Acta Cryst. (1978). B**34**, 3594–3598

The Molecular and Crystal Structure of (Diethylenetriamine)(inosine)platinum(II) Dinitrate Monohydrate

By R. Melanson and F. D. Rochon

Département de Chimie, Université du Québec à Montréal, CP 8888, *Montréal H*3*C* 3*P*8, *Canada*

(*Received* 30 *May* 1978; *accepted* 25 *July* 1978)

[Pt(diethylenetriamine)(inosine)]$(NO_3)_2.H_2O$ forms monoclinic crystals, $a = 6{\cdot}949$ (3), $b = 10{\cdot}698$ (9), $c = 15{\cdot}402$ (9) Å, $\beta = 96{\cdot}12$ (4)°, $Z = 2$, space group $P2_1$. The structure was refined by block-diagonal least-squares analysis to a conventional R factor of 0·040 and R_w of 0·036. The coordination around the Pt atom is square-planar. Inosine is bonded to Pt through the N atom of the five-membered ring. The purine planar group makes an angle of 74° with the Pt coordination plane. The structure is stabilized by an extensive hydrogen-bonding system involving the nitrate ions and the water molecule.

Introduction

Recently, the crystal structure of the [Pt(ethylenediamine)(guanosine)$_2$]$^{2+}$ cation was reported (Bau, Gellert, Lehovec & Louie, 1977; Gellert & Bau, 1975). Intermolecular hydrogen bonding between the $-NH_2$ group of the ethylenediamine ligand and the carbonyl group of the guanine was observed. The authors suggested that this hydrogen bonding might be important in the Pt–DNA interaction in view of the fact that antitumour activity of *cis*-[Pt(amine)$_2X_2$] complexes decreases markedly along the series $NH_3 \sim NH_2R > NHR_2 \gg NR_3$ (Cleare & Hoeschele, 1973).

We are studying the crystal structures of compounds of the type [Pt(diethylenetriamine)(nucleoside)]$^{2+}$ partly to determine the role of the carbonyl group, if any, on the amine ligand. The study of the first compound [Pt(diethylenetriamine)(guanosine)]$(ClO_4)_2$ showed that the role of the diethylenetriamine (= dien) ligand in the hydrogen-bonding system with the carbonyl group is doubtful (Melanson & Rochon, 1978*b*). The carbonyl group of guanosine, O(6), is strongly intermolecularly hydrogen bonded with the amino group of guanosine, N(2). In our second study, the amino group of guanosine was eliminated. We therefore report now the molecular and crystal structure of [Pt(diethylenetriamine)(inosine)]$(NO_3)_2.H_2O$.

Experimental

[Pt(dien)(inosine)]$(NO_3)_2$ was prepared as follows. $AgNO_3$ was added to an aqueous solution of [Pt(dien)Cl]Cl. After filtering off the AgCl precipitate an equimolar amount of inosine was added to the [Pt(dien)H_2O]$(NO_3)_2$ solution. The mixture was stirred, filtered and allowed to slowly evaporate thereby yielding crystals of [Pt(dien)(inosine)]$(NO_3)_2.H_2O$.

A set of precession photographs indicated that the $0k0$, $k = 2n + 1$ reflections were systematic absences indicating the $P2_1$, or $P2_1/m$ space groups. Since the unit cell contained only two molecules and because of the presence of some asymmetric C atoms in the molecules, the centrosymmetric group $P2_1/m$ was eliminated. The $P2_1$ space group was later confirmed by the refinement of the structure.

Crystal data

$PtC_{14}H_{27}N_9O_{12}$, $M_r = 708{\cdot}52$, monoclinic $P2_1$, $a = 6{\cdot}949$ (3), $b = 10{\cdot}698$ (9), $c = 15{\cdot}402$ (9) Å, $\beta = 96{\cdot}12$ (4)°, $Z = 2$, $V = 1138$ (1) Å^3, $D_c = 2{\cdot}067$, $D_m = 2{\cdot}07$ (2) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 65·7 cm^{-1} and $t = 22$ °C.

Collection and reduction of intensity data

Using a Syntex $P\bar{1}$ diffractometer, the intensity data were collected from a crystal having 8 faces with approximate dimensions of 0·11 × 0·12 × 0·4 mm elongated along the a axis. A total of 3496 independent reflections were measured in the region of $2\theta < 60°$ by the $2\theta/\theta$ scan technique using Mo $K\alpha$ radiation. During the data collection, three standard reflections were measured after every 47 reflections. Their variations were less than 2% from their respective means. The reflections for which the intensity was less than $2{\cdot}5\sigma(I)$ were considered as unobserved. The standard deviation $\sigma(I)$ was calculated as was previously described (Melanson & Rochon, 1975). An absorption correction based on the equations of the crystal faces was applied to the 2727 observed reflections. The transmission factors varied from 0·488 to 0·559. The data were then corrected for Lorentz and polarization effects. The scattering factors of Cromer & Waber (1965) were used for Pt, Cl, O, N and C; those of Stewart, Davidson & Simpson (1965) were used for H. The anomalous dispersion terms (Cromer, 1965) of Pt and Cl were included in the calculations.

Structure determination

The position of the Pt atom was easily located from the three-dimensional Patterson map. The positions of all the other atoms, except the H atoms, were obtained by structure factor and Fourier map calculations. A residual peak was identified as a water molecule. The refinement of the parameters was carried out by the block-diagonal least-squares method. In the early stages of refinement, unit weight was assigned to all observed reflections. Later, individual weights were calculated according to the expression $1/w = a + bF_o + cF_o^2$. The constants of the equation were adjusted to make the distribution of $\langle w|\Delta F|^2\rangle$ almost constant with respect to $|F_o|$ and $\sin\theta/\lambda$ (a = 16·004, b = −0·425 and c = 0·00305). All the H atoms, except those of the hydroxyl groups and the water molecules, were fixed at their calculated positions (C—H = 0·95 Å, N—H = 0·85 Å) and assigned isotropic temperature factors of 6·0 Å^2. The refinement of the scale factor, the coordinates and anisotropic temperature factors of all the non-hydrogen atoms converged to $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ = 0·040 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0·036. The standard deviation of an observation of unit weight is 1·27. An attempt was made to locate the remaining H atoms from a final difference Fourier map. Only one H atom in the water molecule was located and refined. The torsion angles within the ribose segment confirmed the expected D configuration of the molecule. The final difference Fourier map did not show peaks higher than 0·8 e Å^{-3}.

The calculations were carried out with a Cyber 73 computer. The programs used have already been described (Melanson & Rochon, 1975).*

Results and discussion

The refined atomic parameters are listed in Table 1. A labelled stereoscopic view of the ion [Pt(dien)-(inosine)]$^{2+}$ is shown in Fig. 1. The bond lengths within the ion are shown on Fig. 2, and the bond angles on Fig. 3.

As expected, inosine is bonded to the Pt atom through the N(7) atom. The coordination around the Pt atom is square-planar. The weighted best plane was calculated through the five atoms. The deviations from this plane are: Pt, 0·0001; N(2), −0·0675; N(4), 0·0121; N(5), −0·0761 and N(7), 0·0027 Å. The angles around Pt are close to the expected 90 and 180° but there are some distortions. The N(2)—Pt—N(4) and

Table 1. *Final structure parameters* (×10^4) *with estimated standard deviations in parentheses*

	x	y	z
Pt	4045·9 (5)	3000	1547·3 (2)
N(1)	8797 (11)	−375 (9)	2311 (6)
N(2)	1758 (13)	2050 (10)	900 (7)
N(3)	6982 (12)	−1023 (9)	3426 (6)
N(4)	3465 (12)	4295 (9)	619 (6)
N(5)	6043 (15)	4208 (10)	2072 (6)
N(6)	6466 (13)	3933 (10)	8870 (6)
N(7)	4575 (12)	1645 (8)	2463 (6)
N(8)	850 (15)	4262 (11)	2816 (7)
N(9)	4191 (12)	320 (9)	3532 (5)
C(1)	1094 (16)	2775 (15)	117 (8)
C(2)	8413 (15)	−1129 (12)	2960 (7)
C(3)	1428 (16)	4126 (12)	236 (8)
C(4)	5838 (14)	−44 (10)	3194 (6)
C(5)	6092 (13)	783 (9)	2516 (6)
C(6)	7680 (13)	655 (10)	2003 (7)
C(7)	4142 (17)	5493 (12)	992 (8)
C(8)	3493 (16)	1322 (10)	3079 (7)
C(9)	6037 (20)	5348 (12)	1459 (8)
C(1′)	3334 (15)	−386 (10)	4231 (7)
C(2′)	4462 (14)	−174 (12)	5130 (7)
C(3′)	3318 (17)	932 (11)	5470 (7)
C(4′)	1302 (16)	709 (11)	5083 (7)
C(5′)	120 (20)	1896 (14)	4915 (9)
O(1)	7609 (14)	3865 (12)	8318 (6)
O(2)	4968 (13)	3360 (11)	8800 (7)
O(3)	6847 (18)	4597 (12)	9508 (7)
O(4)	2197 (17)	4339 (14)	3387 (7)
O(5)	−79 (13)	3273 (17)	2703 (7)
O(6)	8068 (11)	1264 (9)	1385 (5)
O(7)	381 (16)	5152 (11)	2351 (8)
O(8)	6990 (18)	2122 (12)	6972 (7)
O(1′)	1449 (10)	91 (8)	4261 (5)
O(2′)	4335 (13)	−1255 (8)	5620 (5)
O(3′)	3520 (14)	983 (10)	6390 (6)
O(5′)	−1822 (15)	1628 (11)	4586 (9)

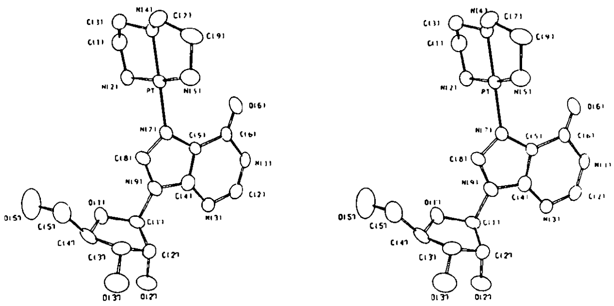

Fig. 1. Stereoscopic view of the [Pt(dien)(inosine)]$^{2+}$ ion.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33836 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

N(4)—Pt—N(5) angles (84·8, 85·4°) are smaller than the N(2)—Pt—N(7) and N(5)—Pt—N(7) angles (93·3, 96·6°). The N(2)—Pt—N(5) angle (169·3°) is also smaller than expected. A slight strain caused by the tridentate ligand is responsible for these deviations from the ideal square-planar coordination. The Pt—N bond lengths (2·00–2·05 Å) are normal and agree well with the published results (Bau *et al.*, 1977; Melanson & Rochon, 1975, 1978*a*,*b*; Louie & Bau, 1977; Cramer & Dahlstrom, 1977; Lock, Bradford, Faggiani, Speranzini, Turner & Zvagulis, 1977).

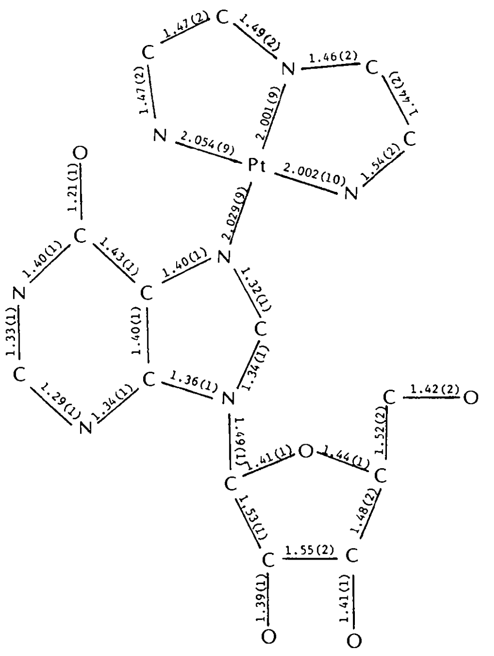

Fig. 2. Bond lengths within the [Pt(dien)(inosine)]$^{2+}$ ion (Å).

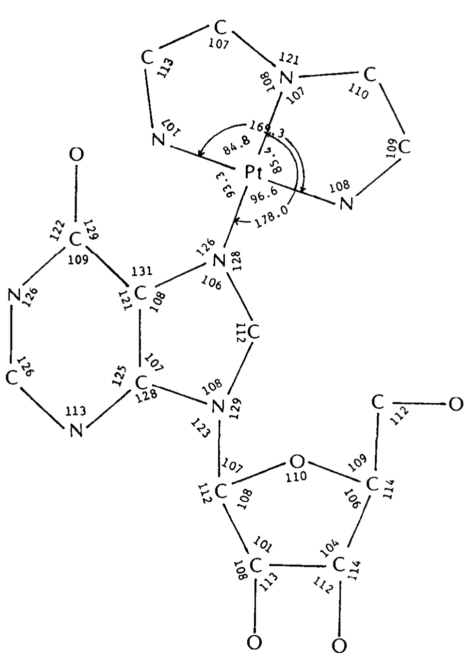

Fig. 3. Bond angles within the [Pt(dien)(inosine)]$^{2+}$ ion (°). The standard deviations are 0·4 to 0·7° for angles involving the Pt atom and 1° for other angles.

The purine group is planar. The weighted best plane was calculated through the nine atoms. The deviations from this plane are: N(7), 0·004; N(9), −0·002; N(3), 0·004; N(1), −0·002; C(8), 0·012; C(4), −0·018; C(5), −0·010; C(6), 0·002 and C(2), 0·014 Å. The deviations of the substituents on the ring are as follows: O(6), 0·049 and C(1′), 0·098 Å (e.s.d. = 0·009 to 0·011 Å). The purine planar group makes an angle of 74·5° with the Pt coordination plane.

The bond lengths in the purine group are similar to those found in inosine rings mentioned in a review by Voet & Rich (1970). They are almost identical to those found in inosine (Munns & Tollin, 1970) and in inosine dihydrate (Thewalt, Bugg & Marsh, 1970). The bond angles are also normal and agree well with the published results mentioned above. The bond angles within the five-membered ring vary from 106 to 112°. In the six-membered ring, the range is from 109 to 126°. As Singh (1965) has pointed out, the internal ring angle at a N atom is greater if the N atom is covalently bound to an extra-annular H atom than if the N atom has no extra-annular attachment. Here C(6)—N(1)—C(2) = 126° while C(2)—N(3)—C(4) = 113°.

The glycosyl bond is normal (1·49 Å) (Voet & Rich, 1970). The angles in the ribose ring are close to the tetrahedral values. O(1′), C(1′), C(2′) and C(4′) are coplanar within 2σ and C(3′) is 0·51 Å distant from that plane on the same side as C(5′) and N(9). This corresponds to the C(3′) *endo* conformation. The dihedral angle between the purine and the ribose planes is 117·7°.

The torsion angles within the ribose group are listed in Table 2. The conventions suggested by Sundaralingam (1969) and by Shefter & Trueblood (1965) have been used. The torsion angle O(1′)C(1′)N(9)-C(8) (φ_{CN}) = 8° and defines an *anti* conformation about

Table 2. *Torsion angles* (°) *in the ribose group*

The conventions suggested by Sundaralingam (1969) and by Shefter & Trueblood (1965) have been used.

O(1′)—C(1′)—N(9)—C(8)	8	φ_{CN} (*anti*)
O(1′)—C(1′)—N(9)—C(4)	−166	
O(1′)—C(4′)—C(5′)—O(5′)	65	φ_{OO} (*gauche*)
C(3′)—C(4′)—C(5′)—O(5′)	−177	φ_{OC} (*trans*)
C(2′)—C(1′)—O(1′)—C(4′)	5	τ_0
C(3′)—C(2′)—C(1′)—O(1′)	−24	τ_1
C(4′)—C(3′)—C(2′)—C(1′)	33	τ_2
O(1′)—C(4′)—C(3′)—C(2′)	−31	τ_3
C(1′)—O(1′)—C(4′)—C(3′)	16	τ_4
O(2′)—C(2′)—C(3′)—O(3′)	40	

the glycosidic bond. The C(5′)–O(5′) bond is in a *gauche–trans* conformation relative to the ribose group: $\varphi_{OO} = 65°$ and $\varphi_{OC} = -177°$.

The bond lengths and angles in the nitrate ions are shown in Table 3. The ions are planar. The bond distances vary from 1·20 to 1·24 Å. The bond angles are close to the theoretical values (119 to 122°).

A packing diagram is shown in Fig. 4. In most nucleoside crystal structures, base stacking plays an important role. In this structure, base stacking is not an important packing factor probably because of the presence of the nitrate ions. This was also observed in the structure of $[Pt(dien)(guanosine)](ClO_4)_2$ where the perchlorate ions are located between the bases (Melanson & Rochon, 1978*b*). Hydrogen bonding is the predominant packing factor in this structure. The most important hydrogen bonds are listed in Table 4.

All the H atoms attached to the O and N atoms of the inosine group are involved in the hydrogen-bonding system. N(1) and O(2′) are hydrogen bonded to O(1) and O(4) respectively of the nitrate ions. O(5′)–H of each ribose group is intermolecularly hydrogen bonded to O(2′). The water molecule O(8) plays an important role in stabilizing the structure. It forms a hydrogen bond with O(7) of the nitrate ion. A second hydrogen bond is formed between the H_2O molecule and O(3′). The bond could be either O(8)–H···O(3′) or O(3′)–H···O(8). In both cases, the angles are favourable since C(3′)–O(3′)···O(8) = 109° and O(7)···O(8)···O(3′) = 102°.

The dien ligand is also involved in the hydrogen bonding. N(5) and N(2) form hydrogen bonds with O(3) and O(5) respectively of the nitrate ions. N(2) might form a second intermolecular hydrogen bond with O(6). The distance is reasonable (2·87 Å) but the angles are less favourable [C(1)–N(2)···O(6) = 99° and Pt–N(2)···O(6) = 133°].

The suggestion that the intermolecular hydrogen bond between the $-NH_2$ of the ethylenediamine ligand and the carbonyl group found in the $[Pt(ethylenediamine)(guanosine)_2]^{2+}$ ion might be an important factor in the Pt–DNA interaction (Bau, Gellert, Lehovec & Louie, 1977; Gellert & Bau, 1975) is not confirmed in the present structure. The role of the carbonyl group in this structure seems less important than the role of the

Table 3. *Bond distances* (Å) *and bond angles* (°) *in the nitrate ions*

N(6)–O(1)	1·23 (1)	N(8)–O(4)	1·22 (2)
N(6)–O(2)	1·20 (1)	N(8)–O(5)	1·24 (2)
N(6)–O(3)	1·22 (2)	N(8)–O(7)	1·22 (2)
O(1)–N(6)–O(2)	122 (1)	O(4)–N(8)–O(5)	121 (1)
O(1)–N(6)–O(3)	120 (1)	O(4)–N(8)–O(7)	121 (1)
O(2)–N(6)–O(3)	119 (1)	O(5)–N(8)–O(7)	119 (1)

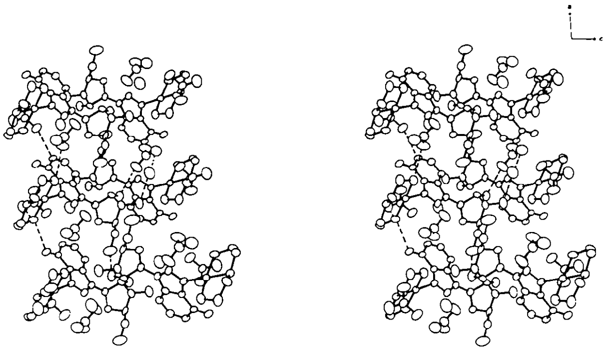

Fig. 4. Stereoscopic diagram of the packing in the $[Pt(dien)(inosine)](NO_3)_2.H_2O$ crystal.

Table 4. *Distances and angles involved in hydrogen bonds*

	Transformation (on third atom)	Distance (Å)		Angle (°)
N(1)–H···O(1) (nitrate)	$2-x, y-\frac{1}{2}, 1-z$	2·89 (1)	C(6)–N(1)···O(1) C(2)–N(1)···O(1)	125 (1) 109 (1)
O(2′)–H···O(4) (nitrate)	$1-x, y-\frac{1}{2}, 1-z$	2·79 (1)	C(2′)–O(2′)···O(4)	91 (1)
O(5′)–H···O(2′)	$-x, \frac{1}{2}+y, 1-z$	2·86 (1)	C(5′)–O(5′)···O(2′)	115 (1)
Involving the water molecule:				
O(8)–H···O(7) (nitrate)	$1-x, \frac{1}{2}-y, 1-z$	2·91 (2)		
O(8)–H···O(3′) or O(3′)–H···O(8)	x,y,z	2·76 (2)	O(7)···O(8)···O(3′) C(3′)–O(3′)···O(8)	102 (1) 109 (1)
Involving the dien ligand:				
N(5)–H···O(5) (nitrate)	$1+x, y, z$	2·94 (1)	C(9)–N(5)···O(5) Pt–N(5)···O(5)	115·(1) 119 (1)
N(2)–H···O(3) (nitrate)	$1-x, y-\frac{1}{2}, 1-z$	2·89 (2)	C(1)–N(2)···O(3) Pt–N(2)···O(3)	113 (1) 107 (1)
N(2)–H···O(6) (doubtful)	$x-1, y, z$	2·87 (1)	C(1)–N(2)···O(6) Pt–N(2)···O(6) O(6)···N(2)···O(3)	99 (1) 133 (1) 97 (1)

water molecule and of the nitrate ions in stabilizing the structure. It is therefore impossible to evaluate at the moment the importance of hydrogen bonding between the amine ligand and the nucleoside in the Pt–DNA interaction. More data are needed in order to discuss in more detail this possible interaction mechanism of platinum drugs.

Grateful acknowledgements are made to the National Research Council of Canada and to the Cancer Research Society Inc., for financial support and to Johnson Matthey & Co. Limited for the gift of potassium chloroplatinite.

References

BAU, R., GELLERT, R. W., LEHOVEC, S. M. & LOUIE, S. (1977). *J. Clin. Hematol. Oncol.* **7**, 51–62.
CLEARE, M. J. & HOESCHELE, J. D. (1973). *Bioinorg. Chem.* **2**, 187–210.
CRAMER, R. E. & DAHLSTROM, P. L. (1977). *J. Clin. Hematol. Oncol.* **7**, 330–337.
CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
DONOHUE, J. & TRUEBLOOD, K. N. (1960). *J. Mol. Biol.* **2**, 363–371.
GELLERT, R. W. & BAU, R. (1975). *J. Am. Chem. Soc.* **97**, 7379–7380.
LOCK, C. J. L., BRADFORD, J., FAGGIANI, R., SPERANZINI, R. A., TURNER, G. & ZVAGULIS, M. (1977). *J. Clin. Hematol. Oncol.* **7**, 63–78.
LOUIE, S. & BAU, R. (1977). *J. Am. Chem. Soc.* **99**, 3874–3876.
MELANSON, R. & ROCHON, F. D. (1975). *Can. J. Chem.* **53**, 1139–1143.
MELANSON, R. & ROCHON, F. D. (1978*a*). *Inorg. Chem.* **17**, 679–681.
MELANSON, R. & ROCHON, F. D. (1978*b*). *Can. J. Chem.* In the press.
MUNNS, A. R. I. & TOLLIN, P. (1970). *Acta Cryst.* B**26**, 1101–1113.
SHEFTER, E. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 1067–1077.
SINGH, C. (1965). *Acta Cryst.* **19**, 861–864.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
SUNDARALINGAM, M. (1969). *Biopolymers*, **7**, 821–860.
THEWALT, U., BUGG, C. E. & MARSH, R. E. (1970). *Acta Cryst.* B**26**, 1089–1100.
VOET, D. & RICH, A. (1970). *Prog. Nucleic Acid Res. Mol. Biol.* **10**, 183–265.

Acta Cryst. (1978). B**34**, 3598–3601

Structure Cristalline du Bromométhanesulfonate d'Argent(I): Ag($BrCH_2SO_3$)

PAR FRANÇOIS CHARBONNIER, RENÉ FAURE ET HENRI LOISELEUR

Laboratoire de Chimie Analytique II, *Université Claude Bernard–Lyon* I, 43 *boulevard du* 11 *novembre* 1918, 69621 *Villeurbanne, France*

(*Reçu le* 17 *avril* 1978, *accepté le* 11 *juillet* 1978)

Silver(I) bromomethanesulphonate, Ag($BrCH_2SO_3$), crystallizes in space group *Pnma* with cell parameters $a = 13\cdot420$ (2), $b = 7\cdot569$ (2), $c = 4\cdot996$ (1) Å and $Z = 4$. Mo $K\bar{\alpha}$ intensities were collected on an automatic four-circle diffractometer and the structure was determined by means of the Patterson function and Fourier syntheses. An anisotropic full-matrix least-squares refinement was performed yielding a final R of 0·053 for the 623 reflexions actually measured. The Ag atoms are located at $\bar{1}$ centres 4(*a*). The bromomethanesulphonato group acts as a hexacoordinating ligand, the symmetry being C_s. Each ligand coordinates four Ag atoms by means of its three sulphonic O atoms and the other two by means of its Br atom. Thus each Ag atom is octahedrally surrounded by four O atoms, in a nearly square configuration, belonging to four different ligands [Ag—O = 2·354 (4) and 2·486 (4) Å], and by two Br atoms, in axial positions, belonging to two other ligands [Ag—Br = 2·970 (5) Å].

Introduction

Une étude structurale des complexes de l'argent(I) avec divers coordinats organiques a été entreprise. Nous avons décrit récemment la structure du méthanesulfonate d'argent, Ag(CH_3SO_3) (Charbonnier, Faure & Loiseleur, 1977). Dans celle-ci le groupement méthanesulfonato grâce à ses atomes d'oxygène se montre pentacoordinant vis-à-vis des atomes d'argent de sorte que le polyèdre de coordination du métal est une bipyramide trigonale dissymétrique. La structure du bromométhanesulfonate d'argent montre une