Olk, R.-M., Olk, B., Dietzsch, W., Kirmse, R. & Hoyer, E. (1992). *Coord. Chem. Rev.* **117**, 99–131, and references therein.
Valade, L., Legros, J.-P., Tejel, C., Pomarede, B., Garreau, B., Bruniquel, M. F. & Cassoux, P. (1991). *Synth. Met.* pp. 41–43, 2268.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 156–166.

Acta Cryst. (1996). C**52**, 541–543

[N,N'-Bis(2-aminoethyl-κN)-N,N'-bis(2-ammonioethyl)ethylenediamine-$\kappa^2 N,N'$]-platinum(II) Bis(tetrachloroplatinate) Trihydrate

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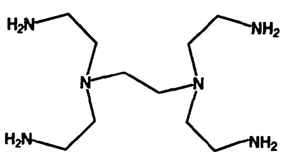
Abstract

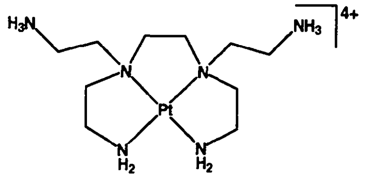
The reaction between K_2PtCl_4 and penten [N,N,N',N'-tetrakis(2-aminoethyl)ethylenediamine] gave a Magnus-type double salt, $[Pt(C_{10}H_{30}N_6)][PtCl_4]_2.3H_2O$, in which the diprotonated penten ligand (pentenH$_2$) serves as a tetradentate chelating ligand. The complex involves an ion pair, $\{[Pt(pentenH_2)][PtCl_4]\}^{2+}$. These two mononuclear units have an attractive interaction for each other, with several hydrogen bonds formed between the amine groups and Cl atoms. The two Pt atoms are shifted out of their ideal coordination planes towards each other and the Pt···Pt distance within this unit is 3.414 (3) Å.

Comment

Our initial interest in penten, (1), lay in its use in the syntheses of binuclear complexes. The reaction between K_2PtCl_4 and penten, conducted at pH 0–5, gave the title complex as the sole product. The complex is a 1:2 salt of a tetravalent $[Pt(pentenH_2)]^{4+}$ cation, (2), and a divalent $PtCl_4^{2-}$ anion, and can be regarded as a Magnus-type double salt. It appears that penten prefers to behave as a tetradentate chelate, implying that the complexation of the two tertiary amines predominantly occurs prior to that of the primary amines.



(1) penten



(2) $[Pt(pentenH_2)]^{4+}$

Fig. 1 shows the structure of the complex salt. A stereodiagram of the crystal packing is shown in Fig. 2. All the C—N distances [1.42 (6)–1.65 (6) Å] indicate single-bond character. The $[Pt(pentenH_2)]^{4+}$ cation shows a large distortion from ideal square-planar geometry due to the strain caused by the three chelate rings, as shown in Table 2. All three coordination planes, however, are judged to be planar in the best-plane calculations performed with the four coordinated atoms, where the four-atom r.m.s. deviations are 0.041, 0.034 and 0.089 Å for the Pt(1), Pt(2) and Pt(3) planes, respectively. One interesting feature is that the Pt(1) and Pt(2) atoms are shifted out of their coordination planes towards each other by 0.14 (2) and 0.026 (8) Å, respectively. The Pt(1)···Pt(2) distance of 3.414 (3) Å is not as short as the distance of 3.25 Å reported for the Magnus green salt $[Pt(NH_3)_4][PtCl_4]$ (Atoji, Richardson & Rundle, 1957), but is comparable to the distance of 3.39 Å reported for $Pt(en)Cl_2$ (en = ethylenediamine) (Martin, Hunter, Kroening & Coley, 1971). These two planes are also attracted to each other, with four hydrogen bonds formed between the amine groups and the Cl atoms (Table 2). Although similar hydrogen-bonding interactions are achieved between the Pt(1) and Pt(3) planes, the Pt(1)···Pt(3) distance of 3.957 (3) Å is too long to be considered as a metal–metal interaction. The dihedral angle between the Pt(1) and Pt(2) planes is 27.6 (8)°, while that between the Pt(1) and Pt(3) planes is 30.6 (8)°. Moreover, this complex ion pair further interacts with neighbouring ion pairs through similar hydrogen bonds, resulting in the formation of a three-dimensional network. In addition, the water molecules also participate in this hydrogen-bonding network. Most of these interactions, however, appear to be insignificant due to the absence of metal–metal interactions. The ion pair formed between the Pt(1) and Pt(2) units in the asymmetric unit is, therefore, the only one which is expected to possess a meaningful metal–metal interaction. In conclusion, this compound can be regarded as a rare example of a double salt which does not have infinite Pt···Pt interactions, but rather has a dimeric Pt···Pt interaction. It is well known that the *d–d* transition of $PtCl_4^{2-}$ in the Magnus green salt is largely red-shifted due to exceptional crystal effects (Martin, Rush, Kroening & Fanwick, 1973). Such a shift in the *d–d* transition is, however, not promoted in the title compound, for both the colour and the UV–visible spectra of the compound resemble those of K_2PtCl_4 in the solid state.

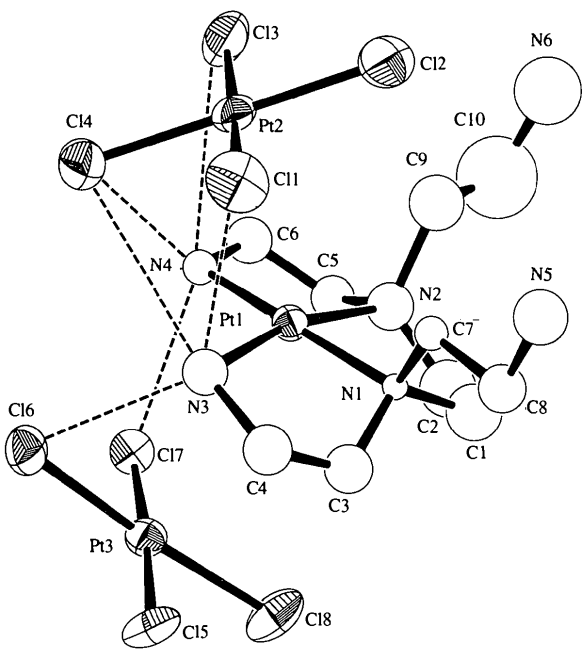


Fig. 1. View of $[Pt(pentenH_2)][PtCl_4]_2$ showing 50% displacement ellipsoids. Water molecules and H atoms are omitted for clarity and hydrogen bonds are shown as dashed lines.

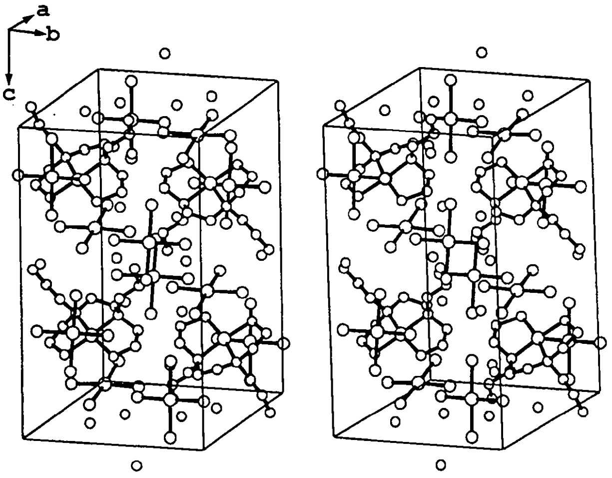


Fig. 2. Stereodiagram of the crystal packing of $[Pt(pentenH_2)]-[PtCl_4]_2.3H_2O$. For clarity, atoms are drawn as ideal spheres and H atoms are omitted.

Experimental

Aziridine, used to prepare penten, was synthesized according to the method of Wystrach, Kaiser & Schaefer (1955), and penten was prepared according to the literature method of Gauss, Moser & Schwarzenbach (1952). For the preparation of the title complex, a solution of penten (0.125 mmol) in 0.1 *M* HCl (2.5 ml) was added dropwise to a solution of K_2PtCl_4 (0.25 mmol) in 0.1 *M* HCl (2.5 ml) over 1 h, during which time the solution was stirred at 353 K. The mixture was stirred at 353 K for a further 4–5 h. On standing the solution at room temperature for 2 days, the product deposited as reddish brown needles (yield 46%). Analysis: calculated for $C_{10}H_{36}Cl_8N_6O_3Pt_3$ C 10.38, H 3.14, N 7.26%; found C 10.40, H 3.28, N 7.26%.

Crystal data

$[Pt(C_{10}H_{30}N_6)][PtCl_4]_2.3H_2O$
$M_r = 1157.33$
Monoclinic
$P2_1/c$
$a = 12.141\ (2)$ Å
$b = 12.010\ (1)$ Å
$c = 19.248\ (2)$ Å
$\beta = 97.03\ (1)^\circ$
$V = 2785.5\ (6)$ Å^3
$Z = 4$
$D_x = 2.760$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 20.13–23.18^\circ$
$\mu = 15.821$ mm^{-1}
$T = 296.0$ K
Plate
0.43 × 0.15 × 0.05 mm
Reddish brown

Data collection

Rigaku AFC-5*S* diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.348$, $T_{max} = 1.000$
5437 measured reflections
5179 independent reflections

1826 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.1338$
$\theta_{max} = 25^\circ$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -22 \rightarrow 22$
3 standard reflections monitored every 150 reflections intensity decay: 0.29%

Refinement

Refinement on *F*
$R = 0.0669$
$wR = 0.0443$
$S = 1.51$
1826 reflections
192 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$ $[\sigma(F)$ from counting statistics]

$(\Delta/\sigma)_{max} = 0.5670$
$\Delta\rho_{max} = 2.23$ e Å^{-3}
$\Delta\rho_{min} = -2.79$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2A)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} for N and C; $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for Pt, Cl and O.

	x	y	z	U_{eq}/U_{iso}
Pt(1)	0.2365 (1)	0.2180 (2)	0.20524 (8)	0.0283 (5)
Pt(2)	−0.0398 (2)	0.1975 (2)	0.1466 (1)	0.0419 (7)
Pt(3)	0.4133 (2)	0.2284 (2)	0.39196 (9)	0.0356 (6)
Cl(1)	−0.059 (1)	0.389 (1)	0.1444 (8)	0.069 (6)
Cl(2)	−0.015 (1)	0.189 (1)	0.0293 (6)	0.074 (5)
Cl(3)	−0.031 (1)	0.007 (1)	0.1491 (8)	0.062 (5)
Cl(4)	−0.0638 (9)	0.203 (1)	0.2639 (5)	0.059 (4)
Cl(5)	0.423 (1)	0.417 (1)	0.3992 (8)	0.055 (5)
Cl(6)	0.2371 (9)	0.235 (1)	0.4247 (5)	0.048 (4)
Cl(7)	0.405 (1)	0.037 (1)	0.3927 (7)	0.052 (5)
Cl(8)	0.5823 (9)	0.224 (1)	0.3490 (6)	0.058 (4)
O(1)	−0.022 (3)	0.118 (3)	0.432 (2)	0.12 (2)
O(2)	0.675 (3)	0.225 (3)	0.178 (2)	0.13 (2)
O(3)	0.668 (3)	0.268 (4)	0.035 (2)	0.13 (2)
N(1)	0.306 (3)	0.337 (2)	0.150 (1)	0.014 (8)
N(2)	0.330 (3)	0.110 (3)	0.153 (2)	0.05 (1)
N(3)	0.180 (3)	0.345 (3)	0.260 (2)	0.04 (1)
N(4)	0.195 (3)	0.080 (3)	0.259 (2)	0.026 (9)

N(5)	0.199 (4)	0.523 (3)	−0.004 (2)	0.06 (1)
N(6)	0.229 (4)	−0.030 (4)	−0.021 (3)	0.10 (1)
C(1)	0.404 (4)	0.293 (5)	0.119 (2)	0.07 (1)
C(2)	0.427 (4)	0.173 (4)	0.145 (3)	0.07 (1)
C(3)	0.334 (5)	0.422 (4)	0.202 (3)	0.05 (1)
C(4)	0.247 (5)	0.456 (4)	0.238 (3)	0.05 (1)
C(5)	0.344 (4)	0.009 (4)	0.202 (2)	0.04 (1)
C(6)	0.244 (5)	−0.021 (4)	0.232 (2)	0.05 (1)
C(7)	0.231 (4)	0.391 (3)	0.093 (2)	0.02 (1)
C(8)	0.283 (5)	0.489 (4)	0.059 (2)	0.05 (1)
C(9)	0.252 (5)	0.067 (4)	0.084 (3)	0.06 (1)
C(10)	0.302 (8)	−0.020 (6)	0.049 (4)	0.14 (2)

Table 2. *Selected geometric parameters (Å, °)*

Pt(1)—N(1)	2.03 (3)	Pt(2)—Cl(3)	2.30 (1)
Pt(1)—N(2)	2.06 (4)	Pt(2)—Cl(4)	2.31 (1)
Pt(1)—N(3)	2.02 (3)	Pt(3)—Cl(5)	2.27 (1)
Pt(1)—N(4)	2.05 (3)	Pt(3)—Cl(6)	2.30 (1)
Pt(2)—Cl(1)	2.32 (1)	Pt(3)—Cl(7)	2.30 (1)
Pt(2)—Cl(2)	2.32 (1)	Pt(3)—Cl(8)	2.31 (1)
N(1)—Pt(1)—N(2)	83 (1)	Cl(2)—Pt(2)—Cl(3)	88.0 (5)
N(1)—Pt(1)—N(3)	86 (1)	Cl(2)—Pt(2)—Cl(4)	179.0 (5)
N(1)—Pt(1)—N(4)	168 (1)	Cl(3)—Pt(2)—Cl(4)	91.0 (5)
N(2)—Pt(1)—N(3)	165 (1)	Cl(5)—Pt(3)—Cl(6)	89.5 (5)
N(2)—Pt(1)—N(4)	85 (1)	Cl(5)—Pt(3)—Cl(7)	176.2 (4)
N(3)—Pt(1)—N(4)	103 (1)	Cl(5)—Pt(3)—Cl(8)	90.2 (5)
Cl(1)—Pt(2)—Cl(2)	92.9 (6)	Cl(6)—Pt(3)—Cl(7)	89.7 (5)
Cl(1)—Pt(2)—Cl(3)	176.7 (5)	Cl(6)—Pt(3)—Cl(8)	174.8 (4)
Cl(1)—Pt(2)—Cl(4)	88.1 (5)	Cl(7)—Pt(3)—Cl(8)	90.9 (5)

Intra- and intermolecular hydrogen-bond contact distances

Cl(1)···N(3)	3.47 (4)	Cl(3)···N(4)	3.36 (4)
Cl(4)···N(3)	3.43 (4)	Cl(4)···N(4)	3.48 (4)
Cl(6)···N(3)	3.43 (4)	Cl(7)···N(4)	3.44 (4)
Cl(1)···N(5^{i})	3.19 (5)	Cl(1)···N(4^{v})	3.49 (3)
Cl(2)···N(6^{ii})	3.22 (5)	Cl(3)···N(6^{ii})	3.24 (6)
Cl(3)···N(3^{iii})	3.29 (4)	Cl(5)···N(6^{iv})	3.26 (5)
Cl(6)···N(5^{iv})	3.45 (4)	Cl(7)···N(5^{iv})	3.47 (4)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, -y, -z$; (iii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Data collection and cell refinement were carried out using *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Metal-atom positions were determined by direct methods (*SAPI90*; Fan, 1990). The remaining non-H atoms were located using the *DIRDIF* program (Parthasarathi, Beurskens & Slot, 1993) and were refined anisotropically by full-matrix least squares. Pt, Cl and O atoms were treated anisotropically, and N and C atoms were treated isotropically. H atoms of the penten ligand were located in their calculated positions (C—H 0.95, N—H 0.87 Å) and were not refined. H atoms of water molecules were not located. Relatively large positive and negative peaks were found in the final difference Fourier map but these were all error peaks located near the Pt and Cl atoms. Best-plane calculations were performed with the *BP70* program developed by Ito (1982). All other calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Atoji, M., Richardson, J. W. & Rundle, R. E. (1957). *J. Am. Chem. Soc.* **79**, 3017–3020.

Fan, H.-F. (1990). *SAPI90. Structure Analysis Programs with Intelligent Control.* Rigaku Corporation, Tokyo, Japan.

Gauss, W., Moser, P. & Schwarzenbach, G. (1952). *Helv. Chim. Acta*, **35**, 2359–2363.

Ito, T. (1982). *Acta Cryst.* A**38**, 869–870.

Martin, D. S. Jr, Hunter, L. D., Kroening, R. & Coley, R. F. (1971). *J. Am. Chem. Soc.* **93**, 5433–5440.

Martin, D. S. Jr, Rush, R. M., Kroening, R. F. & Fanwick, P. E. (1973). *Inorg. Chem.* **12**, 301–305.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software.* Version 1.6c. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Parthasarathi, V., Beurskens, P. T. & Slot, H. J. B. (1983). *Acta Cryst.* A**39**, 351–359.

Wystrach, V. P., Kaiser, D. W. & Schaefer, F. C. (1955). *J. Am. Chem. Soc.* **77**, 5915–5918.

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Nickel(II) Bis(*d*-campholyl-*l*-campholylmethanate)

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Abstract

The title compound, bis{1-[(+)-(1*R*,3*S*)-1,2,2,3-tetramethylcyclopentyl]-3-[(−)-(1*S*,3*R*)-1,2,2,3-tetramethylcyclopentyl]propane-1,3-dionato-*O*,*O*′}nickel(II), [Ni($C_{21}H_{35}O_2$)$_2$], displays interesting stereochemical aspects due to the *meso* configuration of the 1,3-bis(1,2,2,3-tetramethylcyclopentyl)-1,3-propanedionate ligands. The Ni atom lies on an inversion centre, with Ni—O distances of 1.842 (2) and 1.826 (2) Å.

Comment

Chiral metal β-diketonates, *e.g.* europium(III) tris[3-heptafluorobutanoyl-(1*R*)-camphorate] or nickel(II) bis-[3-heptafluorobutanoyl-(1*R*)-camphorate], are important auxiliaries for the discrimination of enantiomers in