Table 2. *Interatomic distances* (Å)

MoGa₁₀ polyhedron		(S,Ga)Ga₁₂ cuboctahedron	
Mo—Ga(1)	2·591 (1)	S,Ga(5)—Ga(1)	3·302 (1)
Ga(2)	2·796 (1)	Ga(2)	2·671 (1)
Ga(3)	2·617 (1)	Ga(1)—Ga(1)	2·801 (1)
Ga(3)	2·629 (1)	Ga(2)	3·212 (1)
Ga(4)	2·558 (0)	Ga(2)	3·286 (1)
Ga(1)—Ga(1)	2·801 (1)		
Ga(2)	3·212 (1)		
Ga(2)	3·286 (1)		
Ga(3)	3·216 (1)		
Ga(4)	3·017 (1)		
Ga(2)—Ga(3)	2·914 (1)		
Ga(3)	3·451 (1)		
Ga(4)	2·920 (1)		
Ga(3)—Ga(3)	2·638 (1)		
Ga(3)	2·754 (1)		
Ga(4)	2·784 (1)		
Ga(4)—Ga(4)	2·642 (0)		

compound (*via* analysis of the Mo–Ga–S phase diagram at 1073 K), the present work presents single crystals of a compound richer in gallium by means of the partial occupation of a twofold site by one additional Ga atom, resulting in an increased density. Both the S and Ga(5) atoms are statistically disordered and have occupation factors a little smaller than 0·5. The occupancies of other atoms do not differ significantly from 1. They were refined, however, in order to check the possibility of the existence of defects at Mo and Ga sites, as was found in Mo_6Ga_{31} and Mo_8Ga_{41} (Yvon, 1974, 1975), but the refinement did not confirm such effects. Attempts to establish a model at lower symmetry, in which the S and Ga sites were ordered, were unsuccessful.

Like the V_8Ga_{41}-type structures (Girgis, Petter & Pupp, 1975; Yvon, 1975) $Mo_8Ga_{41}S$ can be described by two types of coordination polyhedra: $MoGa_{10}$ (Fig. 2*a*) and $(S,Ga)Ga_{12}$ (Fig. 2*b*). The bond lengths (Table 2) within the $MoGa_{10}$ polyhedron are typical, whereas (S,Ga)–Ga distances in the $(S,Ga)Ga_{12}$ cuboctahedron correspond well to usual Ga–Ga bonds; there are,

however, longer than typical S–Ga bond lengths (Goodyear & Steigmann, 1963; Kuhn, Chevy & Chevalier, 1976), consistent with the high temperature factor of sulfur.

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(1,3-Diamino-2-propanol-*N*,*N*′)(malonato-*O*,*O*′)platinum(II) Dihydrate

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Abstract. [Pt(C₃H₂O₄)(C₃H₁₀N₂O)].2H₂O, $M_r =$ 423·2, triclinic, $P\bar{1}$, $a = 7·693$ (2), $b = 8·399$ (2), $c = 11·495$ (2) Å, $\alpha = 108·17$ (2), $\beta = 104·31$ (2), $\gamma =$ 116·67 (2)°, $V = 561·2$ (2) Å³, $Z = 2$, $D_m = 2·50$, $D_x = 2·52$ (3) g cm⁻³, graphite-monochromatized Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 131·8$ cm⁻¹, $F(000) =$

Table 1. *Atomic positional parameters* ($\times 10^4$) *and temperature factors* ($\text{Å}^2 \times 10^3$) *for* $[Pt(C_3H_2O_4)\text{-}(C_3H_{10}N_2O)].2H_2O$

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{12}\cos\gamma + 2U_{13}\cos\beta + 2U_{23}\cos\alpha).$$

	x	y	z	U_{eq}
Pt1	928·4 (4)	1986·7 (3)	4826·5 (2)	12·9
N1	−1237 (10)	101 (9)	2807 (6)	16
C1	−344 (13)	390 (11)	1824 (7)	19
C2	1397 (12)	−4 (12)	1964 (7)	20
O2	638 (10)	−1949 (9)	1856 (6)	26
C3	3495 (12)	1566 (13)	3286 (8)	22
N3	3139 (10)	1459 (10)	4503 (6)	18
C4	3161 (11)	5161 (11)	7710 (7)	17
O4	4580 (10)	6217 (9)	8909 (5)	28
O41	3110 (8)	3705 (8)	6829 (5)	18
C5	1571 (12)	5693 (10)	7203 (7)	20
C6	−822 (11)	3936 (10)	6263 (6)	16
O6	−2229 (9)	4096 (9)	6513 (6)	25
O61	−1319 (9)	2404 (9)	5184 (5)	18
O7	4467 (13)	−1083 (11)	1041 (8)	54
O8	2186 (13)	4659 (12)	865 (8)	58

395·6, $T = 297$ K, $R = 0·0396$, $wR = 0·0520$ for 2564 unique reflections and 136 parameters. The Pt atom is in a square-planar environment. The Pt—N distances [2·025 (6) and 2·028 (6) Å] are significantly shorter than those in the bis(1,3-diamino-2-propanol-*N,N'*)platinum(II) cation (2·058 Å ave.). Other bond distances are normal. The molecule is hydrogen bonded from the ligating amine groups in one molecule to the ligating O atoms of the malonate group in a centrosymmetrically related molecule, forcing a relatively short Pt···Pt' distance [3·1889 (9) Å].

Introduction. *cis*-[PtCl$_2$(NH$_3$)$_2$] is the most widely used anti-cancer drug in North America and its successful use against a variety of cancers has led to a host of other platinum compounds being tested. Toxicity problems appear to be lower with compounds containing organic rings and the incorporation of possible hydrogen-bonding sites increases the aqueous solubility which is sometimes a limitation. To this end, we have synthesized the title compound by the reaction of diiodo(1,3-diamino-2-propanol-*N,N'*)platinum(II) with aqueous silver nitrate. After complete reaction and removal of the silver iodide, treatment of the solution with malonic acid gave the desired product in low yield. Crystals were obtained by evaporation of an aqueous solution at 278 K.

Experimental. Density by suspension in dichloromethane/diiodomethane mixture. Crystal chosen for diffraction: parallelepiped, 0·15 × 0·19 × 0·26 mm, space group $P\bar{1}$, Delaunay reduction showed no hidden symmetry. Unit-cell parameters refined by least-squares fit of positional angles for 15 strong reflections, 19·2 < 2θ < 25·9°, on a Nicolet *P*3 diffractometer at 297 K, monochromated Mo $K\alpha$ radiation, 2870 reflections measured for $2\theta < 55°$. Intensities $0 \le h \le 9$, $-10 \le k \le 10$, $-14 \le l \le 14$, measured by θ–2θ scan

technique. Range of scan rates 4·9 to 29·3° min^{-1} in 2θ. The total-background-time to scan-time ratio is 1:1. Two standard reflections measured every 48 reflections ($4\bar{2}2$ 1·9%, 032 1·6%) showed no instrument instability or crystal decay, even though the colourless crystal turned pale orange after five days of irradiation. Zonal reflections averaged to give 2564 independent reflections, $R_{int} = 0·009$. Reflections with $3\sigma_I \ge I \ge -3\sigma_I$ were treated by the method of French & Wilson (1978). Lp and absorption corrections were made (absorption correction factors, 4·54–8·72), correction applied with the use of the program *PSISCAN* (Calabrese & Burnett, 1980). Structure solved by Patterson method. Anisotropic full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, $w = (\sigma_F^2 + 0·001602 \times F_o^2)^{-1}$. Scale, secondary extinction, positional and anisotropic temperature factors for non-H atoms varied, 136 parameters. H atoms on molecule calculated but not refined. H atoms on O2 and water molecules not included. Final $R = 0·0396$, $wR = 0·0520$, $S = 1·125$. Refinement ended when $(\Delta/\sigma)_{max} = 0·006$. Final difference map revealed electron density max. 1·8 e Å^{-3} near the Pt atom, min. −1·60 e Å^{-3}. Scattering factors from Cromer & Waber (1974). Corrections for anomalous dispersion made for Pt (Cromer & Ibers, 1974). Calculations employed *XTAL* (Stewart & Hall, 1983), *SHELX* (Sheldrick, 1976), *SINBAD* (Altermatt & Brown, 1985) and *SNOOPI* (Davies, 1983) program systems on VAX 8600 computer. Atomic positional parameters and U_{eq} are given in Table 1.

Discussion. The molecule is shown in Fig. 1 and interatomic distances are listed in Table 2.* The molecule contains two six-membered rings with the Pt atom occupying the common vertex. The diaminopropanol ring adopts the chair conformation while the malonate ring is a shallow boat. The four ligating atoms form a square plane; the Pt atom is 0·052 (4) Å out of

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* Lists of structure factors, anisotropic temperature factors, calculated H-atom positions, least-squares planes and dihedral angles, and detailed methods of preparation and analyses have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51688 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
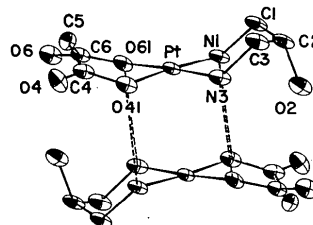

Fig. 1. Two molecules of [Pt(C$_3$H$_2$O$_4$)(C$_3$H$_{10}$N$_2$O)] showing the atom numbering and the hydrogen bonding (broken lines) in the dimer.

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°) *for* [Pt(C$_3$H$_2$O$_4$)(C$_3$H$_{10}$N$_2$O)].2H$_2$O

Pt–N1	2·025 (6)	Pt–N3	2·028 (6)
Pt–O41	2·011 (5)	Pt–O61	2·021 (5)
N1–C1	1·488 (9)	C1–C2	1·50 (1)
C2–C3	1·51 (1)	C2–O2	1·42 (1)
C3–N3	1·51 (1)	O41–C4	1·300 (9)
O4–C4	1·226 (9)	C4–C5	1·53 (1)
C5–C6	1·522 (9)	C6–O6	1·238 (9)
C6–O61	1·292 (8)		

N1–Pt–N3	91·0 (3)	N1–Pt–O41	175·9 (4)
N1–Pt–O61	89·4 (3)	O41–Pt–N3	86·3 (2)
N3–Pt–O61	176·9 (3)	O41–Pt–O61	93·1 (2)
Pt–N1–C1	115·8 (5)	N1–C1–C2	111·9 (6)
O2–C2–C3	108·0 (6)	C2–C3–N3	110·7 (6)
C3–N3–Pt	116·4 (5)	Pt–O41–C4	123·4 (5)
O41–C4–C5	119·1 (6)	O41–C4–O4	120·8 (7)
O4–C4–C5	119·7 (8)	C4–C5–C6	117·4 (6)
C5–C6–O61	119·0 (6)	C5–C6–O6	118·4 (7)
O6–C6–O61	122·3 (7)	C6–O61–Pt	123·2 (5)

Hydrogen bonds

N1···O7[i]	2·92 (1)	N1–H10	1·08
H10···O7[i]	2·03	N1–H10···O7[i]	137
N1···O41[ii]	2·082 (7)	N1–H11	1·09
H11···O41[ii]	2·08	N1–H11···O41[ii]	151
N3···O61[ii]	3·08 (1)	N3–H30	1·08
H30···O61[ii]	2·08	N3–H30···O61[ii]	154
N3···O6[iii]	2·932 (8)	N3–H31	1·08
H31···O6[iii]	1·92	N3–H31···O6[iii]	156
O2···O7	3·15 (1)	O2···O8[iv]	2·728 (9)
O4···O7[v]	2·82 (1)	O4···O8[vi]	2·87 (2)
O6···O8[vii]	2·85 (1)	O7···O8[viii]	3·11 (1)

Atoms are related to those in Table 1 by the following transformations: (i) = $x-1$, y, z; (ii) = $-x$, $-y$, $-z+1$; (iii) = $x+1$, y, z; (iv) = $-x$, $-y$, $-z$; (v) = x, $y+1$, $z+1$; (vi) = $-x+1$, $-y+1$, $-z+1$; (vii) = $-x$, $-y+1$, $-z+1$; (viii) = x, $y-1$, z. No errors are given for parameters involving H atoms since the positions were calculated.

this plane in the same direction as the C atoms attached to the ligating atoms. This deviation from strict planarity is probably caused by the steric requirements of the dimer pairs which the molecules form in the crystal (see Fig. 1). The pairs are held together by hydrogen bonds N1···O61' [2·85 (1) Å] and N3···O41' [2·76 (1) Å]. Since the hydrogen bond distances are somewhat less than the normal closest approach of two non-bonded Pt^{II} atoms (~3·1 Å) [Pt···Pt' 3·1889 (9) Å], the Pt atoms are displaced from the square plane, an effect reported previously (Lippert, Lock, Rosenberg & Zvagulis, 1977).

The chelating angles N1–Pt–N3 [91·0 (3)°] and O41–Pt–O61 [93·1 (2)°] are slightly greater than 90°, in contrast to the bis(diaminopropanol)platinum(II) cation [N–Pt–N', 87·6 (2)°] (Brown & Lock, 1987). This increase in the O–Pt–O and N–Pt–N angles reduces the N1···O61 and N3···O41 separations and may be caused by the intermolecular hydrogen bonding.

The Pt–N distances [Pt–N1 2·025 (6), Pt–N3 2·028 (6) Å] are significantly less than those in the corresponding bis(ligand) complex [Pt–N 2·058 (7), 2·057 (6) Å] (Brown & Lock, 1987) although they lie within the range reported previously for Pt–N bonds

where an N atom is bound to platinum *trans* to an O atom (Faggiani, Lippert, Lock & Rosenberg, 1977*a,b*; Lippert *et al.*, 1977; Britten, Lippert, Lock & Pilon, 1982; Bitha, Child, Hlavka, Lang & Lin, 1988). This probably reflects the lower *trans* influence of an O atom compared to an amine N atom. The Pt—O distances [Pt—O41 2·011 (5), Pt—O61 2·021 (5) Å] lie within the range previously reported for similar compounds (Faggiani *et al.*, 1977*a,b*; Lippert *et al.*, 1977; Bitha *et al.*, 1988). The remaining bond lengths and angles are in agreement with values reported previously for similar structures (Goedkoop & MacGillavry, 1957; Briggman & Oskarsson, 1977; Brown & Lock, 1987).

The packing of the molecules in the unit cell is shown in Fig. 2. The molecules lie in pleated layers roughly perpendicular to [121] so that the molecules are about 38° to the *ac* plane. The water molecules lie almost in these layers, displacement occurring to maximize hydrogen bonding which is extensive. Molecules related by the *a* translation are hydrogen bonded directly [N3···O6 2·932 (8) Å] or through a water molecule [O2···O7 3·15 (1), O7···N1 2·92 (1) Å]. In the *b* direction, the pairs are hydrogen bonded through a water molecule [O6···O8 2·81 (1), O8···O4 2·87 (2) Å]. Within the sheets, the intermolecular hydrogen bonding is through the water molecules [O2···O8 2·728 (9), O8···O4 2·87 (2), O8···O7 3·11 (1), O7···O4 2·82 (1) Å].

The low yield of the desired product from such an apparently simple preparative reaction was unexpected. Clearly, part of the material is precipitated with 'AgI' possibly in silver–platinum complexes of the type discovered by Melanson & Rochon (1987), or Lippert and colleagues (Lippert & Neugebauer, 1982; Schollhorn, Thewalt & Lippert, 1987). In addition, the green supernatant solution from which the crystals were grown also contains excess platinum in unknown complex form. This complexity of reaction products is now, in our experience, a common feature of platinum chemistry.
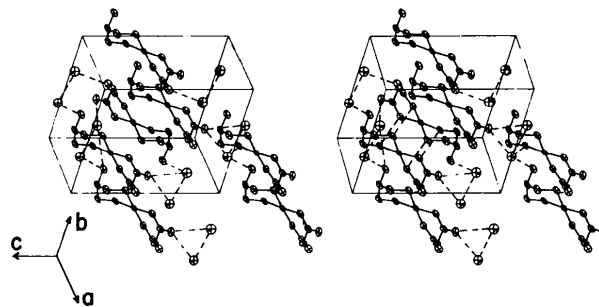
Fig. 2. The packing within the unit cell. Hydrogen bonds are shown by broken lines.

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Structures of the Tetrachloroaluminate Salts of the N-Ethylpyridinium, 2-Ethylpyridinium, Pyridinium and 1-Chloromethyl-1,2,3,4,5,6-hexamethylbenzenium Cations

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Abstract. The crystal structures of four organic-cation tetrachloroaluminate salts have been determined: N-ethylpyridinium tetrachloroaluminate, $[C_7H_{10}N][AlCl_4]$, $M_r = 277.0$, monoclinic, $C2/c$, $a = 14.112$ (3), $b = 12.893$ (5), $c = 14.949$ (3) Å, $\beta = 110.63$ (2)°, $V = 2545.6$ Å^3, $Z = 8$, $D_x = 1.445$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.70926 Å, $\mu = 0.952$ mm^{-1}, $F(000) = 1120$, $T = 295$ K, $R = 0.053$ for 589 unique observed reflections; pyridinium tetrachloroaluminate, $[C_5H_6N][AlCl_4]$, $M_r = 248.9$, orthorhombic, $Cmcm$, $a = 9.204$ (3), $b = 8.314$ (2), $c = 14.001$ (5) Å, $V = 1071.2$ Å^3, $Z = 4$, $D_x = 1.543$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.70926 Å, $\mu = 1.12$ mm^{-1}, $F(000) = 496$, $T = 295$ K, $R = 0.041$ for 356 unique observed reflections; 2-ethylpyridinium tetrachloroaluminate, $[C_7H_{10}N][AlCl_4]$, $M_r = 277.0$, monoclinic, $P2_1/c$, $a = 7.674$ (2), $b = 13.322$ (3), $c = 12.641$ (3) Å, $\beta = 96.18$ (2)°, $V = 1284.8$ Å^3, $Z = 4$, $D_x = 1.432$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.70926 Å, $\mu = 0.944$ mm^{-1}, $F(000) = 560$, $T = 295$ K, $R = 0.064$ for 1134 unique observed reflections; 1-chloromethyl-1,2,3,4,5,6-hexamethylbenzenium tetrachloroaluminate, $[C_{13}H_{20}Cl][AlCl_4]$, $M_r = 380.6$, monoclinic, $P2_1/n$, $a = 8.951$ (2), $b = 12.322$ (2), $c = 16.763$ (4) Å, $\beta = 98.43$ (2)°, $V = 1828.9$ Å^3, $Z = 4$, $D_x = 1.38$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.70926 Å, $\mu = 0.823$ mm^{-1}, $F(000) = 784$, $T = 295$ K, $R = 0.057$ for 1354 unique observed reflections. The structures reveal little or no interaction between the tetrachloroaluminate anions and the cations. The significance of this observation is discussed in the context of tetrachloroaluminate sustained room-temperature melts.

Introduction. That halogenoaluminate salts may exist as liquids under ambient conditions was first realized by Hurley and Wier in 1951 when they reported the properties of the prototypal melts, N-ethylpyridinium [(1)] halogenoaluminates (Hurley & Wier, 1951*a,b*). Activity in this field has steadily increased since 1951, with the related methylpyridinium salts having likewise been investigated (Newman, Tillack, Morgan & Wan,

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