The phenyl rings linked to C(1) and C(2) are each twisted by 7·1 (7)° with respect to the propanedione plane. This value is modified in the rings at C(3) and C(4) [twist angles 18·0 (7) and 9·8 (7)° respectively] by the intermolecular hydrogen bonds. These twists and the C(sp^2)—C(phenyl) bond distances indicate that the electron resonance of propanedione does not extend to the phenyl rings. The hydroxy groups are hydrogen-bonded to adjacent coordinated O atoms. The mean distance is 2·505 (9) Å, similar to that observed in other inorganic compounds with intramolecular hydrogen bonds such as the bis(glyoximato)metal complexes (Solans, Font-Altaba & Briansó, 1983; Nuvan, Briansó, Solans, Font-Altaba & de Matheus, 1983; Solans, Font-Altaba, Bermejo & Alvarez, 1983).

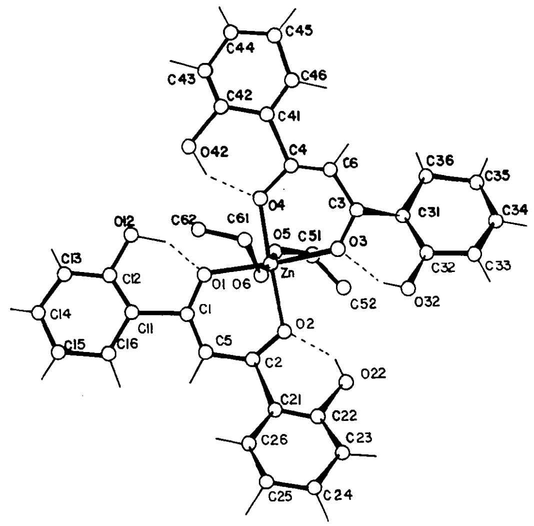

Fig. 1. View of the molecule showing the numbering of the atoms.

This work was sponsored by the University of Barcelona.

References

International Tables for X-ray Crystallography (1974). Vol. IV, p. 150. Birmingham: Kynoch Press.

Llobet, A., Teixidor, F. & Casabó, J. (1983). In preparation.

Niekerk, J. N. van, Schoening, F. R. L. & Talbot, J. H. (1953). *Acta Cryst.* **6**, 720–731.

Nuvan, L. A., Briansó, J. L., Solans, X., Font-Altaba, M. & de Matheus, M. (1983). *Acta Cryst.* C**39**, 211–213.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Smith, G., O'Reilly, E. I., Kennard, C. H. L., Stadnicka, K. & Oleksyn, B. (1981). *Inorg. Chim. Acta*, **47**, 111–120.

Solans, X., Font-Altaba, M., Bermejo, M. J. & Alvarez, S. (1983). *Acta Cryst.* C**39**, 1510–1512.

Solans, X., Font-Altaba, M. & Briansó, J. L. (1983). *Z. Kristallogr.* **162**, 305–312.

Acta Cryst. (1983). C**39**, 1514–1517

One-Dimensional *versus* Three-Dimensional Order in Bis(trimethylenediamine)platinum(II) Dichlorobis(trimethylenediamine)platinum(IV) Tetrafluoroborate, $[Pt(C_3H_{10}N_2)_2][Pt(C_3H_{10}N_2)_2Cl_2](BF_4)_4$, Bis(trimethylenediamine)platinum(II) Dibromobis(trimethylenediamine)platinum(IV) Perchlorate, $[Pt(C_3H_{10}N_2)_2][PtBr_2(C_3H_{10}N_2)_2](ClO_4)_4$ and Bis(trimethylenediamine)platinum(II) Dibromobis(trimethylenediamine)platinum(IV) Tetrafluoroborate, $[Pt(C_3H_{10}N_2)_2][PtBr_2(C_3H_{10}N_2)_2](BF_4)_4$. A Re-Refinement of Their Crystal Structures

By Mario Cannas, Maria Bonaria Lucchesini and Giaime Marongiu

Istituto di Chimica Fisica e Industriale dell'Università, Via Ospedale 72, 09100 *Cagliari, Italy*

(*Received* 3 *March* 1983; *accepted* 27 *June* 1983)

Abstract. The structures of the title compounds, described as three-dimensionally ordered in orthorhombic space group *A*222 [Matsumoto, Yamashita & Kida (1978). *Bull. Chem. Soc. Jpn*, **51**, 3514–3518], have been re-refined in space groups *Amm*2 and $A2_122$ using the original reflection data; better agreement between observed and calculated structure factors was obtained. Re-refinement leads to one-dimensionally ordered structures where no distinction can be made between the two oxidation states of platinum atoms. Moreover, significant differences are obtained for Pt—Br distances, conformation of the chelate rings and anion packing.

Introduction. The title compounds belong to the family of mixed-valence platinum compounds analogous to Wolffram's red salt $[Pt(NH_2CH_2CH_3)_4][Pt(NH_2CH_2CH_3)_4Cl_2]Cl_4.4H_2O$ (Wolffram, 1900), and consist of linear chains of roughly planar [Pt(ligands)] units bridged by halide ions.

0108-2701/83/111514-04$01.50

Most of the crystal structures of these compounds exhibit order in one dimension only (Keller, 1982), in the sense that alternation in Pt^{II}–Pt^{IV} distances along the chain is strictly obeyed, but different chains are slipped statistically along a direction parallel to them, the slipping being just one Pt—*X*···Pt distance; disorder therefore occurs in the directions perpendicular to the chains, which leads to the appearance of diffuse streaks for the odd-layer lines in the Weissenberg photographs of crystals mounted along the chain direction. Intensities of these reflections cannot be evaluated and used in the crystal structure analysis; as a consequence only an average structure can be determined.

Some of these derivatives, however, show weak but sharp reflections in the odd-layer lines perpendicular to the chains; the structures of some of them were described as three-dimensionally ordered (Matsumoto, Yamashita, Ueda & Kida, 1978; Endres, Keller, Martin, Traeger & Novotny, 1980; Matsumoto, Yamashita & Kida, 1978), but recently one-dimensionally ordered structures were proposed for $[Pd(en)_2][Pd(en)_2Cl_2](ClO_4)_4$ (en = ethylenediamine) (Beauchamp, Layek & Theophanides, 1982) and for $[Pt(tn)_2][Pt(tn)_2I_2](ClO_4)_4$ (tn = trimethylenediamine) (Cannas, Marongiu, Martin & Keller, 1983); the presence of diffuse background under the normal Bragg diffraction spots for the odd-layer lines was observed in long-exposure films of the palladium derivative.

In the light of these results we decided to carry out re-refinement of the crystal structures of the trimethylenediamine (tn) derivatives $[Pt(tn)_2][Pt(tn)_2Cl_2](BF_4)_4$, $[Pt(tn)_2][Pt(tn)_2Br_2](ClO_4)_4$ and $[Pt(tn)_2][Pt(tn)_2Br_2](BF_4)_4$, which were reported as three-dimensionally ordered in orthorhombic space group *A*222 (Matsumoto, Yamashita & Kida, 1978, hereafter MYK).

Experimental. Using the original intensity data of MYK we repeated structure-factor calculations in space group *A*222 using the published set of coordinates. The results, given in Table 1, show that the *R* factor jumps from the overall values of 0·08–0·11 to values in the range 0·38–0·48 for *h*-odd reflections, a fact which casts some doubt on the difference reported for $Pt(tn)_2^{2+}$ and $Pt(tn)_2^{4+}$ cations, which should be very sensitive to this category of reflections; moreover, the crystal packing in *A*222 is such that the twofold axis parallel to the chain leads to O(4)···O(4′) contacts which are shorter than the van der Waals radii, while the one passing through Pt and the central carbon atom in the chelate ring leads us to assume an unusual chiral-skew conformation.

Our analysis started by considering the consistency of the possible space groups, *i.e.* *A*222 (No. 21), *A*2*mm* (No. 35), *Amm*2 (No. 38) and *Ammm* (No. 65) with the crystal packing and Patterson map. *Ammm* was ruled out because it would imply a disordered structure with *b*/2 translation and *A*2*mm* because it is not consistent with the packing of the anions.

Using only *h*-odd reflections a three-dimensional Patterson map was calculated for the perchlorate derivative, where this category of reflections is more numerous and have higher F_o values than in fluoroborate ones. The prominent peak in the section $u = 0$ of this map is clearly due to Cl—Cl vectors; its occurrence at $v = 2y_{Cl}$ and $w = 0$ definitely rules out space group *A*222 which would require the occurrence of this peak at $v = 2y$ and $w = 2z$. Space group *Amm*2 was therefore adopted with the perchlorate groups on the mirror planes perpendicular to **a**, platinum atom at 0·25,0,0 and the halogen atoms along the chain at their pertinent Pt—*X* distance. The two chelate groups are necessarily bisected by the other mirror plane and the ambiguity of their relationship about the platinum atom, twofold axis or centre of inversion, was worked out in favour of the latter from the analysis of Cl—C vectors in the *h*-odd Patterson map. Starting coordinates for least-squares refinement were obtained from three-dimensional Fourier syntheses. Refinement was carried out by the block-diagonal least-squares method with a weighting scheme of the type $w = (A + B|F_o| + CF_o^2)^{1/2}$. Final conventional *R* factors ($R = \sum|\Delta F|/\sum|F_o|$) show that agreement is better than in the case of the *A*222 space group; and, most importantly, *h*-odd reflections show a reasonable trend, contrary to what happened in *A*222, where some of the 'strongest' reflections had low calculated *F* values and *vice versa*; the agreement is markedly better in the case of the perchlorate derivative, since 80–90% of the contribution to this category of reflections comes from the anions.*

Discussion. In the resulting structure for the perchlorate, the O···O short contacts are absent because the pertinent perchlorates are no longer coplanar but separated by $\frac{1}{2}$**a**, and the chelate rings adopt the usual chair-like conformation. The mirror relationship among $Pt(tn)_2$ cations stacked along **a** leads to their equivalence and therefore to a one-dimensionally ordered structure and to two independent Pt—*X* distances; as shown in Table 2, the difference between these two distances is, however, in evident contrast with their expected equivalence, casting some doubt on the crystallographic analysis.

A look at the final positional parameters showed that they were very closely related by a twofold screw axis parallel to **a**, which was ruled out because of the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38691 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final conventional agreement factors* ($R = \sum|\Delta F|/\sum|F_o|$) *at the end of refinement in the different space groups*

The number of reflections refers to those coded as observed by MYK.

	Number of reflections		*A*222		*Amm*2		*A*$2_1$22	
	Total	$h=2n+1$	R_{tot}	R_{2n+1}	R_{tot}	R_{2n+1}	R_{tot}	R_{2n+1}
$[Pt(tn)_2][Pt(tn)_2Br_2]\ (ClO_4)_4$	942	415	0·111	0·48	0·070	0·18	0·074	0·20
$[Pt(tn)_2][Pt(tn)_2Br_2]\ (BF_4)_4$	861	176	0·079	0·38	0·065	0·23	0·066	0·28
$[Pt(tn)_2][Pt(tn)_2Cl_2]\ (BF_4)_4$	853*	190	0·077	0·44	0·076	0·34	0·077	0·38

* In the analysis the original set of 1131 observed reflections has been reduced to 853 since 278 very weak and unreliable ones have been coded unobserved.

Table 2. Pt—*X distances* (Å) *from final coordinates in the different space groups*

		*A*222	*Amm*2	*A*$2_1$22
$[Pt(tn)_2]\ [Pt(tn)_2Br_2]\ (ClO_4)_4$	Pt—Br	2·546 (7)	2·44–2·49 (1)	2·47 (1)
	Pt···Br	2·955 (7)	3·06–3·01 (1)	3·03 (1)
$[Pt(tn)_2]\ [Pt(tn)_2Br_2](BF_4)_4$	Pt—Br	2·541 (5)	2·46–2·49 (1)	2·47 (1)
	Pt···Br	2·921 (5)	3·00–2·95 (1)	2·99 (1)
$[Pt(tn)_2]\ [Pt(tn)_2Cl_2](BF_4)_4$	Pt—Cl	2·299 (6)	2·28–2·34 (1)	2·31 (1)
	Pt···Cl	3·096 (6)	3·12–3·06 (1)	3·09 (1)

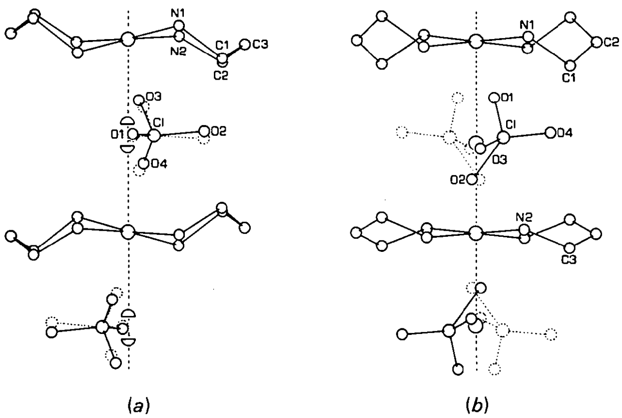

Fig. 1. Projection of the crystal structure of $[Pt(tn)_2][Pt(tn)_2Br_2](ClO_4)_4$ along **c**. (*a*) According to space group *A*$2_1$22, this work; (*b*) according to space group *A*222 (Matsumoto, Yamashita & Kida, 1978). In (*a*) the possible mirror plane through the perchlorate group, as expected in space group *Amm*2, is clearly evident.

presence of a few odd *h*00 reflections, whose structure-factor values are, however, hardly significant. They were therefore omitted and refinement carried out in the *A*$2_1$22 space group which is still consistent with the findings of the *h*-odd Patterson map. Although the number of refined parameters is lower in *A*$2_1$22 (57) than in *Amm*2 (74) comparable agreement factors were obtained, as shown in Table 1.

The general features of the crystal structures in *A*$2_1$22 are very close to those derived in *Amm*2; in fact, as shown in Fig. 1, the chair conformation of the chelate rings and their relative positions is such that their diad relationship is very close to a mirror relationship; the significant structural difference is that the screw axis leads to only one crystallographically independent Pt—*X* distance.

As shown in Table 2 the values of Pt—Cl distances fall in a narrow range in the three space groups, while the values found for Pt—Br distances in our analysis

Table 3. *Final positional parameters* ($\times 10^4$) *for refinement in A*$2_1$22

B_{eq} (for Pt, Cl, Br) $= \frac{1}{3}\sum B_{ii}$.

	x	*y*	*z*	B_{eq} or B(Å^2)
$[Pt(tn)_2]\ [Pt(tn)_2Br_2]\ (ClO_4)_4$				
Pt	0	0	0	1·33 (10)
Br	2249 (4)	0	0	2·63 (15)
Cl	2522 (5)	3063 (3)	732 (4)	2·4 (2)
O(1)	2504 (26)	3989 (25)	140 (23)	7·4 (7)
O(2)	2398 (23)	3183 (15)	2103 (21)	5·2 (4)
O(3)	1611 (23)	2428 (16)	302 (25)	5·0 (5)
O(4)	3702 (30)	2652 (16)	434 (25)	4·5 (4)
N(1)	−343 (26)	1086 (21)	1392 (34)	3·7 (6)
N(2)	−67 (11)	−1045 (8)	1402 (13)	1·01 (16)
C(1)	520 (24)	913 (18)	2606 (25)	2·7 (4)
C(2)	623 (26)	−955 (20)	2551 (27)	4·1 (5)
C(3)	129 (25)	81 (20)	3220 (32)	4·0 (6)
$[Pt(tn)_2]\ [Pt(tn)_2Br_2]\ (BF_4)_4$				
Pt	0	0	0	1·20 (18)
Br	2261 (2)	0	0	2·2 (2)
B	2632 (28)	3072 (15)	738 (18)	1·4 (3)
F(1)	2619 (31)	3916 (14)	61 (15)	5·6 (4)
F(2)	2390 (41)	3258 (15)	2082 (19)	6·5 (5)
F(3)	1483 (24)	2561 (22)	414 (26)	6·9 (5)
F(4)	3550 (22)	2580 (21)	387 (24)	6·0 (5)
N(1)	−186 (23)	1065 (21)	1394 (27)	4·0 (5)
N(2)	−152 (18)	−1069 (15)	1385 (20)	2·2 (3)
C(1)	544 (29)	884 (25)	2650 (29)	3·5 (5)
C(2)	516 (29)	−865 (25)	2713 (29)	3·5 (5)
C(3)	133 (22)	−66 (55)	3304 (23)	3·5 (4)
$[Pt(tn)_2]\ [Pt(tn)_2Cl_2]\ (BF_4)_4$				
Pt	0	0	0	1·9 (2)
Cl	2140 (8)	0	0	2·9 (3)
B	2307 (15)	3059 (10)	716 (13)	0·2 (2)
F(1)	2662 (31)	3875 (15)	33 (20)	6·3 (5)
F(2)	2631 (50)	3292 (19)	2019 (24)	7·7 (7)
F(3)	1428 (22)	2572 (19)	406 (22)	5·7 (5)
F(4)	3517 (30)	2521 (26)	435 (31)	9·2 (8)
N(1)	−172 (25)	1156 (18)	1428 (25)	4·1 (5)
N(2)	−198 (15)	−1008 (11)	1362 (15)	1·2 (3)
C(1)	593 (22)	935 (17)	2579 (22)	1·9 (5)
C(2)	476 (41)	−893 (31)	2670 (40)	5·9 (5)
C(3)	219 (20)	146 (18)	3291 (21)	2·2 (5)

compare well with those in analogous compounds (Beauchamp, Layek & Theophanides, 1982, and references quoted therein) and are significantly different from those reported by MYK.

The values of bond distances and angles in the chelate ligands and perchlorate groups are in the same range as those reported by MYK.

The results of our analysis lead to the conclusion that the $A2_122$ space group is the one which better describes the structures of these compounds, which should therefore be considered as one-dimensionally rather than three-dimensionally ordered. Final positional parameters are given in Table 3.

References

BEAUCHAMP, A. L., LAYEK, D. & THEOPHANIDES, T. (1982). *Acta Cryst.* B**38**, 1158–1164.
CANNAS, M., MARONGIU, G., MARTIN, R. & KELLER, H. J. (1983). *Z. Naturforsch.* Submitted.
ENDRES, H., KELLER, H. J., MARTIN, R., TRAEGER, U. & NOVOTNY, M. (1980). *Acta Cryst.* B**36**, 35–39.
KELLER, H. J. (1982). In *Extended Linear Chain Compounds*, edited by J. S. MILLER, pp. 357–407, and references quoted therein. New York: Plenum.
MATSUMOTO, N., YAMASHITA, M. & KIDA, S. (1978). *Bull. Chem. Soc. Jpn*, **51**, 3514–3518.
MATSUMOTO, N., YAMASHITA, M., UEDA, I. & KIDA, S. (1978). *Mem. Fac. Sci. Kyushu Univ. Ser. C*, **11**, 209–216.
WOLFFRAM, H. (1900). Dissertation, Königsberg.

Acta Cryst. (1983). C**39**, 1517–1519

{N-[N-(3-Hydroxy-5-hydroxymethyl-2-methyl-4-pyridylmethylene)glycyl]glycinato(2—)}nickel(II) Trihydrate, $[Ni(C_{12}H_{13}N_3O_5)].3H_2O$

BY SANTE CAPASSO AND CARLO ANDREA MATTIA

Istituto Chimico-Università, Via Mezzocannone 4, 80134 *Napoli, Italy*

RAFFAELLA PULITI

Istituto per la Chimica di Molecole di Interesse Biologico CNR, Via Toiano 2, 80072 *Arco Felice, Napoli, Italy*

AND ADRIANA ZAGARI

Istituto Chimico-Università, Via Mezzocannone 4, 80134 *Napoli, Italy*

(*Received* 9 *May* 1983; *accepted* 27 *June* 1983)

Abstract. $M_r = 392{\cdot}01$, triclinic, $P\bar{1}$, $a = 7{\cdot}082$ (1), $b = 9{\cdot}004$ (1), $c = 12{\cdot}425$ (1) Å, $\alpha = 97{\cdot}5$ (1), $\beta = 89{\cdot}6$ (1), $\gamma = 100{\cdot}1$ (1)°, $U = 773{\cdot}2$ (3) Å^3, $Z = 2$, $D_x = 1{\cdot}68$, $D_m = 1{\cdot}70$ Mg m^{-3} (by flotation method), $F(000) = 408$, λ(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 2·2 mm^{-1}, room temperature, final $R = 0{\cdot}050$ for 1802 observed reflections. The Ni^{2+} ion is coordinated by the tetradentate ligand in a square-planar arrangement. The packing is determined by hydrogen bonds between the complex and the water molecules and by weak interactions between the stacked planar molecules of the complex.

Introduction. The Schiff-base derivatives of pyridoxal or salicylaldehyde with amino acids, in the presence of metal ions, have been used as model catalysts for a large number of biological reactions (Snell, Braunstein, Severin & Torchinskii, 1968). For this reason their properties have been extensively studied in solution (Abbott & Martell 1970; Wroblesky & Long, 1977) and in the solid state (Capasso, Giordano, Mattia, Mazzarella & Ripamonti, 1974; Dawes & Waters, 1982). We have extended this study to metal complexes of pyridoxal Schiff bases containing di- and tripeptides and in this paper we present the crystal structure of $[Ni(C_{12}H_{13}N_3O_5)].3H_2O$.

Experimental. Red prisms from aqueous methanol solution, 0·55 × 0·08 × 0·04 mm, Enraf–Nonius CAD-4F diffractometer, Ni-filtered Cu $K\alpha$ radiation, lattice parameters from 20 reflections (20° < θ < 27°); data collection: ω–θ scan, 3180 independent reflections with $\theta \le 75°$, $-8 \le h \le 8$, $-10 \le k \le 10$, $0 \le l \le 14$, 1805 with $I \ge 3\sigma(I)$. Three standard reflections ($40\bar{1}$, $\bar{2}1\bar{5}$, $\bar{1}40$) monitored at intervals of 5 h (5% variation), Lp correction, absorption ignored, Patterson and Fourier methods, anisotropic full matrix (on F), H from $\Delta\rho$ synthesis isotropic, not refined. Three reflections (100, 001, $\bar{1}10$ measured improperly due to asymmetric background) excluded from final cycles of refinement. Final $R = 0{\cdot}050$, $R_w = 0{\cdot}056$, $w = 1/\sigma^2(F_o)$, 1802 observations, 217 variables; final $(\Delta/\sigma)_{max} = 0{\cdot}41$. max. and min. heights in final $\Delta\rho$ map 0·5 and −0·4 e Å^{-3}, no correction for secondary extinction; scattering factors from *International Tables for X-ray Crystallography* (1974), Enraf–Nonius *SDP* software and PDP 11/34 computer of the 'Centro di Metodologie Chimico-fisiche dell'Università di Napoli'.

0108-2701/83/111517-03$01.50