

Figure 2. Comparison of bond lengths in sites 1 ($W^VI O_6$) and 2 ($W^{IV} O_6$). O_D designates the unshared outermost oxygen, O_A is one of the central oxygen atoms, O_B are bridging octahedra belonging to different W_3O_{13} groups, and O_C are bridging the octahedra of a same W_3O_{13} group. The arrow shows the direction of the W_1 - W_2 displacement.

placement toward the center of a W_3O_{13} group (see Figure 2). This is also reflected in the W_2O_C distances which have decreased to 1.80 Å, while the W_2O_B distances have increased to 2.04 Å. Thus there seems to be a tendency for the tungsten atoms to move toward the other tungsten atoms of a same

W_3O_{13} group, and we think that the driving force for this process is the building up of a $W^{IV}_3O_{13}$ cluster-like group, which necessitates that the three tungsten atoms occupying sites 2 are those belonging to the same W_3O_{13} group. If this is assumed, the W-W distances are found to be 3.31 Å in the three normal groups (which is in the usual range for this type of structure) and 2.50 Å in the type 2 group. This value is strikingly similar to the one (2.51 Å) observed by Mattes¹⁰ in the $W^{IV}_3O_4F_9^{5-}$ ion exhibiting the same general structure with three edge sharing octahedra.

Of course the present study does not definitively prove the existence of $W^{IV}_3O_{13}$ clusters in reduced polyanion and it will be necessary for that to find a compound in which the crystallographic disorder is absent. However it gives a strong additional support to this assumption. A further argument comes from the existence of a brown 6-electron-reduced form of $Nb_2W_4O_{19}^{4-}$.¹¹ This ion is a cis isomer,¹² and its only structural analogy with the metatungstate ion is the possibility of finding three WO_6 octahedra disposed exactly like in a W_3O_{13} group. Finally let us recall that we have shown elsewhere¹ how the cluster hypothesis can account for the final reduction stage of metatungstate, with 32 electrons per mole, that is 8 electrons per W_3O_{13} group. The electronic structure of this kind of cluster with 6 or 8 electrons can be accounted for by Cotton's molecular orbital scheme.^{13,14a,15}

Registry No. $Rb_4H_8[H_2W_{12}O_{40}] \cdot 18H_2O$, 74231-08-6; $Na_6H_2W_{12}O_{40}$, 12141-67-2.

Supplementary Material Available: A listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Trichlorobis(4-cyanopyridine- N^1)iron(III): A Rare Example of a MX_3L_2 Trigonal-Bipyramidal Complex of Iron(III)

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The crystal and molecular structure of the high-spin five-coordinate $FeCl_3(4-cpy)_2$ complex has been determined from three-dimensional X-ray diffraction data. The complex crystallizes in the monoclinic system of space group $P2_1/c$, with the cell dimensions $a = 11.84$ (1) Å, $b = 10.067$ (5) Å, $c = 12.92$ (1) Å, $\beta = 96.6$ (1)°, $Z = 4$ for $d_{\text{calcd}} = 1.60$ g cm⁻³, and $d_m = 1.60$ g cm⁻³. The structure described by 181 variable parameters was refined by full-matrix least-squares methods to conventional and weighted R values of 0.05 and 0.053, respectively, based on 2381 data with $F > 3\sigma(F)$. The coordination polyhedron around iron(III) is a trigonal bipyramid. The three vertices of the equatorial plane are occupied by Cl atoms while the pyridine ring nitrogens complete the environment. The Fe-Cl bond distances are 2.204 (1), 2.216 (1), and 2.229 (1) Å and the axial Fe-N bond distances are 2.232 (3) and 2.213 (3) Å, respectively. The electronic and infrared spectra are also discussed.

Introduction

The coordination chemistry of iron(III) with nitrogen-containing ligands has received a great deal of attention because of the biological implications of iron. As a part of our interest in this chemistry, we have studied the products of the reaction of iron(III) chloride on cyanopyridine (cpy) in non-

aqueous solvents.¹ The 2-, 3-, and 4-cyanopyridines have two potential donor sites, (i) the pyridine ring nitrogen and (ii) the nitrile nitrogen; a competition between those nitrogen

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atoms may occur. Previous studies based upon IR spectra showed that the 2-, 3-, and 4-cyanopyridines are coordinated with the metal ions via the pyridine ring nitrogen only.²⁻⁸

Some other 2-, 3-, and 4-cyanopyridine complexes have been reported to be coordinated by the nitrile nitrogen.⁶⁻⁹ Structural studies on compounds with these ligands are very scanty.¹⁰⁻¹³ The cyanopyridine iron complexes are of additional interest due to the possibility of behaving as ligands with respect to other metal centers.

This work is concerned with a compound of empirical formula $\text{FeCl}_3(4\text{-cpy})_2$. From an X-ray diffraction study, the compound is shown to have a structure very closely related to a trigonal bipyramid. Such a geometry is known for the series MX_3L_2 with $\text{M} = \text{Ti}, \text{V}, \text{or Cr}$, $\text{X} = \text{Cl or Br}$, and $\text{L} = \text{NMe}_3$.¹⁴⁻¹⁶ On the basis of spectroscopic studies, a similar geometry was postulated for the FeCl_3 -diox (diox = dioxane) complex.^{17,18} However, to the best of our knowledge, there is just one structural example of such a geometry for iron(III), the anion $[\text{Fe}(\text{N}_3)_5]^{2-}$.¹⁹ We also herein report electronic and IR spectra and magnetic measurements.

Experimental Section

Preparation of $\text{FeCl}_3(4\text{-cpy})_2$. Ca. 0.002 mol of anhydrous iron(III) chloride was added to ca. 0.007 mol of 4-cyanopyridine in 10 mL of trichloromethane. A deep brown-red color developed. After a few days, a green complex crystallized from this solution. Anal. Calcd for $\text{FeCl}_3(\text{C}_6\text{H}_4\text{N}_2)_2$ (mol wt 370.5): C, 38.91; H, 2.18; N, 15.12; Cl, 28.71. Found: C, 38.86; H, 2.20; N, 15.11; Cl, 28.86.

Magnetic Measurements. The magnetic susceptibility was determined as a function of temperature with a Faraday-type magnetometer, equipped with a continuous-flow cryostat designed by Oxford Instruments. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. The correction for diamagnetism is estimated at $-219 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ from the atomic values of Pascal.²⁰ The magnetic moments at 296, 190, 90, and 9 K were 5.56, 5.51, 5.48, and 4.77 μ_B , respectively.

Spectra. Electronic spectra in different solvents were determined at room temperature with a Beckman UV 5240 spectrophotometer. Electronic spectrum on the solid was recorded with a Beckman DK 2A spectrophotometer after mulling the complex.

Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer. Free ligand and complex were sampled as KBr pellets.

Collection and Reduction of the Intensity Data

Symmetry and systematic absences consistent with the monoclinic space group $P2_1/c$ were determined on precession photographs. Upon exposure to air, the crystals rapidly lost their ability to diffract, presumably through decomposition. The crystal selected for intensity measurements was then mounted in a Lindeman glass capillary and set up about [001] on a laboratory-made, automatic three-circle diffractometer. Accurate cell parameters were obtained by a least-

Table I. Crystal Data and Data Collection Procedures for $\text{FeCl}_3(\text{C}_6\text{H}_4\text{N}_2)_2$

formula	$\text{C}_{12}\text{Cl}_3\text{H}_8\text{FeN}_4$
fw	370.44
space group	$P2_1/c$
a , Å	11.84 (1)
b , Å	10.067 (5)
c , Å	12.92 (1)
β , deg	96.6 (1)
V , Å ³	1529.8
d_m , g cm ⁻³	1.60
d_{calcd} , g cm ⁻³	1.60
recording temp °C	20
cryst shape, mm	6-sided lump, 1.8 × 0.64 × 0.4
radiatn	Mo $K\alpha$ ($\lambda = 0.71069$), graphite monochromator set in front of the detector
linear abs coeff, cm ⁻¹	15.2
extreme transmissn factors	0.456-0.592
detector aperture, mm	$\phi = 3, 230$ from crystal
takeoff angle, deg	3.0
scan type	θ - 2θ
limit Bragg angle, deg	$1.5 < \theta < 25$
bkgd counts, s	4.5 at each end of scan
scan speed, deg in θ /min	5.0
scan range, deg	0.7 below $K\alpha_1$, 0.7 above $K\alpha_2$
data collected	$+h, +k, \pm l$
unique data no.	2694
unique data with $F > 3\sigma(F)$	2381

squares analysis of nine carefully centered reflections chosen from various regions of reciprocal space ($0.2685 < (\sin \theta)/\lambda < 0.4813 \text{ \AA}^{-1}$ with Mo $K\alpha$ radiation). Experimental density d_m was measured by using the floating technique with a tetrachloromethane-dibromoethane mixture. The diffractometer was fitted with a scintillation counter and pulse-height analyzer tuned to accept 90% of the Mo $K\alpha$ peak. Main features of the data collection are summarized in Table I. The intensities of two standard reflections $04\bar{5}$ and $40\bar{4}$ were measured every 100 reflections; no significant fluctuations were observed. If the intensity of the diffracted beam exceeded 10000 counts s⁻¹, corrections for counting loss were made. Lorentz and polarization corrections were applied together with absorption. Each structure factor F was assigned a standard deviation $\sigma = F(\Delta I/2I)$, where I was the integrated intensity and ΔI was the error on it.

Solution and Refinement of the Structure

Computations were performed by using standard programs;²¹ all calculations were carried out on the University's Computing Center CII IRIS 80. For structure factor calculations, the scattering factors were taken from ref 22, including $\Delta f'$ and $\Delta f''$ for iron and chlorine atoms. The agreement factors were defined in the usual way as $R = \sum(|F_o - F_c|)/\sum|F_o|$ and $R_w = \{\sum(w|F_o - F_c|)^2/\sum(w|F_o|)^2\}^{1/2}$. In all least-squares refinement, the quantity minimized was $\sum(w|F_o - F_c|)^2$. A weighting scheme based on counting statistics, $w = 2F/\Delta I$, was used.

The position of iron was unambiguously revealed by a Patterson synthesis. Subsequent Fe-phased Fourier synthesis showed a hexagonal-bipyramidal coordination around iron atom. The six equivalent largest peaks were at the six vertices of the equatorial plane and at a distance 2.18-2.22 Å from Fe. They were related two by two through a pseudo mirror plane containing iron and the two axial peaks. The analytical results make it extremely unlikely that iron is surrounded by six Cl atoms. Either the molecule was disordered or the heavy-atom phasing added a pseudosymmetry. Three trial structures were then set up: the first one with a disordered model and the second and the third with each of the two possible configurations of three peaks, in an attempt to break the false symmetry. The disordered model reached convergence at 0.46 and the two ordered models convergence at 0.523 and 0.42, respectively. An F_o map based on the phases for the best set of structure factors showed up no more anomaly but the positions

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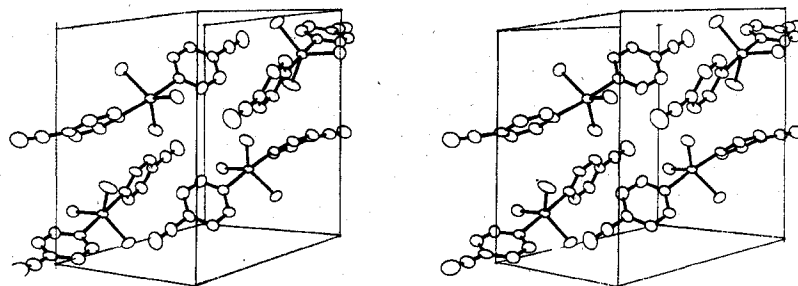


Figure 1. Stereoscopic view showing the molecular packing of $\text{FeCl}_3(4\text{-cpy})_2$ within the unit cell. The thermal ellipsoids are drawn at the 50% probability level.

Table II. Atomic Coordinates ($\times 10^4$) with Esd's in Parentheses

atom	x	y	z
Fe	2278 (0)	4323 (0)	3177 (0)
Cl(1)	2032 (1)	6493 (1)	3137 (1)
Cl(2)	3274 (1)	3526 (1)	4598 (1)
Cl(3)	1575 (1)	3004 (1)	1875 (1)
N(1)	3886 (3)	4568 (3)	2447 (3)
C(1)	4080 (3)	3964 (4)	1556 (3)
C(2)	5108 (4)	4061 (4)	1148 (3)
C(3)	5952 (3)	4841 (4)	1658 (3)
C(4)	5746 (3)	5514 (5)	2556 (3)
C(5)	4711 (3)	5322 (4)	2925 (3)
C(31)	7039 (4)	4962 (4)	1247 (4)
N(31)	7901 (4)	5026 (5)	928 (4)
N(2)	646 (3)	3961 (3)	3810 (2)
C(6)	-226 (3)	4789 (4)	3608 (3)
C(7)	-1324 (3)	4451 (5)	3782 (3)
C(8)	-1523 (3)	3207 (4)	4174 (3)
C(9)	-613 (4)	2369 (4)	4432 (3)
C(10)	451 (4)	2776 (4)	4236 (3)
C(82)	-2685 (4)	2797 (5)	4267 (3)
N(82)	-3598 (4)	2477 (6)	4284 (4)

of all nonhydrogen atoms. Refinement of coordinates, with isotropic temperature factors, gave $R = 0.143$ and $R_w = 0.138$. The introduction of anisotropic thermal parameters dropped R to 0.06 and R_w to 0.063. At this stage the observed structure factors were corrected for absorption. Two further cycles of refinement proved this correction to be significant with $R = 0.057$ and $R_w = 0.059$. H atoms attached to pyridine rings were found on a difference Fourier map and were included as a fixed contribution to F_c at their calculated idealized positions ($\text{C-H} = 1.0 \text{ \AA}$, N-C-H or $\text{C-C-H} = 120^\circ$). They were assigned a thermal parameter 1.0 higher than that of the carbon atom to which they were attached. The final refinement of 181 variables using 2381 observations resulted in $R = 0.050$ and $R_w = 0.053$.

Table III. Anisotropic Thermal Parameters^a

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	3.00 (2)	2.92 (2)	1.89 (2)	0.04 (1)	0.62 (1)	-0.10 (1)
Cl(1)	5.04 (5)	3.07 (4)	4.18 (4)	0.25 (3)	1.64 (3)	0.39 (3)
Cl(2)	3.95 (4)	5.80 (5)	3.40 (4)	0.26 (4)	0.26 (3)	1.74 (4)
Cl(3)	4.65 (5)	7.19 (7)	4.13 (4)	-2.28 (5)	1.75 (4)	-2.85 (5)
N(1)	3.65 (12)	3.49 (13)	2.75 (11)	-0.19 (10)	0.85 (10)	-0.37 (10)
C(1)	4.09 (16)	4.11 (17)	2.75 (14)	-0.56 (13)	1.13 (12)	-0.64 (12)
C(2)	4.65 (18)	4.17 (17)	2.88 (14)	-0.52 (14)	1.48 (13)	-0.48 (13)
C(3)	3.42 (15)	3.56 (15)	3.60 (15)	0.11 (12)	1.14 (12)	0.40 (12)
C(4)	3.62 (16)	4.51 (18)	4.17 (17)	-0.42 (14)	0.46 (13)	-0.88 (15)
C(5)	3.49 (16)	4.65 (19)	3.64 (16)	-0.44 (13)	0.63 (13)	-1.28 (14)
C(31)	4.08 (19)	3.76 (17)	4.97 (20)	-0.47 (14)	1.43 (17)	0.25 (15)
N(31)	5.17 (20)	5.38 (20)	7.82 (27)	-0.99 (16)	-3.03 (19)	-0.55 (19)
N(2)	3.46 (12)	3.46 (12)	2.50 (10)	0.29 (10)	0.83 (9)	0.15 (9)
C(6)	3.65 (16)	3.81 (16)	3.84 (16)	0.64 (13)	0.71 (13)	0.48 (0)
C(7)	3.53 (16)	4.83 (20)	3.94 (16)	0.62 (14)	0.80 (13)	0.30 (15)
C(8)	3.81 (16)	4.70 (18)	2.31 (13)	-0.31 (13)	0.94 (11)	-0.35 (12)
C(9)	4.24 (17)	4.36 (18)	3.90 (17)	0.10 (15)	1.38 (14)	0.89 (14)
C(10)	3.94 (16)	3.88 (17)	4.02 (17)	0.49 (13)	1.14 (13)	0.98 (14)
C(82)	4.02 (20)	6.11 (24)	3.65 (16)	-0.18 (17)	1.12 (14)	0.66 (17)
N(82)	4.17 (19)	8.94 (32)	6.32 (24)	-1.13 (19)	1.49 (16)	1.29 (22)

^a These parameters are in \AA^2 . The temperature factor is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}k lb^{*}c^{*})]$.

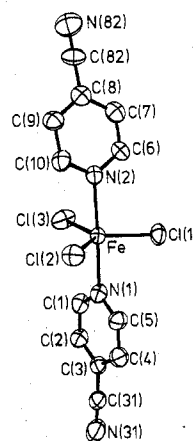


Figure 2. Perspective view of the molecular structure with the atom numbering scheme.

Considering the satisfactory adjustment between F_o and F_c at low diffraction angles, it was not necessary to introduce secondary extinction parameter.

Final atomic coordinates for all nonhydrogen atoms and anisotropic thermal parameters are reported in Tables II and III. Bond distances and angles, with esd's calculated from the full variance-covariance matrix, and the equations of important molecular planes are given in Tables IV and V. A list of observed and calculated structure factors is available as supplementary material.

Description and Discussion of the Structure

The crystal consists of discrete molecular units $\text{FeCl}_3(4\text{-cpy})_2$ separated by normal van der Waals contacts. Figure 1 shows a stereoscopic view of the molecular packing within the unit

Table IV. Interatomic Distances (Å) and Bond Angles (Deg)

Fe-Cl(1)	2.204 (1)	N(1)-C(1)	1.344 (5)	N(2)-C(6)	1.330 (5)
Fe-Cl(2)	2.216 (1)	C(1)-C(2)	1.384 (6)	C(6)-C(7)	1.386 (6)
Fe-Cl(3)	2.229 (1)	C(2)-C(3)	1.378 (6)	C(7)-C(8)	1.381 (6)
Fe-N(1)	2.232 (3)	C(3)-C(4)	1.389 (6)	C(8)-C(9)	1.379 (6)
Fe-N(2)	2.213 (3)	C(4)-C(5)	1.377 (6)	C(9)-C(10)	1.376 (6)
		C(5)-N(1)	1.333 (5)	C(10)-N(2)	1.344 (5)
		C(3)-C(31)	1.452 (6)	C(8)-C(82)	1.454 (6)
		C(31)-N(31)	1.146 (5)	C(82)-N(82)	1.130 (7)
Cl(1)-Fe-Cl(2)	115.77 (6)	C(1)-N(1)-C(5)	117.7 (3)	C(10)-N(2)-C(6)	118.1 (3)
Cl(1)-Fe-Cl(3)	122.39 (5)	N(1)-C(1)-C(2)	122.6 (4)	N(2)-C(6)-C(7)	122.3 (4)
Cl(2)-Fe-Cl(3)	121.84 (6)	C(1)-C(2)-C(3)	118.6 (3)	C(6)-C(7)-C(8)	119.0 (4)
N(1)-Fe-Cl(1)	89.84 (9)	C(2)-C(3)-C(4)	119.3 (4)	C(7)-C(8)-C(9)	118.8 (4)
N(1)-Fe-Cl(2)	89.54 (9)	C(3)-C(4)-C(5)	117.9 (4)	C(8)-C(9)-C(10)	118.6 (4)
N(1)-Fe-Cl(3)	90.58 (9)	C(4)-C(5)-N(1)	123.6 (4)	C(9)-C(10)-N(2)	122.9 (4)
N(2)-Fe-Cl(1)	93.05 (9)	C(4)-C(3)-C(31)	120.8 (4)	C(9)-C(8)-C(82)	121.7 (4)
N(2)-Fe-Cl(2)	92.20 (8)	C(2)-C(3)-C(31)	119.8 (4)	C(7)-C(8)-C(82)	119.4 (4)
N(2)-Fe-Cl(3)	85.07 (8)	C(3)-C(31)-N(31)	178.4 (7)	C(8)-C(82)-N(82)	176.5 (5)
N(1)-Fe-N(2)	175.59 (15)	Fe-N(1)-C(3)	176.5 (1)	Fe-N(2)-C(8)	166.9 (1)

Table V. Least-Squares Plane Calculations^a

	Equations of Planes			
I	10.618x + 1.080y - 6.831z = 0.7158			
II	3.523x - 7.957y + 6.435z = -0.698			
III	0.658x + 3.885y + 11.738z = 6.066			
IV	3.850x - 8.026y + 6.048z = -0.669			
Deviations from the Planes (Å)				
atom	plane I	plane II	plane III	plane IV
Fe	0.000 (0)	0.106 (4) ^b	-0.508 (4) ^b	-0.001 (0)
Cl(1)	0.000 (1)	-1.733 (4) ^b	0.272 (4) ^b	-1.862 (3) ^b
Cl(2)	0.000 (1)	2.006 (4) ^b	0.916 (4) ^b	1.881 (2) ^b
Cl(3)	0.000 (1)	0.069 (4) ^b	-2.595 (4) ^b	-0.002 (1)
N(1)	2.232 (1) ^b	0.007 (3)	-0.022 (3)	-0.022 (3)
C(1)		-0.017 (4)	-0.000 (0) ^b	-0.000 (0) ^b
C(2)		0.005 (4)	0.071 (2) ^b	0.071 (2) ^b
C(3)		0.010 (4)	0.078 (4)	0.078 (4)
C(4)		-0.020 (4)	0.002 (3) ^b	0.002 (3) ^b
C(5)		0.006 (4)	-0.020 (1) ^b	-0.020 (1) ^b
C(31)		0.033 (4) ^b	0.151 (3) ^b	0.151 (3) ^b
N(31)		0.080 (3) ^b	0.238 (2) ^b	0.238 (2) ^b
N(2)	-2.205 (1) ^b		-0.013 (3)	0.043 (3)
C(6)			0.014 (4)	-1.080 (4) ^b
C(7)			0.015 (4)	-1.125 (3) ^b
C(8)			-0.021 (4)	0.033 (4)
C(9)			0.016 (4)	1.212 (2) ^b
C(10)			0.014 (4)	1.177 (2) ^b
C(82)			-0.148 (4) ^b	-0.029 (3) ^b
N(82)			-0.312 (4) ^b	-0.113 (3) ^b
Dihedral Angles (Deg) between Planes				
plane A	plane B	angle		
I	II	92.4 (1)		
I	III	106.9 (1)		
II	III	77.7 (2)		

^a In the equations, x, y, and z represent fractional coordinates with respect to the crystallographic axes. The table gives the displacement (Å) of the specified atom from the plane. ^b Not included in least-squares plane calculation.

cell. The molecular geometry with the atom numbering scheme is shown in Figure 2. The iron atom is located at the center of a trigonal bipyramid. The three vertices of the equatorial plane are occupied by the Cl atoms while the pyridine ring nitrogen atoms complete the environment. To the best of our knowledge there is only one structural study of a trigonal-bipyramidal geometry for iron(III) complexes which concerns the $[\text{Fe}(\text{N}_3)_5]^{2-}$ anion.¹⁹ Such a geometry for FeCl_3 derivatives is unusual since these complexes are commonly found to be $(\text{FeCl}_4)^-(\text{FeCl}_2\text{L}_4)^+$.²³

Table VI. Intramolecular Distances (Å) < 3.5 Å

Cl(1)-N(1)	3.132 (3)	Cl(2)-C(10)	3.406 (4)
Cl(1)-N(2)	3.205 (3)	Cl(2)-C(5)	3.419 (5)
Cl(1)-C(6)	3.291 (4)	Cl(3)-N(2)	3.003 (3)
Cl(1)-C(5)	3.425 (4)	Cl(3)-N(1)	3.170 (3)
Cl(2)-N(1)	3.133 (3)	Cl(3)-C(1)	3.191 (4)
Cl(2)-N(2)	3.192 (3)	Cl(3)-C(10)	3.472 (5)

Table VII. Fe-Cl Bond Distances (Å) for Iron(III) Complexes in Different Geometries

compd	geometry	Fe-Cl	ref
$[\text{FeCl}_4]^-$	tetrahedral	2.183 (1) ^c	25
$[\text{Cl}_3\text{FeOFeCl}_3]^{2-}$	tetrahedral	2.213 (3) ^c	26
chlorohemin	square pyramidal	2.218	24
$[\text{Fe}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2\text{Cl}]$	square pyramidal	2.27	27
$[\text{Fe}(\text{SALPA})\text{Cl}]_2^a$	distorted square pyramidal	2.226 (6)	28
$\text{Fe}(\text{SANE})_2\text{Cl}^b$	distorted square pyramidal	2.251 (5)	28
$\text{FeCl}_3(4\text{-cpy})_2$	trigonal bipyramidal	2.216 (1) ^c	this study

^a SALPA = *N*-(3-hydroxypropyl)salicylaldehyde. ^b SANE = *N*-(2-phenylethyl)salicylaldehyde. ^c Mean value.

Although the molecule has the point symmetry C_1 from crystallography, the actual symmetry of the coordination polyhedron is C_3 , within experimental error, and is only slightly distorted from D_{3h} symmetry. The three Cl and Fe atoms make up a planar system, the maximum deviation from this plane being less than one standard deviation (Table V).

The distortions from the idealized D_{3h} point symmetry occur not only in the three Cl-Fe-Cl angles (122.4 (5), 121.8 (6) and 115.8 (6)°), which deviate from 120°, but also in the nonlinearity of the N(1)-Fe-N(2) group (175.6 (2)°). If the Fe-N(1) bond is perpendicular to the equatorial plane (90.3°), the Fe-N(2) bond is bent towards the Cl(3) atom, making an angle of about 5° with the normal to this plane; this point will be discussed later.

The lengths of the two independent iron-nitrogen bonds (2.214 (3) and 2.231 (3) Å) do not differ significantly. The mean value (2.223 (3) Å) is considerably longer than the bond length observed in high-spin iron(III) either with trigonal-bipyramidal geometry as $[\text{Fe}(\text{N}_3)_5]^{2-}$ ¹⁹ where the mean Fe-N distance is 2.02 Å or with square-pyramidal geometry such as chlorohemin, 2.062 Å.²⁴ The lengthening in the title compound cannot be related to selective placement of electrons in the d orbitals since $\text{FeCl}_3(4\text{-cpy})_2$ and $[\text{Fe}(\text{N}_3)_5]^{2-}$ are both high-spin d⁵. An argument might be to invoke atom-atom repulsion between the nitrogen atoms and the chlorine atoms.

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Table VIII. Structural Parameters of Trigonal-Bipyramidal Metal Complexes (MX₃L₂)

compd	electron config	bond dist, Å		bond angles, deg		ref
		M-X	M-L	X-M-X	L-M-L	
TiBr ₃ (NMe ₃) ₂	d ¹	2.442 (6)	2.30 (6)	121.3 (2)	179.4 (11)	14
		2.442 (6)	2.27 (4)	121.3 (2)		
		2.404 (10)		117.5 (3)		
VCl ₃ (NMe ₃) ₂	d ²	2.241 (4)	2.195 (14)	121.0 (1)	179.0 (5)	15
		2.241 (4)	2.232 (12)	121.0 (1)		
		2.236 (5)		118.1 (2)		
CrCl ₃ (NMe ₃) ₂	d ³	2.216 (7)	2.198 (17)	124.2 (2)	178.8 (5)	16
		2.216 (7)	2.168 (20)	111.4 (2)		
		2.244 (8)		115.8 (6)		
FeCl ₃ (4-cpy) ₂	d ⁵	2.216 (1)	2.232 (3)	115.8 (6)	176 (2)	this study
		2.229 (1)	2.213 (3)	122.4 (5)		
		2.204 (1)		121.8 (6)		
NiBr ₃ (PPhMe ₂) ₂	d ⁷	2.349 (2)	2.263 (3)	110.63 (9)	178.8 (1)	29
		2.375 (2)	2.273 (3)	132.71 (9)		
		2.339 (2)		116.66 (9)		
[NiCl ₃ (L ⁺ CH ₃) ₂] ⁺ ^a	d ⁸	2.281 (3)	2.218 (7)	119.5 (1)	175.9 (2)	30
		2.302 (3)	2.235 (7)	118.2 (1)		
		2.315 (3)		122.3 (1)		
[CuCl ₃ (L ⁺ CH ₃) ₂] ⁺ ^a	d ⁹	2.345 (6)	2.13 (1)	119.4 (2)	176.4 (5)	30
		2.349 (5)	2.16 (1)	118.3 (2)		
		2.353 (5)		122.3 (2)		

^a L⁺CH₃ = *N*-methyl-1,4-diazabicyclo[2.2.2]octonium ion.

It is worthy of note that the Cl-N intramolecular distances (Table VI) vary from 3.003 (3) to 3.205 (3) Å and they are similar to the values found for the corresponding bonds in VCl₃(NMe₃)₂¹⁵ and CrCl₃(NMe₃)₂¹⁶ of 3.15 and 3.10 Å, respectively (mean value).

Let us now consider the iron-chlorine distances. Although a direct comparison of the Fe-Cl bond lengths with those in other complexes containing iron in such a trigonal-bipyramidal geometry is precluded by the lack of structural data, it appears from Table VII that the Fe-Cl distance of 2.216 Å (mean value) is within the normal range for iron(III) complexes in different geometries. The difference in the Fe-Cl lengths, in our compound, of 2.204 (1), 2.216 (1) and 2.229 (1) Å is also observed for other trigonal-bipyramidal metal complexes MX₃L₂ (Table VIII).

An important feature of this structure is the fact that all the atoms lie in three distinct planes (Table V); the first one is the equatorial plane Fe, Cl(1), Cl(2), and Cl(3), the second one contains one of the pyridine rings (N(1) to C(5)), Fe, and Cl(3), and the third one contains the other pyridine ring and Fe. These three planes are such that their intersection lines almost make up an orthogonal system, centered at the Fe atom. In the trigonal-bipyramidal geometry it is well-known that the e'' orbitals (d_{xy}, d_{yz}) are purely π orbitals.³¹ A 90° dihedral angle between the pyridine rings would enable each p lone pair of both nitrogen atoms to form a π bond with the d_{xy} and d_{yz} orbitals, respectively. The dihedral angle observed between the pyridine rings is 77°. It may be argued that the occurrence of π bonding would result in a shortening of the Fe-N bond; such a shortening is not observed. However, we have pointed out (vide supra) that the long Fe-N distances may be related to atomic repulsions.

Another interesting feature appears in the bending of one of the pyridine rings (N(2) to C(8)) toward the Cl(3) atom (Figure 3). The Fe-Cl(3) bond is in a plane nearly perpen-

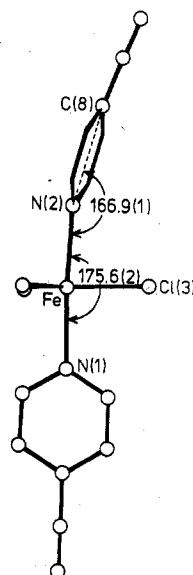


Figure 3. View showing the bending toward Cl(3) of the N(2) pyridine ring.

dicular to that pyridine ring. The departure of the Cl-Fe-Cl angles from the ideal 120° may be responsible for such a deformation. Since the Cl(1)-Fe-Cl(2) angle (115.8 (6)°) is less than 120°, the resultant of the electronic repulsions which occur between the pyridine π cloud and the nonbonding electrons of Cl(1), Cl(2), and Cl(3) is directed toward Cl(3) and forces the ring to bend away from Cl(1) and Cl(2). However this motion toward Cl(3) is restricted by the atomic repulsion between Cl(3) and N(2) which are separated by 3 Å, a very short van der Waals contact. As a result, the Fe-N(2)-C(8) angle (166.9 (1)°) deviates appreciably from 180°.

Electronic Spectra

The electronic spectra of the complex were recorded between (5-50) × 10³ cm⁻¹ in the solid state and in solution. The spectrum of the solid is not significantly different from the spectrum recorded in an ethanol solution (Figure 4), but it is different from those in methanol and acetonitrile solutions. The pentacoordinated structure of the solid complex is probably retained in ethanol, but spectra modifications in other solvents may indicate a reaction of FeCl₃(4-cpy)₂ with the

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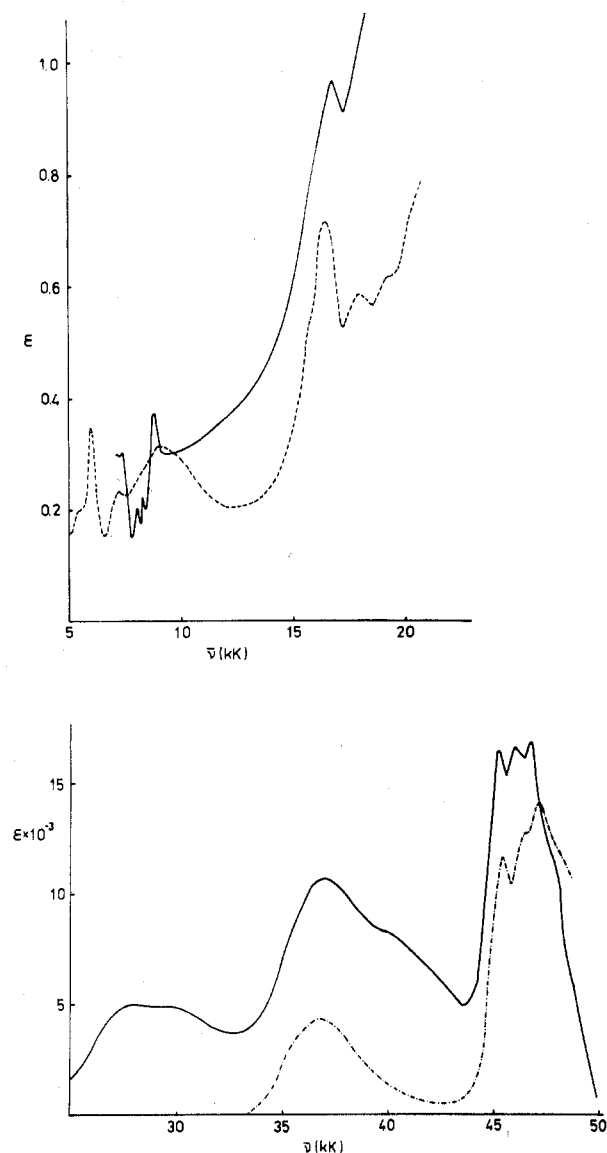


Figure 4. Absorption spectra of $\text{FeCl}_3(4\text{-cpy})_2$ in $\text{C}_2\text{H}_5\text{OH}$ (—), of $\text{FeCl}_3(4\text{-cpy})_2$ (solid-state spectrum (arbitrary scale)) (---), and of 4-cpy in $\text{C}_2\text{H}_5\text{OH}$ (-.-).

solvent. The complex $\text{FeCl}_3(4\text{-cpy})_3$ can be obtained as crystals when a solution of $\text{FeCl}_3(4\text{-cpy})_2$ in CH_3OH is allowed to stand at room temperature.³²

The electronic spectrum of iron(III) in approximately D_{3h} symmetry exhibits many very weak absorption bands (see Figure 4) between 5×10^3 and $20 \times 10^3 \text{ cm}^{-1}$ and several strong absorption bands in the region $(20\text{--}50) \times 10^3 \text{ cm}^{-1}$.

Although a complete assignment of the whole spectrum has not been attempted, the bands in the region $(5\text{--}20) \times 10^3 \text{ cm}^{-1}$ have their origin in spin-forbidden transitions from the ground sextet state to the quartet levels.³³ The high intensity of the bands between $(20\text{--}33) \times 10^3 \text{ cm}^{-1}$ is suggestive of charge-transfer character. Finally the bands in the region $(33\text{--}50) \times 10^3 \text{ cm}^{-1}$ are assigned to internal transitions within the cyanopyridine ligands. As far as we know, this is the first report of the electronic spectrum of a genuine high-spin iron(III) complex with a trigonal-bipyramidal symmetry. For the supposed trigonal-bipyramidal complex of FeCl_3diox ^{17,18} the electronic spectrum has been reported,¹⁷ but the actual structure of this complex is unknown.

Infrared Spectra

No change in the nitrile stretching frequency (2240 cm^{-1}) of the complex from that of the free base is consistent with the crystallographic data: the pyridine nitrogen is coordinated to the metal. The comparison of the pyridine bands of 4-cpy ($1595, 1545, 1500, \text{ and } 1415 \text{ cm}^{-1}$) and its complex ($1612, 1545, 1500, \text{ and } 1416 \text{ cm}^{-1}$) shows that the bands are somewhat shifted to higher energy, also indicating that the pyridine group is coordinated to the metal. The striking features of the far-infrared spectrum are an intense broad band at 378 cm^{-1} and a peak of medium intensity observed at 480 cm^{-1} . The true molecular symmetry around iron(III) atom is C_1 , but a reasonable approximate symmetry is D_{3h} . Accordingly to D_{3h} symmetry our complex should show one $\nu(\text{Fe}\text{--}\text{Cl})$ vibration (e') and one $\nu(\text{Fe}\text{--}\text{N})$ vibration (a''_2). The band at 378 cm^{-1} may be attributed to the $\nu(\text{Fe}\text{--}\text{Cl})$ vibration. It is close to $\nu(\text{Fe}\text{--}\text{Cl})$ in FeCl_3diox ,^{17,18} where a trigonal-bipyramidal environment was suggested. In the $[\text{FeCl}_5]^{2-}$ species $\nu(\text{Fe}\text{--}\text{Cl})$ vibration has been found at 336 cm^{-1} .³⁴ On the basis of the values reported for the $\nu(\text{Fe}\text{--}\text{Cl})$ vibration, it is difficult to coin the correct symmetry about iron(III) because in the tetrahedral anion $[\text{FeCl}_4]^-$ the single IR-active $\nu(\text{Fe}\text{--}\text{Cl})$ occurs at ca. 380 cm^{-1} .

It is difficult to justify the assignment of the band at 480 cm^{-1} to the iron-nitrogen vibration, because the majority values reported for some $\nu(\text{M}\text{--}\text{N}_{\text{py}})$ vibrations are found at ca. $200\text{--}287 \text{ cm}^{-1}$.³⁵ Moreover increasing the effective mass of the ring by CN substitution would result in a lower $\nu(\text{M}\text{--}\text{N})$. So we supposed that the $\nu(\text{Fe}\text{--}\text{N})$ vibration would be expected to occur below 200 cm^{-1} , the frequency limit of the infrared spectrometer used.

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Registry No. $\text{FeCl}_3(4\text{-cpy})_2$, 74298-05-8.

Supplementary Material Available: A listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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