

(Minshall & Sheldrick, 1978), but shorter than those in [(pic)<sub>2</sub>H][WBr<sub>4</sub>(pic)<sub>2</sub>], 2.77 Å, and [(pyH)<sub>2</sub>]-[(Cl<sub>3</sub>Fe)<sub>2</sub>O(py)], 2.75 Å (Drew, McKee & Nelson, 1978).

The angle between the N(3)–C(33) and N(4)–C(43) directions is 15.5°. Pyridine rings are twisted by 76°. The corresponding values in [(pic)<sub>2</sub>H]<sup>+</sup> are 7 and 24°. This difference could be the reason for the closer contact of the two N atoms in the [(pic)<sub>2</sub>H]<sup>+</sup> case.

All four pyridine rings are planar within 0.02 Å. Distances and angles are normal. The shortest interionic interaction is between C(43)(*x*, *y*, *z*) and C(45)(–*x*, 1–*y*, 1–*z*), 3.40 (2) Å.

We are indebted to the Boris Kidrič Foundation and the University of Ljubljana for assistance.

*Acta Cryst.* (1979). B35, 3030–3032

### 3-Cyanopyridinium Tetrachloroferrate(III)–3-Cyanopyridine

BY JEAN-CLAUDE DARAN, YVES JEANNIN AND LILIANA MARIA MARTIN

*Université Pierre et Marie Curie, Laboratoire de Chimie des Métaux de Transition, ERA n° 608, 4 place Jussieu, 75230 Paris CEDEX 05, France*

(Received 3 July 1979; accepted 25 July 1979)

**Abstract.** [C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>][FeCl<sub>4</sub>].C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>, *M<sub>r</sub>* = 406.8, *C*2/*c*, *a* = 33.520 (5), *b* = 7.586 (1), *c* = 14.610 (4) Å, β = 107.9 (2)°, *V* = 3535.2 Å<sup>3</sup>, *D<sub>m</sub>* = 1.55 (2); *D<sub>x</sub>* = 1.53 Mg m<sup>–3</sup>, *Z* = 8. Final *R<sub>w</sub>* = 0.049 for 1556 counter reflexions. The unit cell contains tetrahedral tetrachloroferrate anions, 3-cyanopyridinium cations and 3-cyanopyridine molecules. N–H···N hydrogen bonding occurs between the cation and the solvent molecule.

**Introduction.** The crystal structure study of the title compound was undertaken after the compound appeared as a by-product during a series of reactions between iron(III) chloride and cyanopyridine. Anhydrous iron(III) chloride was added to a large excess of 3-cyanopyridine in dichloromethane. An intense brown-red colour developed. The reaction seemed to be quite complex. If the mixture was immediately filtered to remove excess iron(III) chloride, a yellow complex crystallized from the filtrate. The crystals were washed with ether and dried.

The crystal system was determined from precession photographs (Mo *K*α, λ = 0.71069 Å). Systematic extinctions *h*0*l*, *l* = 2*n* + 1, *hkl*, *h* + *k* = 2*n* + 1

#### References

- BRENČIČ, J. V., ČEH, B. & KRIŽELJ, C. (1977). *Vest. Slov. Kem. Drus.* **24**, 41–46 (in English).  
 BRENČIČ, J. V., ČEH, B. & ŠEGEDIN, P. (1979). *J. Inorg. Nucl. Chem.* In the press.  
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.  
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 DREW, M. G. B., MCKEE, V. & NELSON, S. M. (1978). *J. Chem. Soc. Dalton Trans.* pp. 80–84.  
 LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.  
 MINSHALL, P. C. & SHELDRIK, G. M. (1978). *Acta Cryst.* **B34**, 1378–1380.  
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.  
 ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

indicated space group *C*2/*c*. *D<sub>m</sub>* was measured by flotation in a tetrachloromethane–dichloromethane mixture.

A crystal 0.6 × 0.3 × 0.1 mm was set up about [001] on an automatic four-circle diffractometer and cell dimensions and orientation matrix were obtained by least squares from the setting angles of nine reflexions. The intensities of 3099 independent reflexions with sin θ/λ < 0.59 Å<sup>–1</sup> were measured by a θ/2θ scan at room temperature. Mo *K*α radiation and a take-off angle of 3° were used with a graphite monochromator set in front of the counter. An asymmetric scan starting 0.5° before the *K*α<sub>1</sub> peak and finishing 0.7° after the *K*α<sub>2</sub> peak was used because of tailing of the diffraction peaks. The scan speed was 1.5° min<sup>–1</sup>. The measurements were corrected for Lorentz and polarization effects. No absorption correction was applied (μ = 1.47 mm<sup>–1</sup>). Each structure factor was assigned a standard deviation σ = (F × ΔI)/I where *I* was the integrated intensity and ΔI the error. Of the 3099 reflexions, only 1556 with *F* > 3σ were used in subsequent calculations.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974), including *f'*

and  $f''$ . The agreement factors were defined as  $R = \sum |F_o| - |F_c| / \sum |F_o|$  and  $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2 \}^{1/2}$ . A weighting scheme based on counting statistics,  $w = 2F/\sigma$ , was used.

The structure was solved with *MULTAN 77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The *E* map showed the positions of the Fe and Cl atoms. C and N atoms were found from a Fourier synthesis. Atomic positions were refined by full-matrix least squares with isotropic then anisotropic temperature factors. A difference map based on the heavy atoms gave the positions of all the H atoms. One of the ring N atoms had a H atom attached which identified the cyanopyridinium cation; the other ring was solvent cyanopyridine. These atoms were included in the last two cycles of refinement in calculated positions [ $d(\text{C}-\text{H})$ ,  $d(\text{N}-\text{H}) = 1.0 \text{ \AA}$ ], but were not refined; their temperature factors were constrained to be the same as those of the atom to which they were bound. Convergence was reached at  $R = 0.067$  and  $R_w = 0.049$ .

Non-hydrogen atomic parameters are given in Table 1.\* Bond distances and angles, with e.s.d.'s calculated from the full variance-covariance matrix, are given in Table 2 and Fig. 1, and the equations of important molecular planes in Table 3. A view of the molecular packing is illustrated in Fig. 2.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34704 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) of the non-hydrogen atoms with e.s.d.'s in parentheses

	x	y	z
Fe	3668 (0)	1046 (2)	4892 (1)
Cl(1)	4001 (1)	856 (4)	3820 (2)
Cl(2)	3282 (1)	-1307 (5)	4809 (3)
Cl(3)	4127 (1)	1312 (6)	6323 (2)
Cl(4)	3273 (1)	3381 (4)	4569 (3)
N(1)	1434 (3)	465 (13)	2515 (6)
C(1)	1600 (4)	2048 (17)	2524 (8)
C(2)	2005 (3)	2324 (15)	3058 (8)
C(3)	2239 (3)	952 (21)	3608 (7)
C(4)	2060 (4)	-630 (16)	3573 (8)
C(5)	1642 (4)	-859 (17)	3023 (8)
C(21)	2179 (4)	4080 (22)	3075 (9)
N(21)	2317 (4)	5396 (15)	3056 (11)
N(2)	697 (2)	1178 (14)	1100 (5)
C(6)	749 (3)	1062 (17)	223 (8)
C(7)	453 (3)	1741 (14)	-602 (7)
C(8)	95 (3)	2458 (15)	-516 (7)
C(9)	33 (3)	2539 (15)	380 (8)
C(10)	351 (4)	1882 (17)	1157 (7)
C(72)	534 (3)	1574 (15)	-1535 (8)
N(72)	605 (3)	1384 (19)	-2214 (7)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in the  $[\text{FeCl}_4]^-$  anion with e.s.d.'s in parentheses

Fe-Cl(1)	2.188 (3)	Cl(1)-Fe-Cl(2)	109.3 (2)
Fe-Cl(2)	2.187 (4)	Cl(1)-Fe-Cl(3)	109.1 (1)
Fe-Cl(3)	2.190 (3)	Cl(1)-Fe-Cl(4)	108.0 (1)
Fe-Cl(4)	2.175 (4)	Cl(2)-Fe-Cl(3)	110.9 (2)
		Cl(2)-Fe-Cl(4)	110.0 (1)
		Cl(3)-Fe-Cl(4)	109.5 (2)

Table 3. Least-squares planes and displacements ( $\text{\AA}$ ) of the specified atoms from the planes

In the equations,  $x$ ,  $y$  and  $z$  represent fractional coordinates with respect to the crystallographic axes.

Plane 1: ring N(1) to C(5)

$$\text{Equation of plane: } 19.214x - 1.996y - 13.366z = -0.7032$$

N(1)	0.005 (10)	C(5)	-0.011 (13)
C(1)	-0.006 (13)	H(11)	-0.041 (13)
C(2)	0.005 (13)	C(20)	-0.033 (13)
C(3)	-0.008 (12)	N(21)	-0.006 (13)
C(4)	0.011 (13)		

Plane 2: ring N(2) to C(10)

$$\text{Equation of plane: } 13.948x + 6.801y + 0.234z = 1.792$$

N(2)	0.007 (10)	C(9)	-0.009 (11)
C(6)	-0.019 (12)	C(10)	0.005 (12)
C(7)	0.010 (10)	C(72)	-0.012 (12)
C(8)	0.010 (11)	N(72)	-0.059 (12)

Angle between planes 1 and 2:  $96.6 (6)^\circ$

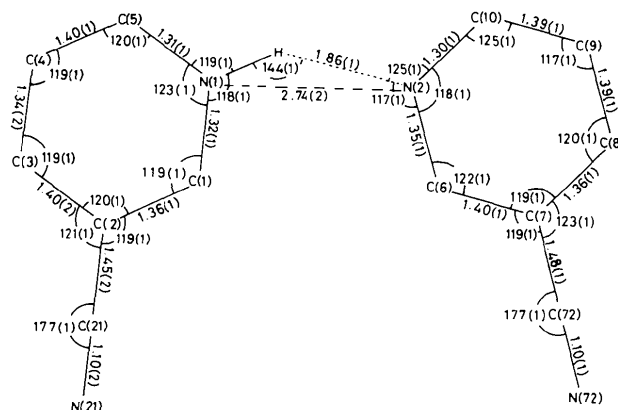


Fig. 1. Distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses in the 3-cyanopyridinium cation and 3-cyanopyridine.

**Discussion.** The asymmetric unit of the crystal contains one tetrachloroferrate anion, one 3-cyanopyridinium cation and one molecule of 3-cyanopyridine.

There have been several structural determinations involving the tetrahedral  $[\text{FeCl}_4]^-$  anion. Among the most accurate are those of  $[\text{PCl}_4][\text{FeCl}_4]$  (Kistenmacher & Stucky, 1968) and  $[\text{Fe}(\text{NCMe})_6][\text{FeCl}_4]_2$

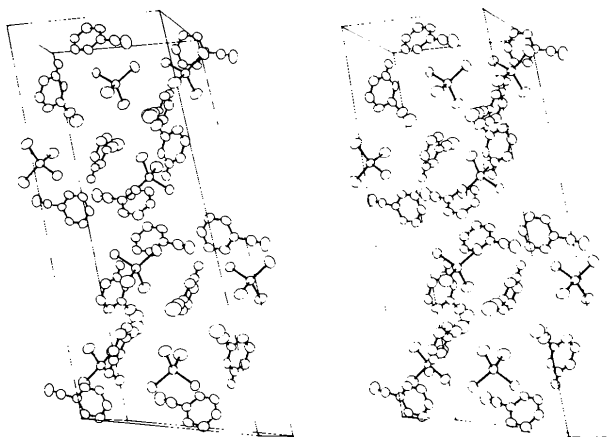


Fig. 2. Stereoscopic view of the unit cell of  $[\text{C}_6\text{H}_5\text{N}_2][\text{FeCl}_4] \cdot \text{C}_6\text{H}_4\text{N}_2$ . The ellipsoids represent 50% electron probability.

(Constant, Daran & Jeannin, 1972) in which the Fe—Cl lengths are 2.182–2.187 (1) and 2.180–2.186 (2) Å respectively. In the present work, the Fe—Cl lengths range from 2.175 to 2.190 Å, with no systematic variation. The Cl—Fe—Cl angles are all close to the tetrahedral value, the mean being 109.5°.

The dimensions of the pyridine rings are roughly the same as those found in 4-cyanopyridine (Laing, Sparrow & Sommerville, 1971) and 3-aminopyridine (Chao, Schempp & Rosenstein, 1975). Resonance is likely to be responsible for the shortening of the exocyclic C—C bond from the single-bond value of 1.54 Å to the observed lengths 1.45 (2) and 1.48 (1) Å. Within experimental error, these values are similar to 1.43 Å (mean value) found in 4-cyanophenol (Higashi & Osaki, 1977) and 1.439 (8) Å in 4-cyanopyridine (Laing,

Sparrow & Sommerville, 1971). The difference in length in the C≡N triple bond, 1.14 Å (mean value) for 4-cyanophenol and 4-cyanopyridine and 1.10 (1) Å for 3-cyanopyridine (this work), might be related to positional substitution of the  $\pi$ -electron withdrawing CN group on the pyridine ring. Unfortunately the lack of more numerous and more accurate crystallographic data of such compounds precludes a definite conclusion.

There is an intermolecular hydrogen bond of the type N—H...N between the cation and the 3-cyanopyridine molecule, Fig. 1. A similar intermolecular hydrogen bond was found in pyridinium  $\mu$ -oxo-bis[trichloroferrate(III)]-pyridine (Drew, McKee & Nelson, 1978) with a N...N contact of 2.747 Å and a N—H...N angle of 160°.

#### References

- CHAO, M., SCHEMPP, E. & ROSENSTEIN, R. D. (1975). *Acta Cryst.* B31, 2924–2926.  
 CONSTANT, G., DARAN, J. C. & JEANNIN, Y. (1972). *J. Organomet. Chem.* 44, 353–363.  
 DREW, M. G. B., MCKEE, V. & NELSON, S. M. (1978). *J. Chem. Soc. Dalton Trans.* pp. 80–84.  
 HIGASHI, T. & OSAKI, K. (1977). *Acta Cryst.* B33, 607–609. *International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 KISTENMACHER, T. J. & STUCKY, G. D. (1968). *Inorg. Chem.* 7, 2150–2155.  
 LAING, M., SPARROW, N. & SOMMERVILLE, P. (1971). *Acta Cryst.* B27, 1986–1990.  
 MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.

*Acta Cryst.* (1979). B35, 3032–3034

## Bis(oxamide oximato)platinum(II)—Ammonium Chloride

BY HELMUT ENDRES

*Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, 6900 Heidelberg 1, Federal Republic of Germany*

(Received 15 February 1979; accepted 16 July 1979)

**Abstract.**  $[\text{Pt}(\text{C}_2\text{H}_5\text{N}_4\text{O}_2)_2] \cdot \text{NH}_4\text{Cl}$ ,  $\text{C}_4\text{H}_{10}\text{N}_8\text{O}_4\text{Pt} \cdot \text{NH}_4\text{Cl}$ ,  $M_r = 481.76$ , monoclinic,  $P2_1/a$ ,  $a = 7.268$  (1),  $b = 23.567$  (4),  $c = 7.174$  (2) Å,  $\beta = 90.85$  (2)°,  $V = 1228$  Å<sup>3</sup>,  $Z = 4$ ,  $d_c = 2.60$  Mg m<sup>-3</sup>. The structure was solved by Patterson and Fourier methods and refined by least squares to  $R = 0.050$  for 3788 independent diffractometer data. The structure

shows a network of H bridges *via* the Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup> ions as well as stronger intermolecular than intramolecular H bridges between oxime O atoms. The planar complex units form stacks along *a*.

**Introduction.** Complexes of oxamide oxime (diaminoglyoxime, oaoH<sub>2</sub>) with metals of the Ni triad are