

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 π -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 μ -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)°, $V = 1228$ Å³, $Z = 4$, $d_c = 2.60$ Mg m⁻³. 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⁻ and NH₄⁺ 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, oaoH₂) with metals of the Ni triad are

interesting as starting materials for the synthesis of solids with highly anisotropic physical properties, the amino groups acting as centers for structural variation. Such a structural variation could be brought about (apart from chemical attack at the amino N) by fixing additional molecules or ions *via* H bridges. This idea was also outlined by Brown & Wroblewski (1979). Hitherto we have reported the structures of Ni complexes with oaoH_2 (Endres, 1978, 1979). The structures of two Co complexes of oaoH_2 are also known (Bekaroglu, Sarisaban, Koray & Ziegler, 1977; Bekaroglu, Sarisaban, Koray, Nuber, Weidenhammer, Weiss & Ziegler, 1978).

The title compound can be prepared by adding dropwise a solution of 415 mg $\text{K}_2[\text{PtCl}_4]$ and 2 g NH_4Cl in 100 ml H_2O to a boiling solution of 240 mg oaoH_2 in 100 ml H_2O . The solution is filtered while hot and allowed to cool to room temperature. Red needles (which are presently being studied) together with a green-brown amorphous body precipitate. They are filtered off and the mother liquor is concentrated to a few ml by evaporation on a sand bath. After cooling to room temperature golden-yellow crystals of the title compound precipitate, and are isolated by filtration. The crystal used in the structure determination was prepared by slow diffusion of $\text{K}_2[\text{PtCl}_4]$ and oaoH_2 in a U-tube filled with aqueous NH_4Cl solution. The identity of the crystals obtained (together with elementary Pt) with the product of the former reaction is proved by Weissenberg photographs.

The crystal system, systematic extinctions and approximate lattice constants were determined from rotating-crystal and Weissenberg photographs (Cu $K\alpha$ radiation). Exact lattice constants (see *Abstract*) were calculated by least squares (Berdiesinski & Nuber, 1966) from the θ values of 56 reflections centered on a

diffractometer. Data collection on a computer-controlled single-crystal diffractometer (Siemens AED, Mo $K\alpha$ radiation, θ - 2θ scans, five-value method, $4^\circ < 2\theta < 76^\circ$) yielded 3788 observed independent reflections with $I > 3.0\sigma(I)$. They were corrected for Lorentz and polarization factors only. The irregularly shaped crystal had an approximate volume of 0.002 mm^3 , no absorption correction was applied ($\mu = 12.26 \text{ mm}^{-1}$). During data collection, the intensities of two check reflections diminished by about 12%. A corresponding linear correction to the observed intensities was applied.

The position of Pt was derived from a Patterson synthesis; the atoms of the ligands were located from Fourier syntheses. The positions of N and Cl of the NH_4Cl , which was not expected at this time, became evident on a difference Fourier map. H positions could not be determined. Least-squares refinement with anisotropic temperature factors for Pt and isotropic ones for the other atoms gave $R = 0.057$; refinement with anisotropic temperature factors converged to $R = 0.050$ (maximum shift/error = 0.4).*

Calculations were carried out on Siemens 301 (Anorganisch-Chemisches Institut Heidelberg) and IBM 370/168 (Universitätsrechenzentrum Heidelberg) computers with programs from the XRAY system (Stewart, Kundell & Baldwin, 1970). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates are listed in Table 1. Fig. 1 shows an *ORTEP* plot (Johnson, 1965) of the molecule with bond distances and angles. The molecule is nearly planar: If the plane is defined by Pt and the four oxime N, the maximum deviation of these atoms

Table 1. Atomic coordinates ($\times 10^4$)

	x	y	z
Pt	2811 (1)	403.8 (2)	390 (1)
Cl	184 (5)	2024 (1)	3890 (5)
O(1)	3132 (14)	-688 (4)	2625 (11)
O(2)	1533 (12)	423 (3)	-3529 (10)
O(3)	2462 (14)	1431 (3)	-2025 (11)
O(4)	4241 (12)	467 (3)	4339 (11)
N(1)	2646 (14)	-430 (4)	983 (11)
N(2)	1923 (13)	94 (3)	-2002 (11)
N(3)	3002 (15)	1221 (4)	-338 (12)
N(4)	3737 (13)	755 (4)	2746 (11)
N(5)	1870 (15)	-1329 (4)	-226 (14)
N(6)	1025 (14)	-721 (4)	-3667 (12)
N(7)	3932 (16)	2132 (4)	562 (14)
N(8)	4912 (15)	1590 (4)	4126 (13)
N(9)	2589 (17)	2783 (4)	7240 (13)
C(1)	2042 (15)	-757 (4)	-376 (14)
C(2)	1610 (14)	-457 (4)	-2141 (13)
C(3)	3668 (16)	1581 (4)	919 (14)
C(4)	4132 (15)	1304 (4)	2722 (13)

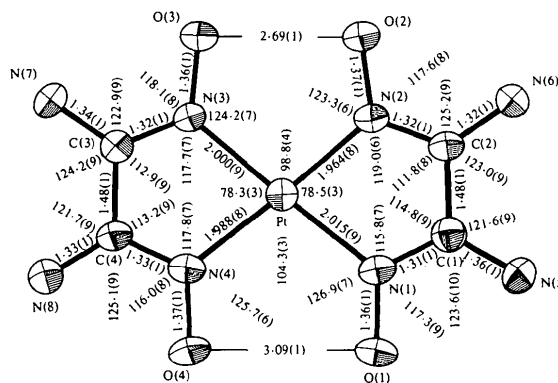


Fig. 1. The $[\text{Pt}(\text{oaoH})_2]$ molecule with bond distances (Å) and angles ($^\circ$).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34613 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

from the plane is 0.015 Å. The amino N(7) and N(8) exhibit the maximum deviation of the rest of the molecule from this plane, 0.16 and 0.23 Å respectively. The molecules form stacks along *x*, the molecular planes being slightly inclined with respect to *x* (Fig. 2). The molecules within a stack are inter-related by the inversion centers at 0,0,0 and $\frac{1}{2}, 0, 0$, hence all the molecular planes are parallel. The planes are practically equidistant. The separations, given by the distances of the adjacent Pt to the molecular plane as defined above, are 3.43 and 3.45 Å. This is the usual interplanar distance of planar molecules with a delocalized π system. The arrangement of the molecules within a stack brings Pt nearly perpendicularly above and below N(1) and C(2) of the adjacent molecules. Distances and angles are included in Fig. 2. Fig. 3 shows a projection on to the *yz* plane. The network of

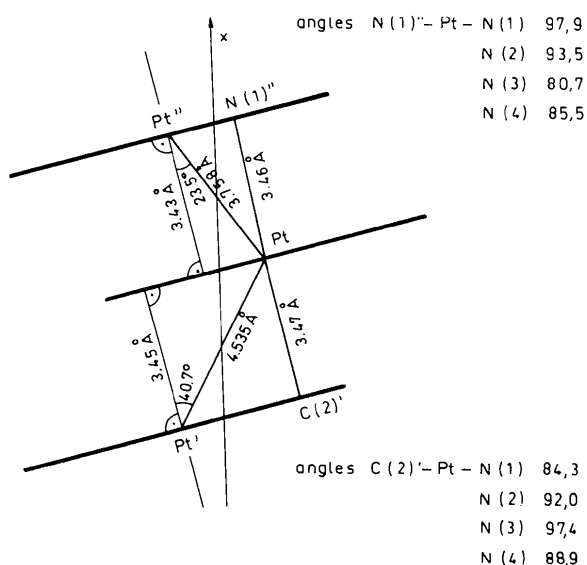


Fig. 2. Schematic projection of a stack parallel to the molecular planes showing relevant distances (Å) and angles (°). Pt' is related to Pt by the inversion center at 0,0,0, Pt'' by the inversion center at $\frac{1}{2}, 0, 0$.

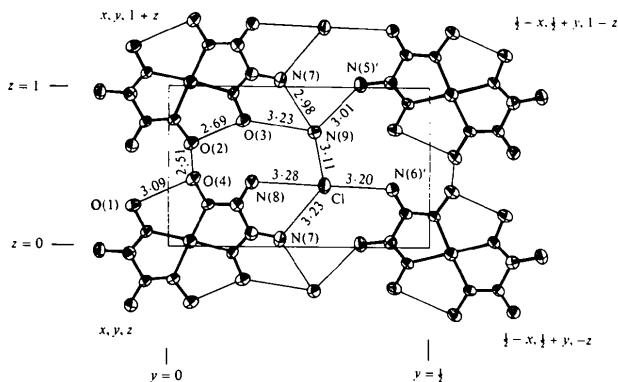


Fig. 3. Projection on to the *yz* plane showing the shortest intermolecular contacts (Å). The atoms of the molecule in the lower left corner have the coordinates given in Table 1. The other molecules shown are generated by the indicated symmetry operations.

short intermolecular contacts is indicated. One of the two usual *intramolecular* H bridges between the oxime O atoms has not been formed [O(1)-O(4) 3.09 Å]. Instead, there exists an *intermolecular* H bridge [O(4)-O'(2) 2.51 Å] linking complex molecules of adjacent stacks. Thus, the stacks are linked to sheets parallel to the *xz* plane at $y = 0$ and $y = \frac{1}{2}$. To my knowledge, this formation of an intermolecular rather than an intramolecular H bridge has never been observed in bis-(dioximato) complexes. Coupling between the sheets at $y = 0$ and $y = \frac{1}{2}$ occurs *via* the NH₄Cl, which is present as an ion pair: The very short N(9)-Cl distance of 3.11 Å, as compared to the distance 3.36 Å in crystalline NH₄Cl (Wyckoff, 1963), hints at strong H bonding. Similarly, the Cl⁻ ion lies at short distances from amino N atoms of complex molecules of adjacent sheets. These distances [to N(7), N(8), N'(6)] are also shorter than the N-Cl distance in crystalline NH₄Cl and probably signify H bonding. A similar ion-pair incorporation has been observed before in another dioximato complex, the AgClO₄ adduct of bis(1,2-benzoquinone dioximato)platinum(II) (Endres, Mégnamisi-Bélobbé, Keller & Weiss, 1976). In both cases the ion-pair inclusion does not allow the formation of a columnar structure, which is the usual structural feature in bis(1,2-dione dioximato) complexes (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977). The inclusion of dimethylformamide in crystals of [Ni(oaoH)₂] has the same effect (Endres, 1978), whereas the incorporation of H₂O may even have a tendency to stabilize a regularly stacked structure, as observed in [Ni(oaoH)₂·2H₂O] (Endres, 1979).

References

- BEKAROGLU, Ö., SARISABAN, S., KORAY, A. R., NUBER, B., WEIDENHAMMER, K., WEISS, J. & ZIEGLER, M. (1978). *Acta Cryst.* **B34**, 3591-3593.
- BEKAROGLU, Ö., SARISABAN, S., KORAY, A. R. & ZIEGLER, M. (1977). *Z. Naturforsch. Teil B*, **32**, 387-392.
- BERDESINSKI, W. & NUBER, B. (1966). *Neues Jahrb. Mineral. Abh.* **104**, 113-146.
- BROWN, D. B. & WROBLESKI, J. T. (1979). *Molecular Metals*, edited by W. E. HATFIELD. New York, London: Plenum. In the press.
- ENDRES, H. (1978). *Acta Cryst.* **B34**, 2306-2309.
- ENDRES, H. (1979). *Acta Cryst.* **B35**, 625-627.
- ENDRES, H., KELLER, H. J., LEHMANN, R., POVEDA, A., RUPP, H. H. & VAN DE SAND, H. (1977). *Z. Naturforsch. Teil B*, **32**, 516-527.
- ENDRES, H., MÉGNAMISI-BÉLOBBÉ, M., KELLER, H. J. & WEISS, J. (1976). *Acta Cryst.* **B32**, 457-460.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- WYCKOFF, R. W. G. (1963). *Crystal Structures*, p. 104. New York, London, Sydney: John Wiley.