Refinement

Refinement on F^2
$R(F) = 0.028$
$wR(F^2) = 0.072$
$S = 1.204$
4572 reflections
238 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 2.1830P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.799$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.643$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0022 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.02 (3)

Table 1. *Selected bond lengths (Å)*

Cd1—O8^{i}	2.188 (3)	Cd2—O5	2.207 (3)
Cd1—O7	2.217 (3)	Cd2—O12^{ii}	2.226 (3)
Cd1—O1W	2.257 (3)	Cd2—O2^{iii}	2.244 (3)
Cd1—O1	2.296 (3)	Cd2—O11	2.247 (3)
Cd1—O3	2.314 (2)	Cd2—O10	2.406 (3)
Cd1—O9	2.400 (3)	Cd2—O4	2.425 (3)

Symmetry codes: (i) $\frac{1}{2}+x, -\frac{3}{2}-y, -1-z$; (ii) $x-\frac{1}{2}, -\frac{1}{2}-y, -1-z$; (iii) $-x, \frac{1}{2}+y, -\frac{1}{2}-z$.

Table 2. *Contact distances and hydrogen-bonding geometry (Å, °)*

O1$W\cdots$O6^{i}	2.613 (6)	O2$W\cdots$O4W^{i}	2.795 (9)
O1$W\cdots$O2^{ii}	2.843 (4)	O2$W\cdots$O4^{iv}	2.841 (5)
O1$W\cdots$O8^{iii}	2.925 (5)	O3$W\cdots$O4W^{v}	2.817 (9)
O2$W\cdots$O5	2.753 (6)	O3$W\cdots$O1^{vi}	2.891 (6)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3O$\cdots$O3W^{ii}	0.820	1.805	2.584 (5)	158.26
O4—H4O$\cdots$O9	0.820	2.121	2.896 (4)	157.52
O4—H4O$\cdots$O3	0.820	2.316	2.769 (3)	115.44
O9—H9O$\cdots$O4W^{ii}	0.820	2.009	2.785 (7)	157.66
O10—H10O$\cdots$O4W^{i}	0.820	2.313	3.085 (7)	156.86

Symmetry codes: (i) $-1-x, y-\frac{1}{2}, -\frac{1}{2}-z$; (ii) $-x, y-\frac{1}{2}, -\frac{1}{2}-z$; (iii) $\frac{1}{2}+x, -\frac{3}{2}-y, -1-z$; (iv) $x-1, y, z$; (v) $1+x, y, z$; (vi) $1-x, \frac{1}{2}+y, -\frac{1}{2}-z$.

H atoms from the tartrate molecules were located from difference syntheses, in positions reliable enough to determine the intermolecular hydrogen bonding. In the final refinement, such positions were fixed, maintaining the geometry, and refined with fixed individual isotropic displacement parameters [$U_{\rm iso} = 1.2U_{\rm eq}$(C) and $1.5U_{\rm eq}$(O hydroxyl)] using a riding model with C—H distances of 0.98 Å and O—H distances of 0.82 Å. Water H atoms could not be located.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*4 (Harms, 1996). Program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *PARST*95 (Nardelli, 1995).

CG-S, JG-P, TL and MET would like to thank the University of La Laguna for financial support (226/54/98).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1241). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Bostelaar, L. J., de Graaff, R. A. G., Hulsbergen, F. B., Reedijk, J. & Sachtler, W. M. H. (1984). *Inorg. Chem.* **23**, 2294–2297.

Brown, I. D. (1992). *Acta Cryst.* B**48**, 553–572.

Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Gonzalez-Platas, J., Gonzalez-Silgo, C. & Ruiz-Perez, C. (1999). *J. Appl. Cryst.* **32**, 341–344.

Harms, K. (1996). *XCAD*4. *Program for the Lp Correction of Nonius CAD-4 Diffractometer Data*. University of Marburg, Germany.

Henisch, H. K. (1970). In *Crystal Growth in Gels*. Pittsburgh: The Pennsylvania State University Press.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

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

Prout, C. K., Carruthers, J. R. & Rossoti, F. J. C. (1971). *J. Chem. Soc. A*, pp. 3336–3342.

Ruiz-Pérez, C., Hernández-Molina, M., González-Silgo, C., López, T., Yanes, C. & Solans, X. (1996). *Acta Cryst.* C**52**, 2473–2475.

Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL97*. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Templeton, L. K., Templeton, D. H., Zhang, D. & Zalkin, A. (1985). *Acta Cryst.* C**41**, 363–365.

Torres, M. E., López, T., Peraza, J., Stockel, J., González-Silgo, C., Ruiz-Pérez, C. & Lorenzo-Luis, P. A. (1998). *J. Appl. Phys.* **84**, 5729–5732.

Acta Cryst. (1999). C**55**, 712–714

Bis[iodo(N,N,N',N'',N''-pentamethyldiethylenetriamine-κ^3N)platinum(II)] di-μ-iodo-bis[diiodoplatinate(II)]

Francesco P. Fanizzi, Francesco P. Intini, Luciana Maresca, Giovanni Natile and Concetta Pacifico

Dipartimento Farmaco-Chimico, Università di Bari, via E. Orabona 4, 70125 Bari, Italy. E-mail: natile@farmchim.uniba.it

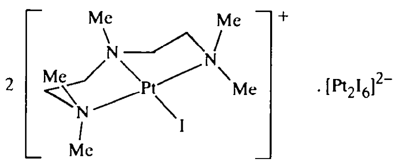
(*Received 10 November 1998; accepted 9 December 1998*)

Abstract

The title compound, $2[PtI(C_9H_{23}N_3)][Pt_2I_6]$ or $2[Pt(Me_5dien)I][Pt_2I_6]$, where Me_5dien is pentamethyldiethylenetriamine, has been synthesized and its X-ray structure solved. In the asymmetric unit, there are two platinum(II) complex moieties, *i.e.* $[Pt(Me_5dien)I]^+$ cations, in which the metal has distorted square-planar coordination geometry, and half an iodo-bridged $[Pt_2I_6]^{2-}$ anion, in which the Pt center has a regular square-planar arrangement.

Comment

In our current studies on the coordination of amide ligands to platinum(II), we have synthesized and structurally characterized the complex [Pt(Me$_5$dien)(acetamide-*O*)]$^{2+}$, (2) (Cini *et al.*, 1998). The use of a sterically encumbered ligand, such as pentamethyldiethylenetriamine (Me$_5$dien), rendered the *O*-bonded amide complex particularly stable, not only in organic solvents, but also in water, where solvolysis takes place with a rate constant as low as 8.7×10^{-5} s^{-1}. It is to be recalled that the corresponding complex with the unsubstitued dien ligand reacts instantaneously with moisture in chlorinated solvents, releasing the amide and forming the aqua species. Our study on [Pt(Me$_5$dien)(amide)]$^{2+}$ was, to the best of our knowledge, the first structural determination of a platinum complex containing the Me$_5$dien ligand. Only structural data on platinum complexes with an unsubstituted or partially substituted diethylenetriamine ligand (dien) can be found in the literature (Fairlie *et al.*, 1994; Melanson *et al.*, 1975; Melanson & Rochon, 1979; Durley *et al.*, 1980; Fanizzi *et al.*, 1986). In one case, the Me$_5$dien ligand was coordinated to a lithium cation and the platinum was present in the counter-anion [Pt(CH$_2$CH$_2$CH$_2$CH$_2$)$_2$]$^{2-}$ (Fröhlich *et al.*, 1994). The case of palladium, for which two complexes with the Me$_5$dien ligand have been structurally characterized (Markies *et al.*, 1992, 1994), is different. The [Pt(Me$_5$dien)(amide)]$^{2+}$ complex cation has a synthetic precursor in complex salt (1), which has also been characterized by X-ray analysis, and the structure has been determined and is reported in the present communication.



(1)

Compound (1) consists of [Pt(Me$_5$dien)I]$^+$ cations and [Pt$_2$I$_6$]$^{2-}$ anions. In the cations, the four coordination sites in the square-planar structure are occupied by three N atoms of Me$_5$dien and one iodine ligand. The distances Pt—N1 and Pt—N3 (terminal N atoms), and Pt—N2 (central nitrogen) found in compound (2) (Cini *et al.*, 1998) were 2.056 (5), 2.065 (5) and 2.007 (5) Å, respectively. The slightly longer Pt—N2 distance found in the present case is indicative of a greater *trans* influence exerted by the I with respect to the O atom. The N1—Pt—N2 and N2—Pt—N3 angles are also slightly smaller than those found in compound (2) [86.3 (2) and 86.5 (2)°, respectively], while the N1—Pt—I1 and N3—Pt—I1 angles are greater than the N1—Pt—O1 and N3—Pt—O1 angles in complex (2) [93.0 (2) and 93.6 (2)°, respectively], which is in agreement with the greater steric hindrance of the I atom. The deviations (Nardelli, 1996) of the atoms from the least-squares plane defined by the metal and donor atoms are: Pt −0.0006 (5), I1 −0.001 (1), N1 0.152 (8), N2 −0.090 (7) and N3 0.155 (7) Å. Interestingly, there is a tetrahedral distortion of the platinum coordination sphere in the present case, while the distortion was pyramidal in compound (2). In the latter case, the presence of an attractive interaction between the metal atom and an amide NH group could be responsible for the observed geometry. The Pt—I1 bond distance is in agreement with the values of Pt—I lengths observed previously for [Pt(Et$_4$dien)I]$^+$ [2.616 (2) Å; Durley *et al.*, 1980].

The halogen-bridged [Pt$_2$I$_6$]$^{2-}$ anion is perfectly planar and centrosymmetric; the greatest deviation from the coordination sphere is 0.006 (1) Å and involves the I2 atom. The X-ray structure of a similar anion has already been reported in the literature, however, in one case (Martin-Gil *et al.*, 1985), there was a twofold axis of symmetry and the Pt—I distances were equivalent in pairs, and in a second case (Rogers *et al.*, 1984), all Pt—I distances in the [Pt$_2$I$_6$]$^{2-}$ anion were different from one another. Similar to the present case, a symmetry center was present in the [Pt$_2$Br$_6$]$^{2-}$ complex reported by Stephenson (1964). Crystal-packing effects could be responsible for the different symmetry of the [Pt$_2$I$_6$]$^{2-}$ anion in the different salts.

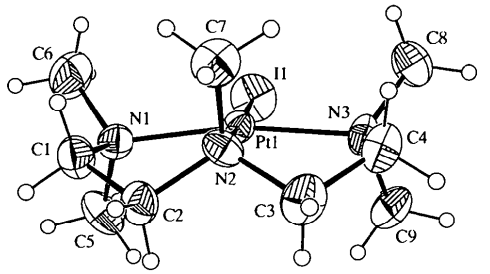


Fig. 1. The molecular structure of the [Pt(Me$_5$dien)I]$^+$ cation shown with 50% probability ellipsoids.

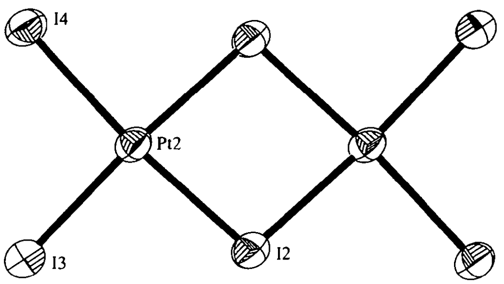


Fig. 2. The molecular structure of the [Pt$_2$I$_6$]$^{2-}$ anion shown with 50% probability ellipsoids.

Experimental

K_2PtCl_4 (0.5 g, 0.0012 mol) was dissolved in water and treated with KI (0.82 g, 0.0049 mol). After stirring for 5 min at 323 K, a stoichiometric amount of Me_5dien (0.207 g, 0.0012 mol) was added and stirring continued for 1 h. The green precipitate which formed was collected by filtration, washed with water and dried in a stream of dry air. Crystals were obtained by slow evaporation of an acetone–water solution of the compound [yield: 0.55 g (67%)]. Found: C 10.1, H 2.2, N 3.9%; calculated for $C_{18}H_{46}I_8N_6Pt_4$: C 10.1, H 2.2, N 3.9%. The ^{1}H NMR spectrum of an acetone-d_6 solution of compound (1) shows three signals for N—Me groups at δ 3.37, 3.28 and 3.11 of relative intensities 3:6:6, and two signals for the protons of the ethylene chains at δ 3.82 and 4.20.

Crystal data

$2[PtI(C_9H_{23}N_3)][Pt_2I_6]$
$M_r = 2142.16$
Monoclinic
$P2_1/c$
$a = 14.084 (5)$ Å
$b = 14.047 (5)$ Å
$c = 10.402 (5)$ Å
$\beta = 93.463 (5)^\circ$
$V = 2054 (1)$ Å^3
$Z = 4$
$D_x = 3.463$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 60 reflections
$\theta = 2\text{–}20^\circ$
$\mu = 19.608$ mm^{-1}
$T = 293 (2)$ K
Platelet
0.25 × 0.20 × 0.20 mm
Intense green

Data collection

Philips PW1100 diffractometer
$\omega\text{–}2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.017$, $T_{\max} = 0.020$
5994 measured reflections
5994 independent reflections
3490 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.040$
$\theta_{\max} = 30.01^\circ$
$h = -19 \rightarrow 19$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 180 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.079$
$S = 0.841$
5994 reflections
168 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0280P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.57$ e Å^{-3} (close to Pt)
$\Delta\rho_{\min} = -1.30$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pt1—N2	2.034 (7)	Pt2—I2	2.586 (1)
Pt1—N1	2.061 (8)	Pt2—I2$^{\rm i}$	2.595 (1)
Pt1—N3	2.074 (7)	Pt2—I4	2.596 (1)
Pt1—I1	2.613 (1)	Pt2—I3	2.601 (1)
N2—Pt1—N1	84.7 (3)	N3—Pt1—I1	95.0 (2)
N2—Pt1—N3	85.5 (3)	I2—Pt2—I2$^{\rm i}$	84.61 (3)
N1—Pt1—N3	166.7 (3)	I2—Pt2—I4	174.90 (3)
N2—Pt1—I1	177.5 (2)	I2—Pt2—I3	90.96 (3)
N1—Pt1—I1	95.2 (2)		

Symmetry code: (i) $1 - x, -y, 1 - z$.

All non-H atoms were located from electron-density maps and were refined anisotropically by full-matrix least squares. H atoms were placed at geometrically calculated positions and included in the full-matrix least-squares cycles fixing isotropic displacement parameters (U) for methylene or methyl H atoms at $1.2U_{\rm eq}$ and $1.5U_{\rm eq}$, respectively, where $U_{\rm eq}$ is the value of the parent C atoms.

Data collection: local program. Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1996). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997). Software used to prepare material for publication: *SHELXL*97 and *PARST*97 (Nardelli, 1996).

The authors gratefully acknowledge Dr Marcello Merli (University of Pavia) for the data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1394). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterno, A. G. G., Polidoro, G. & Spagna, R. (1996). *SIR*97. *A Program for the Automatic Solution and Refinement of Crystal Structures*. University of Bari, Italy.
Cini, R., Intini, F. P., Maresca, L., Pacifico, C. & Natile, G. (1998). *Eur. J. Inorg. Chem.* **9**, 1305–1312.
Durley, R. C. E., Waltz, W. L. & Robertson, B. E. (1980). *Can. J. Chem.* **58**, 664–668.
Fairlie, D. P., Woon, T. C., Wickramasinghe, W. A. & Willis, A. C. (1994). *Inorg. Chem.* **33**, 6425–6428.
Fanizzi, F. P., Natile, G., Lanfranchi, M., Tiripicchio, A., Clark, R. J. H. & Kurmoo, M. (1986). *J. Chem. Soc. Dalton Trans.* pp. 273–278.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Fröhlinch, H. O., Wyrwa, R., Görls, H. & Pieper, U. (1994). *J. Organomet. Chem.* **471**, 23–27.
Markies, B. A., Wijkens, P., Boersma, J., Kooijman, H., Veldman, N., Spek, A. L. & van Koten, G. (1994). *Organometallics*, **13**, 3244–3258.
Markies, B. A., Wijkens, P., Kooijman, H., Spek, A. L., Boersma, J. & van Koten, G. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1420–1423.
Martin-Gil, J., Martin-Gil, F. J., Pérez-Méndez, M. & Fayos, J. (1985). *Z. Kristallogr.* **173**, 179–183.
Melanson, R., Hulbert, J. & Rochon, F. D. (1975). *Can. J. Chem.* **53**, 1139–1143.
Melanson, R. & Rochon, F. D. (1979). *Can. J. Chem.* **57**, 57–61.
Nardelli, M. (1996). *PARST*97. *A System of Computer Routines for Calculating Molecular Parameters from the Results of Crystal Structure Analysis*. University of Parma, Italy.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Rogers, R. D., Isci, H. & Mason, W. R. (1984). *J. Crystallogr. Spectrosc. Res.* **14**, 383–392.
Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Stephenson, N. C. (1964). *Acta Cryst.* **17**, 587–591.