Synthesis and Crystal Structure of the First Trinuclear Chloride-bridged Platinum(II) Complex with Mutually Perpendicular Co-ordination Planes: *cyclo*-Tri-μ-chloro-tris[chloro(1-hydroxy-1-imino-2,2-dimethylpropane)platinum(II)]–Dichloromethane (0.5/1)†

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The first trinuclear chloride-bridged platinum(II) compound has been obtained by disproportionation of *cis*-$[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]_2\}_2]$ **1**. Two compounds result from the disproportionation, which contain one and three amide molecules per platinum atom (compounds **2** and **3** respectively). Compound **2**, which crystallizes from dichloromethane as orange hexagonal prisms, contains discrete molecules of $[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]\}_3]$. The co-ordination geometry of each metal centre is square planar; two *cis* positions are occupied by bridging chloride ions, and a terminal chloride and the nitrogen atom of an amide ligand (iminol form) complete the co-ordination sphere. The co-ordination planes of the three platinum atoms are mutually perpendicular with a dihedral angle of 99.2(2)°. The structure is strongly related to that of the β form of $PtCl_2$ (Pt_6Cl_{12} molecules). Compound **2** incorporates exactly one half of the Pt_6Cl_{12} cube and saturates the vacant co-ordination sites, made available by splitting of the bridges across the two halves of the cube, with amide ligands. The complex, as a whole, assumes a calyx-type shape and two molecules of complex take up one molecule of solvent (CH_2Cl_2).

In a previous paper we described a novel dimeric platinum(II) complex, *cis*-$[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]_2\}_2]$ **1**, in which the two platinum units are held together by four interplanar hydrogen bonds and a weak intermetallic linkage.[1] Compound **1** disproportionates spontaneously in chlorinated solvents to give two species which contain one and three amide molecules per platinum atom (compounds **2** and **3** respectively).

We now report on the crystal and molecular structure of compound **2** which proved to be a cyclic trimer, $[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]\}_3]$, with mutually orthogonal metal co-ordination planes. The novel structure is strongly reminiscent of the cubic structure found for the β form of $PtCl_2$ (Pt_6Cl_{12} units)[2] and gives new insight into the chemistry of platinum.

Experimental

Compound *cis*-$[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]_2\}_2]$ **1** was prepared by the procedure reported previously[1] *via* hydrolysis of *cis*-$[PtCl_2\{N{\equiv}CC(CH_3)_3\}_2]$.[1] The nitrile complex, dissolved in dichloromethane, was treated first with excess powdered potassium hydroxide to give $K_2[PtCl_2\{HN{=}C(O)C(CH_3)_3\}_2]$ and then with an excess of HCl in cold water to form the amido species *cis*-$[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]_2\}_2]$ **1** in nearly quantitative yield.

Compound **1** is unstable in chlorinated solvents (*e.g.* dichloromethane) where it isomerizes to the more stable isomer *trans*-$[PtCl_2\{HN{=}C(OH)C(CH_3)_3\}_2]$. If the decomposition reaction is performed in a medium with a smaller solvating capacity than dichloromethane, two intermediate species are obtained. They contain one and three amide molecules per platinum atom, compounds **2** and **3** respectively. In a typical experiment compound **1** (0.5 mmol) was dissolved in the minimum volume of dichloromethane (3 cm^3) and *n*-hexane (20 cm^3) added to precipitate a significant amount of the starting material. The mixture was left to stand for a few days whereupon a mixture of the disproportionation products, $[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]\}_3]$ **2** and *cis*-$[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]_2[H_2NC(O)C(CH_3)_3]\}_2]$ **3**, was formed in 50% yield. Crystals of the two compounds, having different colours and shapes, were separated mechanically (Found: C, 16.7; H, 3.0; Cl, 19.5; N, 3.7. Calc. for $C_{15}H_{33}Cl_6N_3O_3Pt_3$ **2**: C, 16.4; H, 3.0; Cl, 19.3; N, 3.8%).

Compound $K[PtCl_3\{HN{=}C(OH)C(CH_3)_3\}]$ **4** was prepared for comparison. The compound $K[PtCl_3\{N{\equiv}CC(CH_3)_3\}]$ (1 mmol)[1] dissolved in the minimum volume of water (4–6 cm^3) and cooled to 0 °C was treated with a slight excess of KOH (1.2 mmol). The solution was stirred for 1 h at 0 °C and then treated with 3 mol dm^{-3} HCl until the pH reached 3. The solvent was evaporated under reduced pressure and the solid residue extracted with MeOH. The alcoholic solution, after evaporation of the solvent, afforded a yellow solid of $K[PtCl_3\{HN{=}C(OH)C(CH_3)_3\}]$ **4** (yield 70%) (Found: C, 13.5; H, 2.4; Cl, 24.3; N, 3.2. Calc. for $C_5H_{11}Cl_3KNOPt$: C, 13.6; H, 2.5; Cl, 24.1; N, 3.2%).

Crystal-structure Determination.—Orange, hexagonal prisms of $[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]\}_3]$ **2** were obtained from dichloromethane–hexane (1 : 1, v/v). The prisms showed some cracks and deformities. A fragment of dimensions *ca.* 0.25 × 0.25 × 0.35 mm was selected and mounted on a glass fibre for data collection. Experimental details for the data collection, structure solution and refinement are listed in Table 1. Unit-cell parameters were obtained by least-squares refinement of 35 carefully centred reflections chosen from different regions of reciprocal space (2θ, 11–30°). The intensities were obtained after Lorentz and polarization corrections. An absorption correction was applied *via* the ψ-scan technique on three reflections. The poor quality of the crystal was reflected in the relatively high value of R_{int}

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

(0.11). 4120 Reflections (±*h*, ±*k*, *l*) were collected at 22 °C; 1369 were unique and 1207 observed [$F > 4\sigma(F)$]. Values of R_{int} for the monoclinic lattices were in the range 0.301–0.311 whereas R_{int} for the triclinic system was 0.024 (52 equivalences).

The structure was solved by conventional Patterson and Fourier methods (direct methods produced the correct atomic positions for the Pt, Cl and N atoms) and refined by full-matrix least-squares techniques. The Pt, Cl, O and N atoms were treated anisotropically and the C atoms isotropically at a certain stage of the refinement. At that point the Fourier difference map showed two sets of three peaks each, around the C(2) carbon atom. This was interpreted as disorder of the *tert*-butyl group. The atoms C(3), C(4) and C(5), and C(6), C(7) and C(8), were assigned to the two sets respectively. The sum of the occupancy factors (s.o.f.) for the two sets of terminal carbon atoms was constrained to 1. The two s.o.f. values converged to 0.48(6) for C(3), C(4) and C(5), and to 0.52(6) for C(6), C(7) and C(8), respectively. The thermal parameters converged to reasonable values. In the final cycles of refinement the Pt, Cl, N, O, C(1) and C(2) atoms were treated anisotropically: the C(3)–C(8) atoms were considered isotropic. An attempt to refine all the C atoms anisotropically resulted in some atoms that were 'not positively defined'. This is probably due to both the poor quality of the crystal and the high disorder of the terminal methyl groups.

The H atom linked to N was included in the refinement *via* the AFIX option of SHELX 76.[3] Its thermal parameter was fixed at 0.080 Å^2, a value greater than the average $(U_{11} + U_{22} + U_{33})/2 = 0.068$ found for the N atom.

The Fourier-difference synthesis also showed a peak at $X/a = Y/b = Z/c = 0.0429$ and six more peaks around it at a distance of *ca.* 1.80 Å. These seven peaks were attributed to a dichloromethane molecule whose C atom is located on the three-fold axis. The molecule must be subject to two types of statistical disorder. First, each Cl and H atom of the molecule can assume three positions related by the three-fold axis; secondly, the dichloromethane molecule can assume either of two positions related by the centre of symmetry. For these reasons the occupancy of the C and Cl atoms was fixed at 0.167.

Table 1 Experimental details for the crystallographic analysis of $[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]\}_3]$ **2**

Formula	$C_{15}H_{33}Cl_6N_3O_3Pt_3\cdot 0.5CH_2Cl_2$
M	1143.9
Space group	$R\bar{3}$ (no. 148)
Rhombohedral setting	
a/Å	12.230(8)
α/°	105.36(3)
U/Å^3	1587(2)
D_c/g cm^{-3}	2.394
Z	2
F(000)	1050
Hexagonal setting	
a/Å	19.435(8)
c/Å	14.526(8)
Colour, dimensions/mm	Orange, 0.25 × 0.25 × 0.35
μ(Mo-Kα)/cm^{-1}	139.5
Diffractometer	Siemens P4
λ/Å	0.710 73
Scan range/°	$5 < 2\theta < 45$
Scan type	ω–2θ
Scan speed/° s^{-1}	0.06
Intensity control parameters	Three standard reflections (1 2 2, 5 −3 −1, 0 5 −1) periodically measured (2 h): no significant change in intensity
No. of data collected at 22 °C	4120 ($R_{\text{int}} = 0.11$)
No. of independent observed reflections [$F > 4\sigma(F)$]	1207
$R = \Sigma\|F_o - \|F_c\|\|/\Sigma F_o$	0.0578
$R' = \Sigma\sqrt{w}\|F_o - \|F_c\|\|/\Sigma\sqrt{w}F_o$	0.0584
Weighting scheme, $w = a/[\sigma^2(F) + bF^2]$	*a* converged to 2.5274 *b* converged to 0.001 11
No. of parameters refined	101

By using this model the *R* and *R'* values converged to 0.0578 and 0.0584, respectively. Attempts to solve and refine the structure in the triclinic system were unsuccessful. The set of coordinates for the triclinic $P\bar{1}$ space group was refined anisotropically for the Pt, Cl, N, O and C atoms. The agreement factor values converged to 0.1034 and 0.1067 for *R* and *R'*, respectively. More than 100 correlation matrix elements were greater than 0.5 and a C atom was not positively defined.

The scattering factors were those of SHELX 76[3] and SHELX 86[4] and of ref. 5. All the calculations were carried out on VAX 6610 and IBM 3090 computers using the SHELX and PARST[6] computer packages. Final atomic coordinates are listed in Table 2. The triclinic data set (4120 reflections) is available from the authors on request.

Additional material available from the Cambridge Crystallographic Data Centre comprises the thermal parameters.

Results

Compound **2** was expected to be a dimer by analogy with the structures of other platinum(II) complexes containing three donor groups per platinum atom. The mononuclear complex $K[PtCl_3\{HN{=}C(OH)C(CH_3)_3\}]$ **4**, containing one amide and three chloride ions per platinum atom, was prepared for comparison.

The ^{1}H NMR spectra revealed that in both cases (**2** and **4**) the amide was in the iminol form (one OH and one NH resonance signal at δ 10.20 and 7.20 and at δ 11.16 and 7.06 for **2** and **4**, respectively). The two compounds had rather different chemical shifts, in particular the hydroxyl proton was *ca.* 1 ppm to lower field in the anionic complex **4** compared with the neutral complex **2**.

In the IR spectra, bands at 3340 and 3060 cm^{-1} for complex **2** and at 3350 and 3280 cm^{-1} for complex **4** were observed, which are assigned to NH and OH stretching vibrations, respectively.[7] These data indicate that the hydroxyl proton is more shielded and the O–H bond weaker in the neutral complex **2** compared with the anionic species. **4**. This could be taken as an indication of the presence of a strong hydrogen bond involving the hydroxyl group in **2**.

Table 2 Atomic coordinates (× 10^4) of $[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]\}_3]$ **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt	2624(1)	2272(1)	4235(1)
Cl(1)	2790(4)	4301(4)	4632(4)
Cl(2)	664(5)	1841(6)	4240(7)
O	927(16)	−507(16)	4130(24)
N	2568(15)	558(13)	3880(15)
H(N)	3340(15)	463(13)	3650(15)
C(1)	1894(17)	−458(18)	3838(15)
C(2)	2103(18)	−1672(17)	3528(18)
C(3)[a]	3474(26)	−1442(46)	3830(52)
C(4)[a]	1643(64)	−2273(56)	2128(25)
C(5)[a]	1565(70)	−2491(56)	4153(66)
C(6)[a]	3092(48)	−1738(58)	2987(61)
C(7)[a]	2328(51)	−2020(46)	4670(33)
C(8)[a]	887(37)	−2598(45)	2533(48)
C(D)[b]	429	429	429
Cl(1D)[b]	−476(58)	−922(56)	541(81)
Cl(2D)[b]	297(74)	116(123)	−1123(42)

[a] The occupancy factor (s.o.f.) for the C(3), C(4) and C(5) atoms was refined as a free variable constrained to sum up to 1 with the corresponding values for C(6), C(7) and C(8). The s.o.f. value was 0.48(6) for C(3), C(4) and C(5) and 0.52(6) for C(6), C(7) and C(8), respectively. [b] The s.o.f. value was fixed at 0.167.

Table 3 Bond distances (Å) for $[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]\}_3]$ **2**

Pt–Cl(1)	2.340(4)	C(1)–C(2)	1.539(27)
Pt–Cl(2)	2.315(5)	C(2)–C(3)[a]	1.548(19)
Pt–N	2.003(15)	C(2)–C(4)[a]	1.547(19)
Pt–Cl(1a)[b]	2.342(4)	C(2)–C(5)[a]	1.531(19)
Pt–Pt(a)[b]	3.527(1)	C(2)–C(6)[a]	1.534(19)
C(1)–O	1.314(24)	C(2)–C(7)[a]	1.543(19)
C(1)–N	1.277(22)	C(2)–C(8)[a]	1.547(19)
H(N)–N	1.08	C(D)–Cl(1D)[c]	1.790(28)
		C(D)–Cl(2D)[c]	1.788(31)

[a] Bond distances were constrained at 1.53 ± 0.02 Å *via* the AFIX instruction of SHELX.[3] [b] Related by the *x,y,z*→*z,x,y* relationship to Cl(1) and Pt, respectively. [c] Bond distances were constrained at 1.80 ± 0.03 Å *via* the AFIX instruction of SHELX.[3]

Table 4 Bond angles (°) for $[\{PtCl_2[HN{=}C(OH)C(CH_3)_3]\}_3]$ **2**

Cl(1)–Pt–Cl(2)	88.1(2)	C(1)–C(2)–C(4)	108.1(20)
Cl(1)–Pt–Cl(1a)*	89.9(2)	C(1)–C(2)–C(5)	113.0(30)
Cl(1)–Pt–N	176.8(5)	C(3)–C(2)–C(4)	99.6(29)
Cl(2)–Pt–Cl(1a)*	177.5(2)	C(3)–C(2)–C(5)	110.9(38)
Cl(2)–Pt–N	95.1(5)	C(4)–C(2)–C(5)	114.2(39)
Cl(1a)–Pt–N	87.0(6)	C(1)–C(2)–C(6)	116.6(31)
Pt–Cl(1)–Pt(a)*	97.7(2)	C(1)–C(2)–C(7)	108.4(20)
Pt–N–C(1)	139.2(16)	C(1)–C(2)–C(8)	104.5(24)
N–C(1)–O	118.8(20)	C(6)–C(2)–C(7)	111.3(36)
N–C(1)–C(2)	127.3(20)	C(6)–C(2)–C(8)	106.3(34)
O–C(1)–C(2)	113.9(19)	C(7)–C(2)–C(8)	109.4(31)
C(1)–C(2)–C(3)	110.4(25)	Cl(1D)–C(D)–Cl(2D)	108.2(26)

* Pt(a) and Cl(1a) related to the asymmetric unit atoms *via* the *x,y,z*→*z,x,y* transformation.

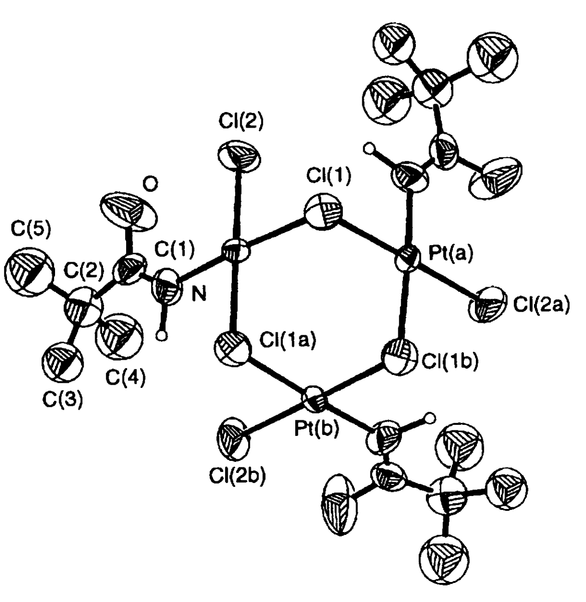
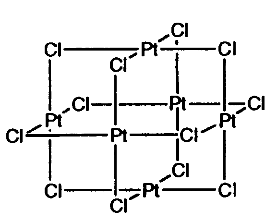
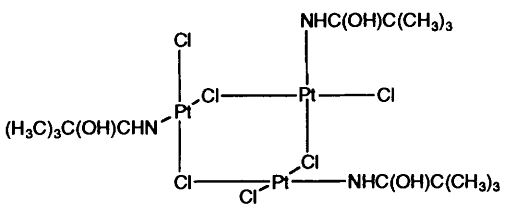


Fig. 1 ORTEP[8] drawing of the complex molecule with the labelling scheme of the asymmetric unit. The ellipsoids enclose 50% probability



Pt_6Cl_{12}



2

Crystal Structure of Complex **2**.—The complex molecule is illustrated in Fig. 1 and bond distances and angles are reported in Tables 3 and 4, respectively.

The co-ordination geometry around each Pt centre is square planar [the Pt atom deviates by 0.024(1) Å from the plane defined by the donor atoms in the direction of the other metal centres]. Two *cis* positions of the co-ordination polyhedron are occupied by a terminal chloride ion [Cl(2)] and by the N atom of an amide ligand, respectively; the other two positions are occupied by bridging chloride ions which link the platinum centre to the other two metallic centres of the trimer. The three-fold crystallographic axis is perpendicular to the triangle formed by the three Pt atoms of the complex molecule and passes through its centroid.

The Pt–Cl(2) bond distance [2.315(5) Å] is slightly shorter than the Pt–Cl(bridging) distances [average 2.340(4) Å] in agreement with those in *cis*- and *trans*-$[PtCl_2(NH_3)_2]$ (averages 2.33 ± 0.01 and 2.32 ± 0.01 Å, respectively),[9] and square-planar platinum(II),[10,11] octahedral platinum(IV) and binuclear platinum(II)[1] and platinum(III) compounds.[12]

The Pt–N bond distance of 2.003(15) Å is almost three times the e.s.d. smaller than those reported for *trans*-$[PtCl_2(NH_3)_2]$ (average 2.05 Å),[9] $[PtCl_2(R_2NCH_2CH_2NR_2)]$ (R = Pr^i, 2.075; Bu^t, 2.087; or CHMePh, 2.044 Å),[10] and other platinum(II) complexes with the same *tert*-butylamide ligand (2.012–2.040 Å).[1]

The iminol tautomeric form of the amide ligands could not be confirmed by X-ray data since no hydrogen atoms could be located from Fourier-difference analysis. However, the geometrical parameters of the ligand are very similar to those found in other platinum complexes containing the same amide in the iminol form.[1,12] The N–C and C–O bond distances are not significantly different, although the former appears to be slightly shorter than the latter.

The co-ordination bond angles are normal, the largest deviation from canonical values being the Cl(2)–Pt–N angle [95.1(5)°]. Also the Pt–Cl–Pt angle [97.7(2)°] is similar to those found in most chloride-bridged platinum clusters (Table 5).[13–22]

Discussion

Most of the Pt^{II} complexes containing chloride bridges are dinuclear and have a coplanar set of metal centres and donor atoms[13–22] {dihedral angle between the two platinum co-ordination planes deviates significantly from 180° only in the case of $[Pt_2Cl_2(SnCl_3)_2(PEt_3)_2]$}.[17] The mean value found for the Pt–Cl–Pt bond angles is 96° and is accompanied by a mean value for the Cl–Pt–Cl angle between bridging chlorides of 84° (Table 5) (in a planar arrangement the sum of these two angles must be equal to 180°). In compound **2** the Pt–Cl–Pt angle [97.7(2)°] is in agreement with those found in dinuclear compounds, however the Cl–Pt–Cl angle between the bridging chlorides is very close to 90° [89.9(2)°] and is permitted by the different arrangement of the platinum subunits.

In compound **2** the chloride bridges are arranged in such a way that the resulting co-ordination planes are mutually orthogonal [dihedral angle 99.2(2)°]. The overall structure is strongly related to that of the β form of $PtCl_2$.[2] Crystals of the latter contain discrete Pt_6Cl_{12} molecules arranged in a cubic cluster with the six co-ordination planes almost at right angles with respect to each other. Compound **2**

Table 5 The Pt–X–Pt and X–Pt–X bond angles (°) of some bi- and tri-nuclear platinum complexes with Cl or OH bridges together with the dihedral angle (°) between the co-ordination planes (α)

Compound	Pt–Cl–Pt	Cl–Pt–Cl	α	Ref.
$[Pt_2Cl_4(PPr^n_3)_2]$	96.4(3)	83.6(3)	180	13
$[Pt_2Cl_4(AsMe_3)_2]$	95.4(2)	84.6(2)	180	14
$[Pt_2Cl_2(COEt)_2(PMe_2Ph)_2]$	96.3(1)	83.7(1)	180	15
$[Pt_2\{P(CMe_2CH_2)Bu^t_2\}_2Cl_2]$	96.1	83.9	180	16
$[Pt_2Cl_2(SnCl_3)_2(PEt_3)_2]$	80.5(3)	84.3(3)		17
$[Pt_2Cl_2\{C(CF_3)=C(CF_3)(SnCl_3)\}_2(PEt_3)_2]$	94.9(1)	85.1(1)	180	18
$[NBu^n_4]_2[Pt_2Cl_2(C_6F_5)_4]$	95.1(1)	84.9(1)	180	19
$[Pt_2Cl_2\{[P(CF_3)_2]_2CMe\}_2]$	94.85(8)	85.15(8)	180	20
$[Pt_2\{P(C_6H_2Me_2CH_2)(C_6H_2Me_3)_2\}_2Cl_2]$	96.43(4)	83.57(4)	180	21
$[Pt_2Cl_4(PEt_3)_2]$	96.5(1)	83.5(1)	180	22
$[Pt_3Cl_6\{HN=C(OH)Bu^t\}_3]$	97.7(2)	89.9(2)	99.2(2)	This work
	Pt–O–Pt	O–Pt–O		
$[Pt_3(OH)_3(NH_3)_6][NO_3]_3$	111(1)	91(1)		23
	118(1)	92(1)		
	123(1)	93(1)		
$[Pt_3(OH)_3(NH_3)_6]_2[SO_4]_3\cdot 6H_2O$	109(1)	88.7(6)		24
	109(1)	90.4(6)		
	109(1)	87.4(7)		
$[Pt_3(OH)_3\{C_6H_{10}(NH_2)_2\}_3]_2[SO_4]_3\cdot 14H_2O$	106.1(7)	86.9(6)		25
	106.3(6)	84.0(6)		
	108.9(7)	86.9(5)		

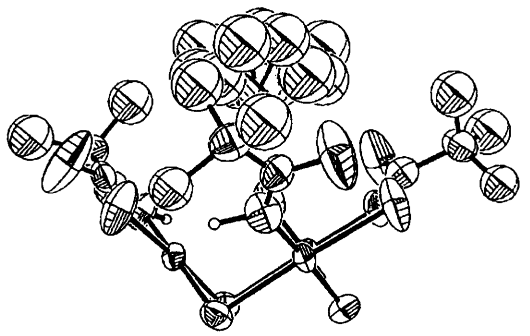


Fig. 2 View of the complex molecule and its proximal CH_2Cl_2 molecule along an axis perpendicular to C_3

incorporates exactly one half of the cubic Pt_6Cl_{12} molecule (*i.e.* Pt_3Cl_6) and saturate the co-ordination sites, made available by splitting of the chloride bridges between the two halves of the cube, with three amide ligands (see below).

It was argued that there is a bonding interaction between the platinum atoms linked by chloride bridges in the structure of Pt_6Cl_{12}. Although the Pt–Pt distances (3.32–3.40 Å) were rather long (sum of the van der Waals radii 3.40–3.60 Å),[26] only an attractive interaction between the two atoms could explain the displacement of the platinum atoms from the plane of the co-ordinated chloride ions towards the other platinum centres (0.040 Å) resulting in a Pt–Cl–Pt angle smaller than 90° [87.5(4)–88.5(4)°]. In compound **2** the displacement of the platinum atoms from the co-ordination planes is very close to those found for the β form of $PtCl_2$ [0.024(1) Å]. The fact that the intermetallic distances in **2** are longer than those found in Pt_6Cl_{12} [3.527(1) Å *cf.* 3.32–3.40 Å] could be the consequence of the open structure of the cluster (half a cube instead of a closed cube) with three rather bulky *tert*-butylamide ligands sitting on the brim of the calyx which can suffer intramolecular steric repulsion.

We have already pointed out that in the case of a platinum trimer with an orthogonal arrangement of co-ordination planes the Cl–Pt–Cl and Pt–Cl–Pt angles can vary independently from one another and they are free to assume the preferred value. The expected value for a Pt–Cl–Pt angle should be close to 109° (tetrahedral geometry of the chloride valence shell) or somewhat less to account for the greater electrostatic repulsion of the unshared lone pairs of electrons. The actual value of the Pt–Cl–Pt angle is 97.7(2)° and can be considered as further evidence in favour of an attractive interaction among the platinum atoms in addition to the displacement of the platinum atoms from the co-ordination planes towards the other metallic centres (0.024 Å) already mentioned. It can be inferred that in compound **2** the entropy cost consequent to the association of three platinum units in a trimer (instead of two units in a dimer) is compensated by the enthalpy gain resulting from less strained chloride bridges and, possibly, intermetallic bonding interactions.

Although compound **2** is the first trinuclear complex of platinum(II) containing chloride bridges that has been identified, similar complexes containing hydroxide bridges have already been reported. Two hydroxide-bridged trimers, with different counter ions, were reported by Rosenberg and co-workers.[23,24] The nitrato species $[Pt_3(OH)_3(NH_3)_6][NO_3]_3$ has little in common with the chloride-bridged trimer described here.[23] The complex contains square-planar units held together by bridging OH^- groups. The trimer, however, has not a trigonal symmetry but a pseudo two-fold axis passes through one Pt and one O atom, the three co-ordination planes being twisted with respect to the pseudo axis. The Pt–O–Pt bond angles are all different and rather large [111(1), 118(1) and 123(1)°, respectively]. Therefore the latter structure differs significantly from the cubic structure of Pt_6Cl_{12}, as well as from the structure of compound **2**, and the very large values of the Pt–O–Pt angles are indicative of the absence of intermetallic attractive interactions although the intermetallic distances remain rather short [Pt(1)–Pt(2) 3.341(2), Pt(1)–Pt(3) 3.440(2), Pt(2)–Pt(3) 3.521(2) Å].

In contrast, the sulfato species $[Pt_3(OH)_3(NH_3)_6]_2[SO_4]_3\cdot 6H_2O$ has a structure strictly related to that of compound **2** with three hydroxides in place of the bridging chlorides and six ammines in place of the three terminal chlorides and the three amide ligands.[24] The dihedral angles between the co-ordination planes are in the range 108.1–111.1° and are greater than those of compound **2**. This allows the Pt–O–Pt angles to assume values in the range 107.8(9)–109.2(11)° very close to the tetrahedral angle. The Pt···Pt distances are rather short 3.282(2)–3.291(2) Å but the Pt atoms are not displaced from the mean co-ordination planes. Therefore, in spite of the close Pt–Pt contacts, no attractive

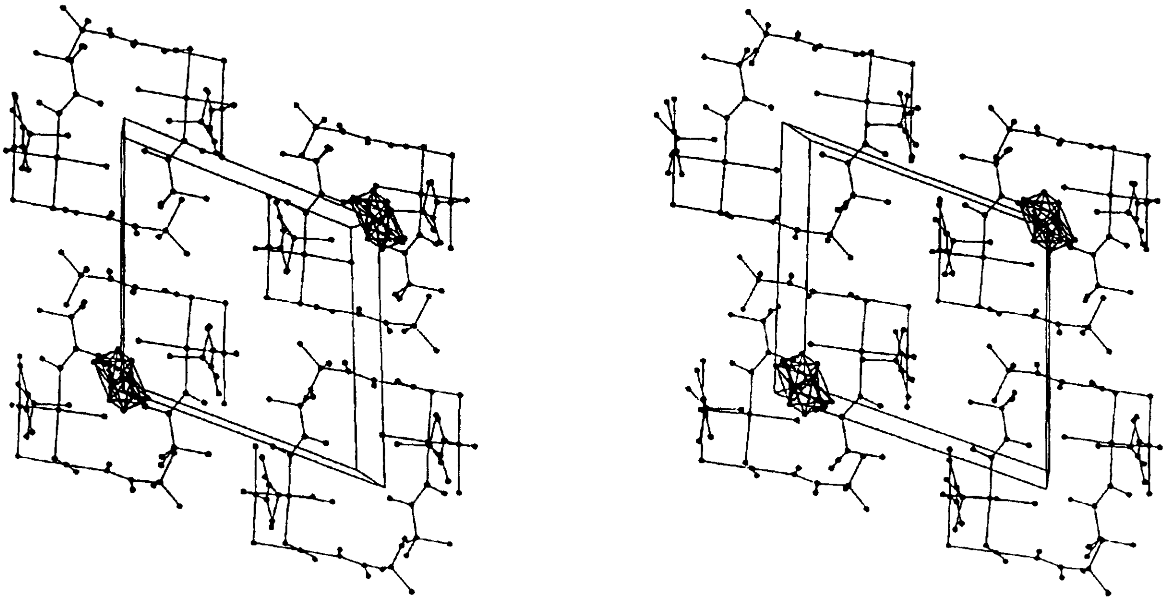


Fig. 3 Stereoview of the crystal packing along the *a* cell edge

interaction seems to take place and the authors assume that in solution the cation is sterically non-rigid and undergoes a rearrangement with inversion of configuration.

A third hydroxide-bridged trimer was reported by Macquet *et al.*[25] The structure is closely related to that of the sulfato species $[Pt_3(OH)_3(NH_3)_6]_2[SO_4]_3\cdot6H_2O$ with three *trans*-1,2-diaminocyclohexane ligands in place of the six ammines. The dihedral angles between the coordination planes are in the range 107.0(4)–109.1(4)° and allow the Pt–O–Pt angles to assume values [106.1(7)–108.9(7)°] very close to the tetrahedral angle. The Pt $\cdots$ Pt distances are rather short [3.251(4)–3.338(3) Å] but no displacement of the Pt atoms from the mean co-ordination planes is observed. Therefore also in this case, in spite of the close Pt–Pt contacts, no intermetallic attractive interactions seem to take place.

We propose that structural considerations, such as the narrowing of a Pt–X–Pt angle below the expected value and the displacement of the platinum atom from the co-ordination plane towards the other metallic centres, are better arguments than the value of the Pt $\cdots$ Pt distance itself to assess the existence of an intermetallic attractive interaction. This is also the case for Pt $\cdots$ H interactions for which a short distance is not necessarily indicative of an agostic interaction [a short distance resulting from geometrical constraints usually causes a downfield shift of the proton resonance; on the contrary a short distance resulting from bonding (agostic) interaction results in an upfield shift of the proton resonance].[27]

Therefore, while the $[Pt_3(NH_3)_6(OH)_3]^{3+}$ trimers appear to be essentially stabilized by the hydroxide bridges, compound **2** is likely to gain stability from a metal–metal interaction. The amide ligands could play a crucial role in favouring the formation of intermetallic interactions. It is worth recalling that compound **1**, having two amides and two chloride ions per platinum(II) cation, has a dimeric structure in which the two units are placed face to face and are linked together by four hydrogen bonds and a direct intermetallic interaction.[1] The intermetallic interaction between platinum(II) units could be favoured by removal of electron charge from filled d orbitals of the metal promoted by the π^* orbital of the amide.

In compound **2** three intramolecular hydrogen bonds link chlorine (terminal) and oxygen atoms, as can be argued from the geometry of the complex molecule [in-plane orientation of the amide ligand with a Cl(2)–Pt–N–C(1) torsion angle of 12(3)°] and from the contact distance O $\cdots$ Cl(2) 2.94(2) Å. The intramolecular O–H $\cdots$ Cl hydrogen bond appears to be particularly strong thus confirming the prediction made on the basis of the IR and NMR data. The NMR data also indicate that the same type of interaction takes place in solution. The geometry of the N–H $\cdots$ Cl(1a) (bridging) groups [N $\cdots$ Cl 3.00(2) Å, N–H $\cdots$ Cl *ca.* 99°] suggests the presence of another intramolecular hydrogen bond. The complex, as a whole, assumes a calyx-type shape and two molecules of complex take up one molecule of solvent with short contacts between the chlorine atoms of the dichloromethane molecule and the methyl carbon [C(4) $\cdots$ Cl(1D) $(-y, -z, -x)$ 3.41(2), C(4) $\cdots$ Cl(2D) (y, z, x) 3.36(2) Å] and oxygen atoms [O $\cdots$ Cl(2D) $(-x, -y, -z)$ 3.79(2) Å] of the amides (Fig. 2). The possibility that this complex can act as a cryptand towards other molecules is under investigation. It is noteworthy that Pt_6Cl_{12} gives adducts (clathrates) with several molecules including benzene, CS_2, $CHCl_3$ and Br_2.[2]

The structure reported in this work does not have any intermolecular Pt $\cdots$ Pt contact shorter than 4 Å. In the $[Pt_3(NH_3)_6(OH)_3]^{3+}$ trimers intermolecular Pt $\cdots$ Pt and Pt $\cdots$ O contacts were observed. The crystal packing (Fig. 3) is stabilized by weak dipole–dipole and hydrophobic interactions which involve *tert*-butyl groups of different molecules [shortest contact: C(3A) $\cdots$ C(4A) $(-z, -x + 1, -y)$ 3.42(2) Å]. The overall structure is characterized by the presence of two types of channels almost parallel to the three-fold axis. One is made up of a stack of Pt_3Cl_3 rings, the other by the *tert*-butyl groups of three adjacent stacks of molecules.

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