Synthesis and Crystal Structure of Bis(1,4,7-triazacyclononane-*NN'*)-platinum(II) Dibromide Dihydrate † and its Facile Oxidation by Oxygen: Characterisation of Bis(1,4,7-triazacyclononane-*NN'N''*)platinum(IV) Tetraperchlorate

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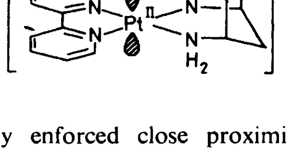
1,4,7-Triazacyclononane (L) reacts with $[PtCl_4]^{2-}$ in aqueous solution to form a variety of complexes containing the potentially tridentate amine as a uni- or bi-dentate ligand. The complex $[Pt^{II}(L)_2]Br_2{\cdot}2H_2O$ containing two bidentate ligands was oxidised by molecular oxygen in aqueous solution to form the octahedral cation $[Pt^{IV}(L)_2]^{4+}$. ^1H N.m.r. spectra indicated that the two cyclic amines were co-ordinated *via* six N-donor atoms. The *X*-ray crystal structure of $[Pt^{II}(L)_2]Br_2{\cdot}2H_2O$ was determined. The complex crystallises in space group $P2/n$, with $a = 8.990(2)$, $b = 7.987(2)$, $c = 14.424(4)$ Å, $\beta = 93.34(2)°$, and $Z = 2$. 1 419 Independent reflections with $I \geqslant 2.5\sigma(I)$ gave $R = 0.0335$. The geometry of the complex cation is essentially square planar with one unco-ordinated nitrogen atom per bound amine ligand.

Square-planar complexes of platinum(II) containing ligands with nitrogen and/or oxygen donor atoms are known to be oxidized by strong oxidants such as chlorine or hydrogen peroxide affording octahedral complexes of platinum(IV).[1] An interesting reaction was reported in 1977 where this $Pt^{II} \longrightarrow Pt^{IV}$ conversion was achieved under very mild conditions [2] (' probably air oxidation '[2]), see equation (i)

$$[Pt^{II}(bipy)Cl_2] + tach \xrightarrow[O(?)]{H_2O} [Pt^{IV}(tach - H_2)(bipy)(H_2O)]Cl_2 \quad (i)$$

where tach = *cis,cis*-1,3,5-triaminocyclohexane and bipy = 2,2'-bipyridine. The ligand tach was shown to be co-ordinated *via* three nitrogen atoms as the dianion (tach − H_2) (two NH^- groups) to Pt^{IV}, which is surrounded in a distorted octahedral manner by nitrogen atoms of the tridentate amine and of the bidentate bipy and one water molecule. We felt that this unusual oxidation might be accompanied by a precursor complex of platinum(II) with a square-planar configuration containing a bidentate *cis,cis*-1,3,5-triaminocyclohexane ligand (see below).



The sterically enforced close proximity of one unco-ordinated NH_2 group of the potentially tridentate ligand to the filled d_{z^2} orbital of the Pt^{II} centre may then facilitate the removal of two electrons from this orbital with concomitant expansion of the first co-ordination sphere of the platinum centre. To test this hypothesis we decided to study the reaction of 1,4,7-triazacyclononane (L) with $[PtCl_4]^{2-}$ in aqueous solution. This cyclic triamine is known to form extremely stable octahedral complexes; the three nitrogen atoms occupying exclusively facial positions.[3,4]

Results and Discussion

Upon mixing aqueous solutions containing equimolar amounts of 1,4,7-triazacyclononane (L) (pH 7) and K_2-$[PtCl_4]$, pink crystals precipitate immediately at room temperature. The u.v.-visible spectrum of an aqueous solution of this material is identical to that of the $[PtCl_4]^{2-}$ chromophore. Elemental analysis and spectroscopic behaviour indicate that the salt $[H_2L][PtCl_4]$ (1), containing the dihydro-cation of the triamine, is formed. Prolonged heating at 80 °C of an aqueous suspension of (1) yields a yellow solution. After adjustment to pH 9—10 and addition of NaBr yellow crystals precipitate upon cooling to 5 °C. Complex (2) (Scheme 1) is formed. If this reaction is carried out at lower pH values (7 or 5) different yellow bromide salts can be obtained, (3) and (4). The palladium analogues of complexes (2) and (3) have been described by Nonoyama and Nonoyama.[5] Complexes (2) and (3) contain a bidentate amine ligand, the unco-ordinated nitrogen of which may be protonated as in (3) or deprotonated as in (2). Assuming a square-planar environment of the platinum(II) centre we suggest that the amine ligand in (4) is only unidentate. Complexes (2), (3), and (4) are not sensitive to oxygen under the above reaction conditions.

The reaction of $[PtCl_4]^{2-}$ with an excess of 1,4,7-triazacyclononane trihydrobromide (1 : 3) (pH 8) at 90 °C under oxygen-free conditions yields a yellow solution from which, upon addition of NaBr and cooling, colourless crystals of (5) precipitate. The elemental analysis reveals the ratio Pt : L : Br : H_2O of 1 : 2 : 2 : 2. The *X*-ray crystal structure of (5)

$$[PtCl_4]^{2-} + 2L \xrightarrow[\text{pH 8}]{\text{NaBr, 90 °C}} [Pt^{II}(L)_2]Br_2{\cdot}2H_2O \quad (ii)$$

shows that the oxidation state of the platinum centre has not changed. Figure 1 shows an ORTEP view of the complex cation with the atom-numbering scheme used. The atomic co-ordinates, bond lengths and selected angles are given in Tables 1 and 2, respectively.

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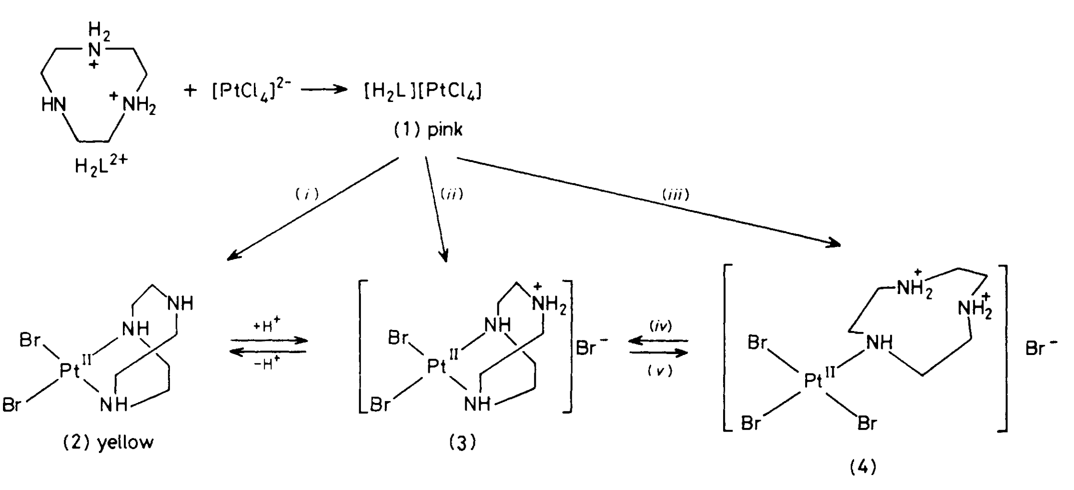
† *Supplementary data available* (No. SUP 23638, 12 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



Scheme 1. (*i*) 80 °C, H_2O, Br^-, pH 10; (*ii*) 90 °C, H_2O, Br^-, pH 7; (*iii*) 90 °C, H_2O, Br^-, pH 5; (*iv*) 70 °C, pH 7; (*v*) pH 3

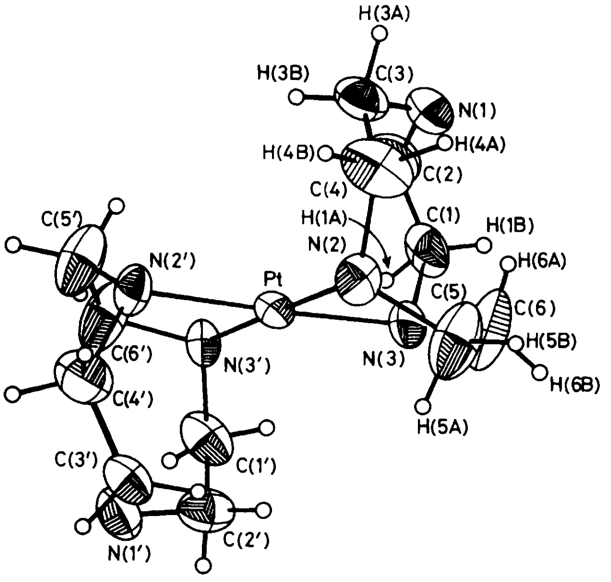


Figure 1. Perspective view of the $[Pt^{II}(L)_2]^{2+}$ cation of (5) showing the atom-labelling scheme. The cation has crystallographically imposed C_2 symmetry (primes represent the positions: $\frac{1}{2} - x$, y, $\frac{1}{2} - z$)

Table 1. Atomic co-ordinates for $[Pt(L)_2]Br_2{\cdot}2H_2O$ (5) with estimated standard deviations in parentheses

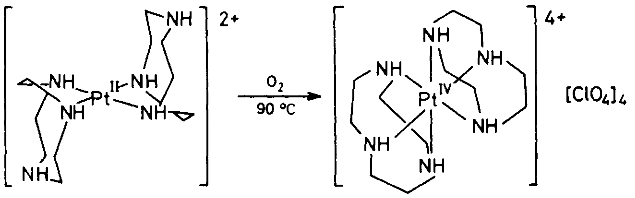
Atom	*x*	*y*	*z*
Pt	0.2500	0.659 16(6)	0.2500
Br	0.183 1(1)	0.163 2(2)	0.420 5(1)
N(1)	−0.098 8(9)	0.665(1)	0.118 7(6)
N(2)	0.091 3(9)	0.488(1)	0.288 6(6)
N(3)	0.089 1(8)	0.832(1)	0.282 8(5)
C(1)	0.017(1)	0.916(1)	0.199 9(10)
C(2)	−0.004(1)	0.817(2)	0.114(1)
C(3)	−0.022(1)	0.504(2)	0.120 2(8)
C(4)	−0.008(2)	0.414(1)	0.212(1)
C(5)	0.008(2)	0.578(2)	0.360 5(9)
C(6)	−0.030(1)	0.746(2)	0.334(1)
O	0.199(1)	0.825(1)	0.574 5(8)

Table 2. Bond lengths (Å) and selected angles (°) for $[Pt(L)_2]Br_2{\cdot}2H_2O$ (5)

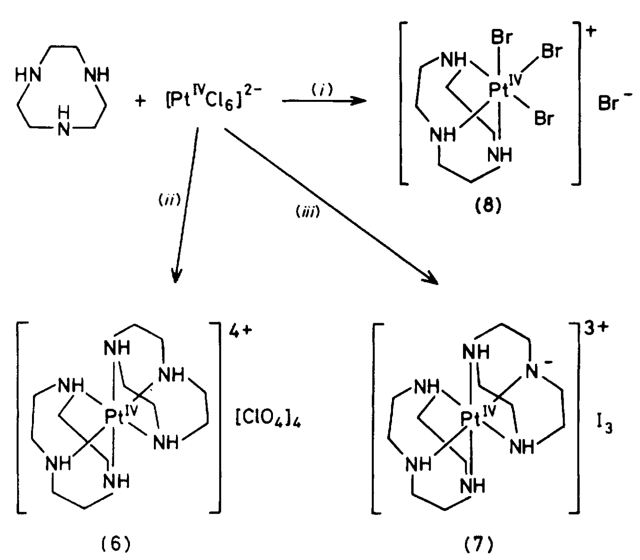
Pt–N(2)	2.077(9)	N(2)–Pt–N(3)	83.0(3)
Pt–N(3)	2.074(9)	N(3)–Pt–N(3')	96.5(5)
N(1)–C(2)	1.49(2)	N(3)–Pt–N(2')	177.6(3)
N(1)–C(3)	1.46(2)	N(2)–Pt–N(2')	97.6(5)
N(2)–C(4)	1.50(1)		
N(2)–C(5)	1.50(1)		
N(3)–C(1)	1.49(2)		
N(3)–C(6)	1.50(2)		

The geometry about the platinum is best described as slightly distorted square planar. The cation has crystallographically imposed C_2 symmetry; the dication contains a two-fold axis. The two amine ligands are co-ordinated to Pt^{II} *via* two nitrogens, respectively. The ligand is bidentate. The unco-ordinated nitrogens are bent away from the *z* axis of the complex in the solid state. The bromide ions are not bound to platinum. The Pt–N bond distances agree well with those found previously in $[Pt^{II}(dien)Cl]^+$ (dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$).[6] Thus it is evident that the platinum(II) centre has not expanded its first co-ordination sphere despite two sterically easily available unco-ordinated nitrogen donors.

Prolonged heating (90 °C) of an aqueous solution of (5) (pH 7) and at the same time bubbling air through the solution (20 h) slowly effects the oxidation of Pt^{II} to Pt^{IV}. A yellow tetraperchlorate, (6), may be precipitated from such solutions (pH 6) or at pH 11 an orange tri-iodide, (7). Identical products are obtained using potassium hexachloroplatinate(IV) as a starting material (Scheme 2) and excess 1,4,7-triazacyclononane. In addition, complex (8) is formed using a L : $[PtCl_6]^{2-}$ ratio of 1 : 1.



(5) (6)



Scheme 2. (*i*) $n = 1$, 80 °C, NaBr; (*ii*) $n = 2$, 80 °C, $NaClO_4$, pH 7; (*iii*) $n = 2$, 80 °C, NaI, pH 11

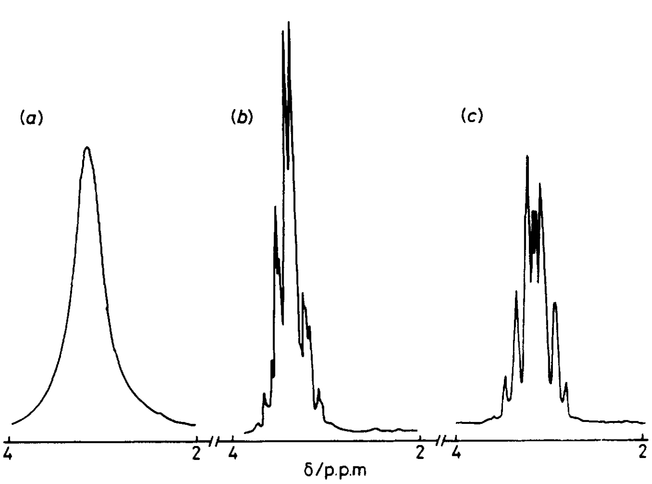


Figure 2. ^1H N.m.r. spectra (80 MHz) of cations (*a*) $[Pt^{II}(L)_2]^{2+}$, (*b*) $[Pt^{IV}(L)_2]^{4+}$, and (*c*) $[Co^{III}(L)_2]^{3+}$ in D_2O (CH_2 signals are shown only)

The u.v.-visible spectrum of (6) in aqueous solution exhibits a well resolved maximum at 240 nm ($\varepsilon = 1.3 \times 10^3$ dm^3 mol^{-1} cm^{-1}) in contrast to that of the cation $[Pt(en)_3]^{4+}$ (en = $H_2NCH_2CH_2NH_2$).[7] Complex (5) exhibits a distinctly different u.v.-visible spectrum with a maximum at 295 nm ($\varepsilon = 94$ dm^3 mol^{-1} cm^{-1}).

The most convincing evidence that (6) has an N_6-donor set was obtained from its ^1H n.m.r. spectrum. Figure 2 shows the ^1H n.m.r. spectra of the cations of complexes (5) and (6) and of the well characterized $[Co(L)_2]Br_3$ [8] measured in D_2O (pH 7). Only the resonances of the methylene protons are detected. Since in $[Co(L)_2]^{3+}$ all six nitrogens of the ligands are co-ordinated to the cobalt(III) centre the $-CH_2-CH_2-$ groups of the ligands adopt a sterically rigid conformation both in the solid state and in solution. Consequently a rather complex signal for the methylene protons is observed at room temperature. A near identical spectrum is observed for (6). Therefore, a rigid conformation of the ligands in (6) is suggested. Interestingly, the ^1H n.m.r. spectrum of (5) in D_2O at room temperature exhibits only one broad unresolved signal indicating fluxional behaviour of some kind for the *NN'*-co-ordinated ligands in (5). It is therefore conceivable that in solution conformations where the unco-ordinated N atoms approach the *z* axis of the platinum(II) centre quite closely are present. This may cause an enhanced oxidizability.

Consistent with the observation that primary and secondary amines and ammine ligands of Pt^{IV} complexes are rather acidic,[9] a deprotonated form of $[Pt^{IV}(L)_2]^{4+}$ has been isolated as the tri-iodide, (7), from alkaline solutions (pH 11) of (6).

Experimental

Preparation of Complexes.—All reactions were carried out in aqueous solution. Infrared spectra were measured in the range 400—4 000 cm^{-1} as KBr plates using a Beckman Acculab 10 instrument. ^1H N.m.r. spectra were recorded as D_2O solutions using a Bruker WP-80 instrument. The ligand 1,4,7-triazacyclononane trihydrobromide was prepared according to procedures described previously.[10,11]

*7-Aza-*1,4-*diazonia-*1,4-*dihydrocyclononane tetrachloroplatinate*(II) (1). 1,4,7-Triazacyclononane trihydrobromide (0.2 g) was dissolved in water (20 cm^3) and neutralized with 20% sodium hydroxide. To this solution sodium tetrachloroplatinate(II) (0.21 g) dissolved in water (20 cm^3) was added at room temperature. Precipitated pink crystals were filtered off, washed with ethanol and diethyl ether and air dried (yield 0.20 h, 87%) (Found: C, 14.9; H, 3.8; Cl, 30.0; N, 9.0; Pt, 41.8. $C_6H_{17}Cl_4N_3Pt$ requires C, 15.4; H, 3.7; Cl, 30.2; N, 9.0; Pt, 41.7%).

Dibromo(1,4,7-*triazacyclononane*-NN')*platinum*(II) (2). To an aqueous solution (50 cm^3) of 1,4,7-triazacyclononane trihydrobromide (1 g) which was neutralized with sodium hydroxide, solid potassium tetrachloroplatinate(II) (1.1 g) was added. The pink precipitate dissolved upon heating to 80 °C affording a clear yellow solution. Sodium bromide (3 g) was added and the pH was adjusted to 9—10 by adding 0.1 mol dm^{-3} NaOH dropwise. Upon cooling yellow crystals precipitated which were filtered off, washed with ethanol and diethyl ether and air dried (yield 1.1 g, 85%) (Found: C, 14.9; H, 3.1; Br, 32.9; N, 8.7; Pt, 39.8. $C_6H_{15}Br_2N_3Pt$ requires C, 14.9; H, 3.1; Br, 33.0; N, 8.7; Pt, 40.3%).

Dibromo(4,7-*diaza*-1-*azonia*-1-*hydrocyclononane*-N^4N^7)-*platinum*(II) *bromide* (3). The above procedure for the preparation of (2) was closely followed but without the addition of NaOH. Instead the neutral reaction solution (pH 7) was cooled to 0 °C. Pale yellow crystals formed which were filtered off, washed with ethanol and diethyl ether and air dried (yield 1 g, 70%) (Found: C, 12.6; H, 2.8; Br, 42.2; N, 7.3. $C_6H_{16}Br_3N_3Pt$ requires C, 12.8; H, 2.9; Br, 42.4; N, 7.4%).

(7-*Aza*-1,4-*diazonia*-1,4-*dihydrocyclononane*-N^7)*tribromoplatinum*(II) *bromide* (4). The reaction was carried out as described for (2) but instead of adding sodium hydroxide the pH of the solution was slowly lowered at 90 °C with concentrated HBr to 5. Upon cooling (0 °C) yellow crystals precipitated which were filtered off, washed with ethanol and diethyl ether and air dried (yield 1.2 g, 67%) (Found: C, 11.1; H, 2.6; Br, 49.1; N, 6.4. $C_6H_{17}Br_4N_3Pt$ requires C, 11.2; H, 2.6; Br, 49.5; N, 6.5%).

Bis(1,4,7-*triazacyclononane*-NN')*platinum*(II) *dibromide dihydrate* (5). The pH of a solution of 1,4,7-triazacyclononane trihydrobromide (1 g) in water (10 cm^3) was adjusted with 1 mol dm^{-3} NaOH to 9. Solid potassium tetrachloroplatinate(II) (0.3 g) was added. A clear yellow solution was obtained after gentle warming to 40 °C for 30 min. Sodium bromide (3.0 g) was added and the solution was kept at 0 °C for 12 h.

Colourless crystals precipitated which were filtered off, washed with ethanol and diethyl ether and air dried (yield 0.33 g, 71%) (Found: C, 22.5; H, 5.1; N, 13.1. $C_{12}H_{34}Br_2N_3O_2Pt$ requires C, 22.2; H, 5.3; N, 12.9%).

Bis(1,4,7-*triazacyclononane*-NN′N″)*platinum*(IV) *tetraperchlorate* (6). To an aqueous solution (20 cm^3) of potassium tetrachloroplatinate(II) (0.5 g), sodium perchlorate (3 g) was added. The solution was quickly heated to 80 °C and cooled in an ice-bath. Precipitated potassium perchlorate was then removed by filtration. To the refluxing solution 1,4,7-triazacyclononane trihydrobromide (1.5 g) dissolved in water (40 cm^3) was added dropwise. A constant stream of air was passed through the refluxing solution for 20 h. The cooled solution (0 °C) was kept for 2 d in the refrigerator during which time yellow crystals precipitated which were filtered off, washed with ethanol and diethyl ether and air dried (yield 0.65 g, 64%) (Found: C, 16.7; H, 3.6; ClO_4, 46.3; N, 9.7. $C_{12}H_{30}Cl_4N_6O_{16}Pt$ requires C, 16.9; H, 3.6; ClO_4, 46.7; N, 9.9%). An identical product was obtained from the reaction of potassium hexachloroplatinate(IV) and excess 1,4,7-triazacyclononane.

(1,4,7-*Triazacyclononane*-NN′N″)(1,4,7-*triazacyclononan-*1-*ido*-NN′N″)*platinum*(IV) *tri-iodide* (7). The pH of a solution (50 cm^3) of 1,4,7-triazacyclononane trihydrobromide (1.5 g) was adjusted to 11 with sodium hydroxide and potassium tetrachloroplatinate(II) (0.5 g) was added. A constant stream of air was passed through the refluxing solution for 20 h. To the still hot solution sodium iodide (3 g) was added. The solution was kept in a refrigerator (0 °C) for 12 h. Orange crystals were filtered off, washed with ethanol and diethyl ether and air dried (yield 1 g, 72%) (Found: C, 16.9; H, 3.6; I, 46.0; N, 16.0. $C_{12}H_{29}I_3N_3Pt$ requires C, 17.3; H, 3.5; I, 45.7; N, 16.1%).

Tribromo(1,4,7-*triazacyclononane*-NN′N″)*platinum*(IV) *bromide* (8). To a neutralized aqueous solution (35 cm^3) of 1,4,7-triazacyclononane trihydrobromide (0.25 g) solid potassium hexachloroplatinate(IV) (0.33 g) was added. The suspension was heated to 80 °C and the pH was adjusted to 8. After 2 h at 80 °C sodium bromide (2 g) was added. Upon cooling (0 °C) yellow needle-shaped crystals precipitated which were filtered off, washed with ethanol and diethyl ether and air dried (yield 0.2 g, 66%) (Found: C, 11.2; H, 2.6; Br, 49.5; N, 6.4. $C_6H_{15}Br_4N_3Pt$ requires C, 11.2; H, 2.4; Br, 49.6; N, 6.5%).

X-*Ray Crystal Structure of* $[Pt^{II}(L)_2]Br_2\cdot 2H_2O$.—Well defined needle-shaped crystals of $[Pt(L)_2]Br_2\cdot 2H_2O$ were obtained by slow recrystallisation from water.

Crystal data. $[Pt(L)_2]Br_2\cdot 2H_2O$, $M = 649.3$, Monoclinic, space group $P2/n$ (C^4_{2h}), $a = 8.990(2)$, $b = 7.987(2)$, $c = 14.424(4)$ Å, $\beta = 93.34(2)°$, $U = 1\,034$ Å^3, $D_m = 1.98(2)$, $Z = 2$, $D_c = 2.035$ g cm^{-3}, $F(000) = 623.8$, $\lambda = 0.710\,69$ Å, $\mu = 107.01$ cm^{-1}, $T = 22$ °C.

Intensity data were collected using a Syntex R3 instrument with Mo-K_α radiation in the θ—2θ scan mode. Data were measured in the range $2 \leqslant 2\theta \leqslant 60°$ with two check reflections being measured every 100 data. 1 065 Independent reflections were collected of which 1 419 with $I > 2.5\sigma(I)$ were considered observed and used in the refinement. Data were corrected for background, attenuators and Lorentz polarization factors and absorption using the SHELX system of programs.[12]

The Pt and Br positions were located from a three-dimensional Patterson synthesis; all other non-hydrogen atoms were located in subsequent Fourier syntheses. The hydrogen atoms of the CH_2 groups were included in the refinement with calculated idealized positions [d(C–H) 0.96 Å, isotropic thermal parameter]. Anisotropic thermal parameters for Pt, Br, C, and N and isotropic parameters for O of water molecules were refined.[12] Hydrogen atoms of N–H groups and H_2O were not located and were omitted in the final cycles of full-matrix least-squares refinement. Final discrepancy factor $R = 0.0335$. No weighting scheme was used. Computations were carried out on a NOVA (General Data) computer using the SHELX system of programs.[12]

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this research.

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Received 8*th December* 1982; *Paper* 2/2050