The Crystal and Molecular Structure of a 4-Nitropyridine *N*-Oxide Adduct of *trans*-Dichlorodiaquocopper(II), CuCl₂(H₂O)₂ . 2(C₅H₄N₂O₃)*

BY R. J. WILLIAMS† AND DON T. CROMER

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544, U.S.A.

AND W. H. WATSON

Chemistry Department, Texas Christian University, Fort Worth, Texas 76129, U.S.A.

The crystal and molecular structure of a 4-nitropyridine N-oxide adduct of dichlorodiaquocopper(II) has been determined by three-dimensional, single-crystal X-ray diffraction methods. The compound crystallizes in the monoclinic space group $P2_1/c$ and has unit-cell parameters: $a = 13\cdot540$ (6), $b = 5\cdot487$ (2), $c = 11\cdot153$ (5) Å and $\beta = 93°37' \pm 2'$. The measured density is $1\cdot79$ g.cm⁻³; with $Z = 2$, the calculated density is $1\cdot807$ g.cm⁻³. An automated four-circle diffractometer was used to measure 1270 unique reflections by the θ–2θ scan technique to a maximum 2θ of 60° with Mo $K\alpha$ radiation. The structure was solved by the heavy-atom method and refined by the full-matrix, least-squares technique to a conventional R factor of $0\cdot043$. The structure consists of *trans* square-planar CuCl₂(H₂O)₂ groups having the amine-oxide oxygen atom of the 4-nitropyridine N-oxide molecule loosely bonded to the copper ion (Cu–O distance $2\cdot635$ (2) Å), thus forming a distorted tetragonal bipyramidal coordination geometry. The water molecules hydrogen-bond through both hydrogen atoms to amine-oxide oxygen atoms to form two-dimensional hydrogen-bonded networks.

Introduction

In the past few years we have conducted a number of studies on the interesting magnetic and structural properties of aromatic amine–oxide complexes of copper (II) halides (Watson, 1969 and references contained therein). In those studies it was observed that the copper(II) ion can assume vastly different coordination geometries depending on the stoichiometric ratio of aromatic amine–oxide to copper halide and on the presence of other constituents in the complex.

The preparations of both the anhydrous 1:1 and 2:1 adduct of 4-nitropyridine N-oxide and CuCl₂ have been reported (Whyman, Copley & Hatfield, 1967; Hatfield, Muto, Jonassen & Paschal, 1965). We have prepared the dihydrate of the 2:1 complex, CuCl₂(H₂O)₂ . 2(C₅H₄N₂O₃), and have determined its structure by using single-crystal X-ray diffraction techniques. We now report the details of this investigation.

This structure was originally solved from film data by one of the authors (RJW) while at Texas Christian University. Intensity data have been retaken by counter methods, and only the results of this latter investigation are given here.

Experimental

Copper(II) chloride dihydrate was obtained from the Allied Chemical Company and 4-nitropyridine *N*-oxide from the Aldrich Chemical Company, Incorporated. Both compounds were used without further purification.

Equimolar amounts of 4-nitropyridine *N*-oxide and copper(II) chloride dihydrate were dissolved separately in ethanol and the solutions were mixed. The anhydrous, golden brown 1:1 complex precipitated immediately. This material was redissolved in 20% aqueous methanol and light green crystals of the 2:1 dihydrate resulted. [*Analysis*. Calculated for (C₅H₄N₂O₃)₂CuCl₂ . 2H₂O: Cu, 14·10; C, 26·65, N, 12·43; H, 2·68%. Found: Cu, 14·16; C, 26·32; N, 12·07; H, 2·69%. EDTA titrations were used in the copper determination (Frite, Abbink & Payne, 1961) and the carbon, hydrogen and nitrogen analysis were done by Scandinavian Microanalytical Laboratories.]

Precession photographs indicated the crystal system to be monoclinic. The lattice constants were obtained from a least-squares analysis of the positions of twelve reflections measured with Mo $K\alpha_1$ radiation ($\lambda = 0\cdot70926$ Å) on an automated Picker diffractometer. The values obtained are: $a = 13\cdot540$ (6), $b = 5\cdot487$ (2), $c = 11\cdot153$ (5) Å and $\beta = 93° 37$ (2)'. Systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$ observed on precession and Weissenberg photographs uniquely determined the space group to be $P2_1/c$.

The density was measured by the flotation method in a mixture of chloroform and bromoform and was found to be $1\cdot79$ g.cm⁻³. The calculated density for $Z = 2$ is $1\cdot807$ g.cm⁻³.

Intensities were measured by using a Picker four-circle diffractometer interfaced with a Digital Equipment Corp. PDP-8 computer. The orientation and data

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collection programs used were modified versions of the Oak Ridge system (Busing, Ellison, Levy, King & Roseberry, 1968). A θ–2θ scan technique was used with steps of 0·05° over a 2° range and a two-second count at each step.

Intensities for one-half the reflection sphere were measured out to $2\theta = 60°$. Zirconium-filtered molybdenum radiation was used. A total of 2429 reflections were collected with each unique reflection, in general, measured twice. Equivalent reflections were compared and averaged to yield a unique data set. The value of a disagreement index, R_d, was 0·019 where $R_d = \sum_n \sum_i |F_{ave} - F_i| / \sum_n \sum_i |F_{ave}|$, F_{ave} is the weighted average

of i equivalent F_i' s, and the summation is taken over all n sets of equivalent reflections.

The crystal used for the intensity measurements was a parallelepiped with dimensions $0·15 \times 0·15 \times 0·22$ mm. Absorption corrections were applied according to the method of Busing & Levy (1957) using a modified version of Burnham's (1962) program ($\mu = 17·3$ cm^{-1}). A total of 1270 unique reflections was observed greater than zero according to the criterion:

$$(I - B) \geq 3·0[I + B + (0·02 I)^2]^{1/2},$$

where I is the integrated peak intensity and B is the normalized background count.

Table 1. *Observed and calculated structure factors for* CuCl₂(H₂O)₂.2(C₅H₄N₂O₃)

Column headings are l, F_o/K, F_c*/K. A minus sign preceding F_o means 'less than'.

Structure determination

The copper ions were assigned to the special position set (0,0,0), (0,½,½) on centers of symmetry, since there are only two formula units in the unit cell. A three-dimensional electron density map was phased from this partial model and all remaining atoms, except one oxygen atom of the nitro-group, were resolved. This atom was located from a subsequent difference-Fourier synthesis.

This model was refined with the LASL anisotropic full-matrix, least-squares programs (Larson, 1970) to give $R = 0.063$ and $R_H = 0.047$ where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_H = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$. A difference-Fourier calculated at this time contained a number of small peaks ranging from 0.53 to 0.97 e.Å^{-3}. Six of these peaks were located at reasonable positions for the six hydrogen atoms in the asymmetric unit and were so assigned. An attempt was made to refine this model with each hydrogen atom given an isotropic temperature factor. However, all hydrogen atoms showed a tendency to move too close to the oxygen atom or carbon atom to which they were bonded. No doubt the electron density maxima are displaced from the hydrogen nuclei toward the bonding atom. To obtain accurate geometrical details of the hydrogen bonding observed in this structure (discussed later), the hydrogen-atom positions were constrained so as yield normal hydrogen distances of C–H, 1.08 Å and O–H, 0.99 Å (*International Tables for X-ray Crystallography*, 1962). Constraints were applied in the least-squares program by using additional equations of condition of the type:

$$D_{ij} - d_{ij} = \sum_n \frac{\partial d_{ij}}{\partial \zeta_n} \Delta \zeta_n \text{, (Waser, 1963)}$$

where D_{ij} is the constraining distance, d_{ij} is the actual distance between atoms i and j, and the ζ_n are the coordinates of the two atoms involved. These equations were given weights equal to $40/\sigma^2 d_{ij}$ where σd_{ij} is the average estimated standard deviation of the C–H and O–H bonds in the structure (0.05 Å). This large

Table 2. *Positional and thermal parameters with standard deviations*

B_{or}

	X	Y	Z	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
Cu	0.0000	0.5000	0.5000	31 (1)	148 (2)	44 (1)	34 (2)	−11 (1)	−22 (2)
Cl	0.8506 (1)	0.6102 (2)	0.4140 (1)	36 (1)	244 (4)	52 (1)	46 (2)	−10 (1)	12 (3)
O(1)	0.9887 (2)	0.7592 (5)	0.1270 (2)	59 (2)	216 (11)	56 (3)	−112 (8)	−44 (4)	69 (9)
O(2)	0.0842 (2)	0.8004 (4)	0.3529 (2)	28 (2)	213 (11)	55 (2)	37 (7)	−5 (3)	−2 (8)
O(3)	0.5386 (2)	0.7239 (7)	0.4217 (3)	37 (2)	598 (18)	100 (3)	−50 (10)	−11 (4)	−36 (13)
O(4)	0.5056 (2)	0.3946 (7)	0.3224 (3)	55 (2)	657 (19)	125 (4)	173 (11)	−3 (5)	−220 (16)
N(1)	0.1803 (2)	0.7546 (6)	0.3537 (3)	36 (2)	138 (11)	43 (3)	14 (8)	7 (4)	8 (9)
N(2)	0.4810 (3)	0.5826 (8)	0.3690 (3)	40 (3)	422 (20)	60 (4)	11 (11)	4 (5)	8 (13)
C(1)	0.2121 (3)	0.5679 (7)	0.2870 (3)	38 (3)	182 (17)	56 (4)	−5 (9)	8 (5)	−63 (11)
C(2)	0.3100 (3)	0.5096 (8)	0.2903 (3)	40 (3)	254 (16)	59 (4)	28 (13)	13 (5)	−59 (16)
C(3)	0.3744 (3)	0.6446 (7)	0.3626 (3)	29 (2)	262 (17)	52 (4)	11 (10)	14 (5)	19 (13)
C(4)	0.3432 (3)	0.8352 (8)	0.4282 (4)	36 (3)	298 (20)	69 (4)	−21 (11)	−13 (5)	−91 (15)
C(5)	0.2451 (3)	0.8881 (8)	0.4243 (4)	45 (3)	202 (16)	64 (4)	−16 (11)	−5 (5)	−81 (14)
H(1)	0.149 (2)	0.478 (6)	0.243 (3)	4.9 (9)					
H(2)	0.332 (2)	0.359 (4)	0.236 (3)	4.2 (9)					
H(3)	0.391 (2)	0.936 (5)	0.491 (2)	4.2 (9)					
H(4)	0.214 (3)	0.036 (5)	0.473 (3)	6.5 (12)					
H(5)	0.960 (2)	0.594 (3)	0.119 (3)	4.8 (11)					
H(6)	0.028 (3)	0.777 (9)	0.205 (2)	7.7 (14)					

$g = 3.39 \times 10^{-5}$
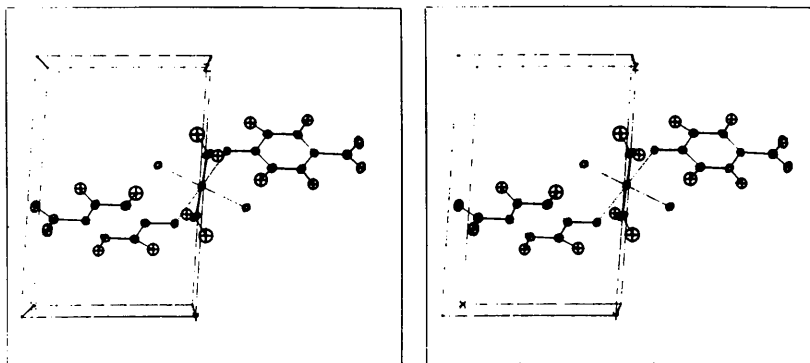
Fig. 1. Stereo pair of the $CuCl_2(H_2O)_2.2(C_5H_4N_2O_3)$ molecule with thermal ellipsoids.

weight was required to force the distance to remain close to the above prescribed values.

This new model was then refined subject to the constraining conditions mentioned above. This last refinement converged to final disagreement indices of $R = 0.043$ and $R_H = 0.032$. The final difference-Fourier yielded two peaks over 0.75 e.Å^{-3}. Both were at or near the copper ion positions and had peak values of 1.4 and 1.3 e.Å^{-3}.

The quantity minimized in the least-squares procedure was $\sum w(F_o - F_c^*)^2$ where

$$F_c^* = KF_c \Big/ \left\{1 + g\left[\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right] \mathrm{Lp}F_c^2\right\}^{1/2},$$

K is a scale factor, g is the extinction parameter (Larson, 1967), Lp is the Lorentz-polarization factor, F_c is the calculated structure factor and

$$w = \frac{4\mathrm{Lp}A}{K^2} \cdot \frac{N_T - N_B}{N_T + N_B + (0.02\ Npk)^2}$$

where A is the transmission factor, N_T is the total count, N_B the background and $Npk = N_T - N_B$ (Stout & Jensen, 1968). For unobserved reflections $w = 0.0$.

The largest $\Delta\xi_i/\sigma(\xi_i)$ after the final cycle of refinement was 0.003, and the average value was approximately 10^{-4} for all positional and thermal parameters. The maximum extinction correction of approximately 11% was applied to the (102) and (11$\bar{3}$) reflections.

The hydrogen scattering factor was taken from Stewart, Davidson & Simpson (1965); those for Cu^{2+}, Cl^-, O, N and C were obtained from Cromer & Waber (1965). Anomalous dispersion corrections were applied to the scattering factors of all atoms except hydrogen (Cromer & Liberman, 1970).

The observed and calculated structure factors are given in Table 1. Final atomic positions and thermal parameters are given in Table 2.

Discussion

A stereographic drawing of the basic molecular unit of the structure of $CuCl_2(H_2O)_2.2(C_5H_4N_2O_3)$ is shown

in Fig. 1. Bond lengths and intermolecular contact distances are given in Table 3 while bond angles are given in Table 4. There are two interesting features in this structure. First, the 4-nitropyridine N-oxide group is not directly bonded to the copper(II) ion as evidenced by the Cu(II)–O distance of 2.635 (2) Å. Instead, the structure is essentially a *trans* square-planar $CuCl_2$ $(H_2O_2)_2$ complex with very weak association in the axial direction to the co-crystallized amine-oxide. Second, there is an extensive two-dimensional hydrogen-bonding network involving the hydrogen atoms of the water molecules in the square-planar $CuCl_2(H_2O)_2$ group and the amine-oxide oxygen atoms on the 4-nitropyridine N-oxide molecules. This hydrogen bonding is shown in Fig. 2, which is a stereographic drawing of the contents of the unit cell where the hydrogen bonds are indicated by dotted lines.

Table 3. *Bond lengths and intermolecular distances*

Bond lengths		Intermolecular distances	
Cu—Cl	2.266 (1) Å	O(1)–O(2)	2.767 (4) Å
Cu—O(1)	1.950 (3)	O(1)–O(2)	2.719 (4)
Cu—O(2)	2.635 (2)	O(2)–H(5)	1.75
O(2)–N(1)	1.325 (3)	O(2)–H(6)	1.78
N(1)–C(1)	1.352 (4)	N(2)–O(3)	2.903 (5)
N(1)–C(5)	1.356 (4)	N(2)–O(4)	2.752 (5)
C(1)–C(2)	1.362 (5)	Cl—O(1)	2.963 (3)
C(2)–C(3)	1.368 (5)	O(1)–H(1)	2.90
C(3)–C(4)	1.359 (5)	O(3)–H(3)	2.28
C(4)–C(5)	1.358 (5)		
C(3)–N(2)	1.480 (5)		
N(2)–O(3)	1.223 (4)		
N(2)–O(4)	1.211 (4)		
O(1)–H(5)	0.99		
O(.)–H(6)	0.99		
C(1)–H(1)	1.08		
C(2)–H(2)	1.08		
C(4)–H(3)	1.08		
C(5)–H(4)	1.08		

It seems unusual that the amine-oxide does not coordinate directly to the metal ion. Direct bonding was observed in our past structure studies of these complexes (Watson, 1969, and references therein). Those studies indicate that the normal Cu–O bond length is

Fig. 2. Stereo view of the $CuCl_2(H_2O)_2.2(C_5H_4N_2O_3)$ structure. The Cu–O(2) bond and the hydrogen bonding are indicated by dotted lines. The view is approximately along x.

1·98 Å. The reason why the present situation is different is likely related to the hydrogen bonding in the crystal. Elongated axial bonds are the rule rather than the exception with six-coordinated copper(II) complexes. In general, the ligand bonded farthest from the copper(II) ion is the one with the smallest effective field strength (Wells, 1962), so we would normally expect the chloride ions to have the elongated bonds. However, in the present case the amine-oxide oxygen atom has sp^3 hybridization to facilitate its participation in the hydrogen-bonding scheme instead of its normal sp^2 hybridization, and this lowers its effective field strength so that it becomes the elongated ligand. The energetically favorable hydrogen-bonding scheme causes the elongation to reach the limits of what might be called bonding, but there is still a certain degree of association since the amine-oxide oxygen atoms are located very close to the ideal D_{4h} positions.

The hydrogen-bonding network is two-dimensional in nature and is perpendicular to the a direction. The two independent amine-oxide oxygen atom to water oxygen atom distances of 2·767 (4) and 2·719 (4) Å agree well with the average distance of 2·77 (13) Å between the hydrogen-bonding species O⁻ and H_2O as
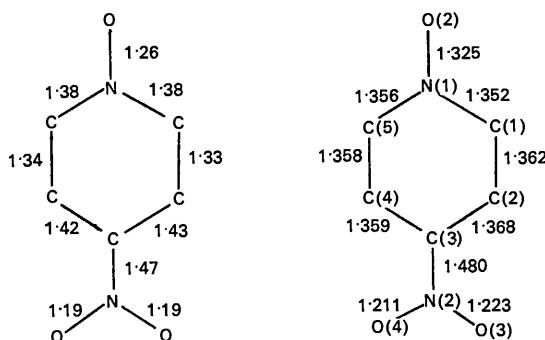
compiled by Wallwork (1962). The amine-oxide oxygen atom to hydrogen atom distances are 1·75 (3) and 1·78 (3) Å. The approximately tetrahedral sp^3 hybridized state of the amine-oxide oxygen atom is evidenced by its six bond angles whose extremes are 95·9 and 121·3° and whose average is 109 (5)°.

The geometrical features of the square planar $CuCl_2$ $(H_2O)_2$ group are very similar to those found in past X-ray and neutron diffraction studies (Harker, 1936; Sager & Watson, 1968; Peterson & Levy, 1957). The Cu–Cl and Cu–OH₂ bond lengths are 2·266 (1) and 1·950 (3) Å, respectively, both in good agreement with the averages from the above references, i. e. Cu–Cl, 2·28 Å and Cu–OH₂, 1·93 Å. The bond angles in the square plane are 91·0 (1) and 89·0 (1)°.

The structure details of the 4-nitropyridine N-oxide group may be compared with those of the free amine-oxide. A quinoidal nature was postulated for this molecule in the crystalline state by Eichhorn (1956). However, the hydrogen bonding or the weak association of the amine-oxide with the copper ion destroys the quinoidal form in the present case as is evidenced by a comparison of bond lengths in Fig. 3.

The amine-oxide N–O bond length is 1·325 (3) Å, a significant increase of over 0·06 Å as compared with the free ligand, indicating a significant decrease in the double-bond nature of this linkage. The C–C and C–N bond lengths are all approximately equal at 1·36 (1) Å.

A least-squares plane with unit weights was fitted to the atoms in the pyridine ring and the atom farthest from this plane is C(4) which is at a distance of 0·013 Å. Although this ring system is essentially planar, the nitro group is not coplanar with it. The plane of the nitro group makes a dihedral angle of approximately 10° with the plane of the pyridine ring.

All calculations performed in this study were done on a CDC 6600 computer using the Los Alamos Scientific Laboratory structure codes.

Fig. 3. A comparison of bond lengths (Å) from two independent studies of the 4-nitropyridine N-oxide molecule.

Table 4. *Bond angles* (°)

Cl—Cu—O(1)	91·0 (1)		O(4)–N(2)–C(3)	117·9 (4)
Cl—Cu—O(2)	88·8 (1)		N(1)–C(1)–C(2)	120·4 (4)
O(1)–Cu—O(2)	94·9 (1)		N(1)–C(1)–H(1)	109·0
H(5)–O(1)–H(6)	111·0		C(2)–C(1)–H(1)	130·0
O(2)–O(1)–O(2)	98·7 (1)		C(1)–C(2)–C(3)	118·2 (4)
Cu—O(2)–N(1)	109·9 (2)		C(1)–C(2)–H(2)	117·0
Cu—O(2)–O(1)	108·7 (1)		C(3)–C(2)–H(2)	124·0
Cu—O(2)–O(1)	110·8 (1)		N(2)–C(3)–C(2)	119·2 (4)
O(1)–O(2)–N(1)	113·1 (2)		N(2)–C(3)–C(4)	119·1 (4)
O(1)–O(2)–O(1)	90·0 (1)		C(2)–C(3)–C(4)	121·7 (4)
Cu—O(2)–H(5)	107·0		C(3)–C(4)–C(5)	119·0 (4)
Cu—O(2)–H(6)	111·0		C(3)–C(4)–H(3)	123·0
N(1)–O(2)–H(5)	121·0		C(5)–C(4)–H(3)	117·0
N(1)–O(2)–H(6)	111·0		N(1)–C(5)–C(4)	119·9 (4)
O(2)–N(1)–C(1)	119·1 (1)		N(1)–C(5)–H(4)	116·0
O(2)–N(1)–C(5)	120·0 (3)		C(4)–C(5)–H(4)	124·0
C(1)–N(1)–C(5)	120·8 (3)		O(1)–H(5)–O(2)	164·0
O(3)–N(2)–O(4)	124·2 (4)		O(1)–H(6)–O(2)	173·0
O(3)–N(2)–C(3)	117·9 (4)			

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The X-ray Crystal Structure of Diethylammonium Tetracyanopalladate

BY S. JÉRÔME-LERUTTE

Cristallographie Approfondie et Physique de l'État Solide, Université de Liège au Sart-Tilman, B-4000 Liège, Belgium

The crystal structure of $[(C_2H_5)_2NH_2]_2Pd(CN)_4$ has been determined by inspection of Patterson bi-dimensional synthesis $(hk0)$ and $(h0l)$ and by refinement of tridimensional intensity data. The space group of the primitive cell is $P\bar{1}$, but a more convenient double cell has been chosen whose space group is $C\bar{1}$, with $a = 15\cdot79 \pm 0\cdot01$, $b = 9\cdot10 \pm 0\cdot01$, $c = 6\cdot35 \pm 0\cdot01$ Å, $\alpha = 84°11' \pm 1'$, $\beta = 92°42' \pm 1'$, $\gamma = 94°5' \pm 1'$. The complex anion is centred on the origin and the distance between two heavy atoms is considerably larger than the corresponding one in the inorganic salts of the $Pd(CN)_4^{2-}$ anion. The latter has the well known square-planar configuration. The four CN ligands are bound to the adjacent cations by H bonds of the $N-H\cdots N$ type, so forming an infinite chain lying in the b axis direction. Neighbouring chains in the $(\bar{2}01)$ direction form planes whose inclination approximates that of the complex group. The stacking of the planes performs the tridimensional structure. The weak van der Waals bonds between chains and between planes is responsible for the important thermal motion of the atoms.

Introduction

The study of the inorganic salts of $Pd(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$ complexes in the solid state started with the structural works of Brasseur & de Rassenfosse (1935, 1936, 1937, 1938). Recently, the tridimensional X-ray analysis of $CaPd(CN)_4.5H_2O$ (Fontaine, 1968) and $Rb_2Pd(CN)_4.H_2O$ (Dupont, 1970) confirmed some structural features that are believed characteristic of the complex group present in the crystal lattice.

In the crystals just mentioned, the square-planar ions are always found in columns parallel to the c-axis direction. The shortest distance between two neighbouring heavy atoms varies from $3\cdot13$ Å in the heptahydrate of Mg^{2+} to $3\cdot72$ Å in the monohydrate of Rb^+. Optical properties such as fluorescence emission (Pt

compounds only), ultraviolet and visible absorption seem to be related to the heavy-metal spacing (Fontaine, Moreau & Simon, 1968). In order to increase the latter, we have replaced the metallic cation by a large organic one and we have studied the structure and properties of such a compound.

Previous preliminary research (Jérôme-Lerutte, 1967) allows us to choose the diethylammonium salt as a specially demonstrative example.

Crystal data

The cell dimensions and space group of the diethylammonium tetracyanoplatinate have already been published (Jérôme-Lerutte, 1967). The palladate is quite isotypic. It is triclinic; $a = 15\cdot79 \pm 0\cdot01$, $b =$