_2Cl_2]Cl{\cdot}OH_2$ crystallised directly from a reaction mixture in methanol–acetonitrile. The magnetic moment and Mössbauer effect parameters are virtually the same as those of the anhydrous compound [1].

The crystals contain *cis*-$[Fe(biim)_2Cl_2]^+$ complexes, hydrogen-bonded with the water molecule

TABLE IV. *(continued)*

C. Hydrogen bonds

H1–Cl2[a]	2.39(4)	O–H1–Cl2[a]	169(3)
H2–Cl3[b]	2.17(4)	O–H2–Cl3[b]	174(3)
HN13–O[c]	2.03(3)	N13–HN13–O[c]	152(3)
HN14–O[c]	2.16(3)	N14–HN14–O[c]	150(3)
HN23–Cl3[d]	2.50(4)	N23–HN23–Cl3[d]	154(4)
HN24–Cl3[d]	2.43(3)	N24–HN24–Cl3[d]	156(3)

[a] −x, 0.5 + y, 1.5 − z. [b] −1 − x, 2 − y, 1 − z. [c] 1 + x, 2.5 − y, 0.5 + z. [d] −x, 2 − y, 1 − z.

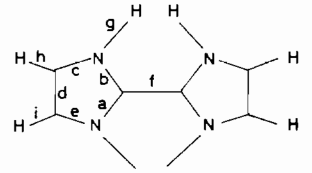
(O, H1, H2) and the chloride ion (Cl3) as shown in Fig. 1. The atom labelling scheme for the complex is given in Fig. 2: the two imidazole rings, m = 1, 2, of each biim ligand, n = 1, 2, are identified by the symbols of the coordinated nitrogen atoms Nnm. Table IV contains selected bond distances and angles.

All biimidazole H–N groups are hydrogen bonded, to the water molecule from biim ligand 1, and to the chloride ion from biim ligand 2. The hydrogen bonding at the water molecule links the chloride ion and two different $[Fe(biim)_2Cl_2]^+$ complexes, one *via* biim and the other at Cl2. It can be seen from Fig. 1 that the chloride ion Cl3 is hydrogen bonded on one side only: the other side is surrounded by H–(C) atoms but at distances too large to be regarded as even weak hydrogen bonds. Thus non-bonding boundary surfaces, apparent between the two sections of Fig. 1, exist in the crystal.

Distances and angles within the coordination sphere are normal. The Fe–N distances, which are significantly unequal, are slightly shorter than those in *cis*-$[Fe(phen)_2Cl_2]^+$ [3], while the Fe–Cl bonds (particularly that involving hydrogen bonded Cl2) are slightly longer.

The non-hydrogen atoms of each imidazole ring are coplanar to within 0.003 Å. However within each biimidazole ligand the two rings are not coplanar,

TABLE V. Statistical Comparison of Imidazole Ring Dimensions[i] in Complexes of 2,2′-Biimidazole and of the 2,2′-Biimidazolate Dianion.

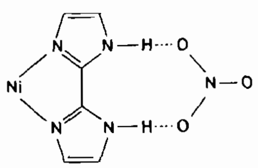


Dimension	$[Fe(biim)_2Cl_2]^+$	$[Ni(biim)_2(OH_2)_2]^{2+}$	$(COD)_2Rh_2(biim\text{-}2H)$	$(CO)_8Rh_4(biim\text{-}2H)_2$
a	1.330[3,1][ii,iii]	1.326[6,5]	1.329[6,3]	1.348[5,4]
b	1.338[2,1]	1.347[4,3]	≡a[iv]	1.335[2,2]
c	1.368[4,2]	1.368[1,1]	1.384[6,3]	1.386[9,6]
d	1.355[6,3]	1.361[1,1]	1.359[5,4]	1.362[14,10]
e	1.373[9,4]	1.377[2,2]	≡c[iv]	1.381[4,3]
f	1.438[1,1]	1.441	1.413[11,8]	1.449
g	0.92[3,1]			
h	0.92[4,2]			
i	0.80[5,2]			
a–b	110.9[2,1]	111.3[4,3]	116.5[7,5]	112.7[9,7]
b–c	107.5[2,1]	107.4[7,5]	102.8[4,2]	105.4[6,5]
a–e	105.78[5,3]	105.5[1,1]	≡b–c[iv]	105.3[11,8]
c–d	106.5[2,1]	106.3[5,4]	109.0[3,2]	108.4[6,4]
d–e	109.3[3,1]	109.7[2,2]	≡c–d[iv]	108.3[4,3]
a–f	117.4[4,2]	118.7[1,1]	121.8[5,2]	115.8[7,5]
b–f	131.7[2,1]	130.1[4,3]	≡a–f[iv]	131.5[1,1]

[i] In each structure the 2,2′-biimidazole ligand possesses virtual twofold symmetry; consequently twofold rotation symmetry, about an axis containing the coordinated metal and bisecting f, has been imposed on the analysis. [ii] Values in square brackets are, respectively, the estimated standard deviations of the sample of values and the sample mean, and refer to the least significant digit quoted. [iii] Individual estimated standard deviations in C–C, C–N distances average to 0.003, 0.005, 0.008 and 0.008 Å respectively for the four structures. [iv] Chemically equivalent dimensions have been combined in the sample for the first listed dimension.

due to twist around the Cn1–Cn2 (n = 1, 2) bonds: the angles between the normals to the imidazole ring planes are 5.2° (n = 1) and 4.6° (n = 2). Consequently individual ligand atoms are displaced by up to 0.06 Å from the least-squares planes of the biimidazole ligands. The iron atom is displaced from the imidazole ring planes, by 0.10, 0.39, 0.36 and 0.22 Å from rings 1 and 2 (n = 1) and 1 and 2 (n = 2) respectively.

The biim ligand dimensions, with higher precision than previously available, have been compared with those of hydrogen-bonded biim, *2*, in $[Ni(biim)_2(OH_2)_2]^{2+}(NO_3)_2$ [2], and those of the doubly deprotonated ligand (biim – 2H) coordinated to two rhodium atoms, *3*, in $(COD)_2Rh_2$(biim – 2H) [8], and to three rhodium atoms, *4*, in $(CO)_8Rh_4$(biim – $2H)_2$ [9]. The virtual geometrical equivalence of the two imidazole rings of the ligand in each case has been incorporated in the statistical analysis reported in Table V. It should be noted that the bond lengths *within* the imidazole rings of biim, particularly in $[Fe(biim)_2Cl_2]^+$, show effective symmetry $a = b$, $c = e$. This leads to the interpretation that the effects of metal coordination, *5*, and hydrogen-bonded protonation, *6*, at imidazole nitrogen atoms have equivalent effects on the ring electronic structure, which is therefore not well represented by the formalism *7*.



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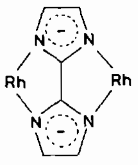

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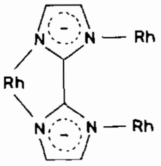

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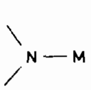

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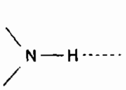

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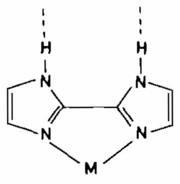

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The C–N bond lengths in 2,2′-biimidazole engaged in two hydrogen bonds and one bidentate metal coordination are not significantly different from those of the 2,2′-biimidazolate dianion engaged in double bidentate metal coordination. The largest difference is in bond *c*. In fact, apart from angular variations enforced by the three different modes of coordination, there is little significant change in ligand dimensions for the various modes of coordination.

Acknowledgement

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