Crystal Structure of Tetraethylammonium μ-Chloro-*abefh*-pentachloro-μ-nitrosyl-nitrosyldiplatinate(II)

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The crystal structure of the title compound has been determined by the heavy-atom method from diffractometer *X*-ray data and refined by full-matrix least-squares to *R* 0·07 for 1688 observed reflections. Crystals are monoclinic, space group $P2_1/c$, a = 20·704(2), b = 10·390(1), c = 14·408(2) Å, β = 106·99(1)°. The novel anion consists of two platinum atoms in square planar and octahedral environments respectively bridged by a chlorine atom and a nitrosyl group, the other nitrosyl group being terminal and equatorial in the co-ordination sphere of the octahedral platinum, *cis* to the bridging nitrosyl and bent towards it (O ··· O′ 2·71 Å, Pt–N–O, 122(5)°). The Pt–Cl bridging bond *trans* to the terminal nitrosyl is significantly longer than the remaining Pt–Cl distances [2·64(1), *cf.* 2·33 (mean) Å]. The N–O bond of the bridging nitrosyl is significantly longer than that of the terminal nitrosyl group [1·27(5), 1·05(6) Å].

ADDITION of an equimolar quantity of potassium nitrite to a solution of potassium tetrachloroplatinate acidified with hydrochloric acid yields a dark green air-sensitive solution from which a bright green stable diamagnetic solid with analysis corresponding to the formula $(Et_4N)[Pt(NO)Cl_4]$ may be precipitated by the addition of tetraethylammonium chloride.[1] To distinguish between the various mono- and poly-meric structures possible for the anion, an *X*-ray structure determination was undertaken.

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[1] J. Lewis, M. J. Ware, and S. B. Wild, unpublished work.

EXPERIMENTAL

$K_2[PtCl_4]$ (0·5 g) was dissolved in the minimum of water (7 ml) and filtered into a Schlenk tube. All dissolved oxygen was removed by bubbling oxygen-free nitrogen through the solution for 15 min and maintaining a nitrogen atmosphere thereafter. The solution was made weakly acidic (*ca.* 0·2M) with concentrated hydrochloric acid and an equimolar amount of $NaNO_2$ (0·083 g) in oxygen-free solution added with constant stirring, yielding a dark olive-green solution. Excess of solid $(Et_4N)Cl$ was added and the solution set aside in the dark for 18 h. A dark green microcrystalline product formed on the side of the Schlenk tube; it was washed briefly with dilute hydrochloric acid and dried *in vacuo* for 1 h [Found: C, 19·7; H, 4·0; N, 4·8; Cl, 27·1. Calc. for $[Et_4N][Pt(NO)Cl_4]$: C, 19·3; H, 4·1; N, 5·6; Cl, 28·3. Calc. for $[Et_4N][Pt(NO)Cl_3]$: C, 20·8; H, 4·4; N, 6·1; Cl, 23·0%.

Crystal Data.—$C_8H_{20}Cl_3N_2OPt$, $M = 461·6$, Monoclinic, $a = 20·704 \pm 0·002$, $b = 10·390 \pm 0·001$, $c = 14·408 \pm 0·002$ Å, $\beta = 106·994$ (0·008)°, $U = 2964·2 \pm 0·6$ Å^3, D_m (by flotation) = 2·04 ± 0·02 g cm^3, $D_c = 2·07$ g cm^{-3}, $Z = 8$, $F(000) = 1752$. Cu-K_α radiation (Ni-filtered), $\lambda = 1·5418$ Å;[2] μ(Cu-K_α) = 229 cm^{-1}. Space group $P2_1/c$ (C_{2h}^5, No. 14).[3]

A single compact polyhedral crystal 0·09 × 0·09 × 0·09 mm was selected; during structure solution it became apparent that this crystal did not correspond to the analytical composition of the bulk and that it was atypically large. Cell dimensions were obtained by a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex P$\bar{1}$ four-circle diffractometer. A unique set of data in the range $2\theta < 100°$ were collected by use of a 2θ—θ scan (3052 independent reflections, of which 1688 were $>3\sigma$ and used in the refinement and computation of the structure). All data processing and computation was carried out on the CDC 6200 computer at the University of Western Australia with a local adaptation of the *X*-ray '72 programme system.[4]

Scattering factors were for the neutral atoms,[5] platinum and chlorine[6] being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[7] No pronounced extinction effects were observed and no correction applied. Data were corrected for absorption.

Solution of the structure was by conventional Patterson and Fourier heavy-atom methods, the final stages of refinement being carried out by use of a full-matrix procedure, thermal anisotropy being refined for the heavy atoms according to the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hlb^*c^* + 2U_{23}klb^*c^*)]$. In the final least-squares cycle, all parameter shifts were $<0·02\sigma$, unit weights being applied to all reflections, yielding a final R of 0·068, R' $[= \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|)^{\frac{1}{2}}]$ of 0·079; a final difference map showed no significant features.*

RESULTS

Description of the Structure.—The crystals of the complex are composed of discrete $[Et_4N]^+$ cations and $[Pt_2(NO)_2Cl_6]^{2-}$ anions, the asymmetric unit comprising one $[Et_4N]_2[Pt_2(NO)_2Cl_6]$ formula unit. Final atomic co-ordinates are in Table 1. The geometries of the $[Et_4N]^+$ cations are normal within the wide limits of experimental error (Table 1). The unit-cell contents and atom numbering system are shown in Figures 1 and 2.

The anion structure is novel. The two platinum atoms separated by 3·287(3) Å are bridged by a chlorine atom Cl(3) and an unusual bridging nitrosyl group, N(1)–O(1). (The assumption has been made throughout the determination that the nitrosyl group bonds *via* the nitrogen rather than the oxygen.) Pt(1) has a square-planar environment comprised of three chlorine atoms: Cl(1) and Cl(2) at 2·30, 2·27(1) Å are non-bridging while the third [Cl(3) 2·34(1) Å] bridges to Pt(2). The remaining co-ordination position is filled by the nitrogen of the bridging nitrosyl group [Pt(1)–N(1) 1·89(4) Å]. The environment of Pt(1) does not deviate significantly from planarity (Table 3).

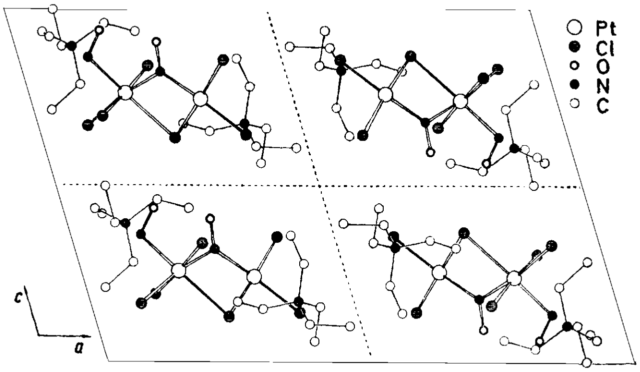

FIGURE 1 Unit-cell contents projected down *b*

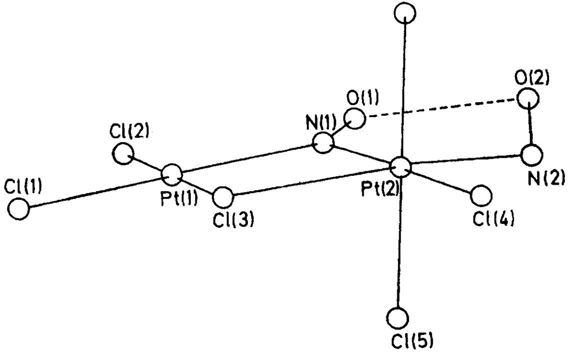

FIGURE 2 The anion with atomic numbering system

Pt(2) is in a distorted octahedral environment consisting of four chlorine atoms Cl(3)–(6) [Cl(3) bridging] and the two nitrosyls [N(1)–O(1) bridging], the latter being mutually *cis* and equatorial. The axial bonds Pt(2)–Cl(5,6) [2·35(1), 2·33(1)] are shorter than those in the equatorial positions and comparable with Pt(1)–Cl(1,2). In the plane, Pt(2)–Cl(4) [2·38(1) Å] is also of the same order; however, the distance to the bridging chlorine Cl(3) is much longer

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* Structure factors are listed in Supplementary Publication No. SUP 20861 (12 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[2] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1969, p. 169.

[3] Ref. 2, vol. I, 1965, p. 59.

[4] *X*-Ray system, version of June 1972, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A.

[5] Ref. 2, p. 202 *ff.*

[6] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[7] Ref. 2, p. 215.

TABLE 1

Atomic fractional cell co-ordinates of the asymmetric unit with isotropic thermal parameters ($\times 10^2$), and least-squares estimated standard deviations in final digit in parentheses

Atom	*x*	*y*	*z*	10^2U/Å^2
(*a*) Cation (1)				
N(10)	0·391(1)	0·618(3)	0·111(2)	6·3(9)
C(11)	0·393(2)	0·591(4)	0·221(3)	7·9(13)
C(12)	0·467(2)	0·582(5)	0·291(3)	8·3(14)
C(21)	0·319(2)	0·599(4)	0·047(3)	6·4(12)
C(22)	0·266(2)	0·680(5)	0·064(3)	9·2(5)
C(31)	0·440(2)	0·544(4)	0·075(3)	6·5(12)
C(32)	0·429(2)	0·395(4)	0·081(3)	7·6(12)
C(41)	0·409(2)	0·765(4)	0·107(3)	5·7(10)
C(42)	0·406(2)	0·819(4)	0·008(3)	8·5(14)
(*b*) Cation (2)				
N(20)	0·105(2)	0·494(3)	0·319(2)	7·3(9)
C(51)	0·097(3)	0·604(6)	0·391(4)	12·8(21)
C(52)	0·020(2)	0·625(5)	0·379(3)	8·7(13)
C(61)	0·071(3)	0·530(6)	0·210(4)	10·2(17)
C(62)	0·086(2)	0·445(5)	0·139(3)	9·7(16)
C(71)	0·181(3)	0·468(5)	0·340(4)	10·0(16)
C(72)	0·219(2)	0·586(5)	0·315(4)	10·1(17)
C(81)	0·070(3)	0·362(6)	0·332(4)	10·6(17)
C(82)	0·093(3)	0·319(5)	0·440(4)	10·4(17)
(*c*) Anion				
Pt(1)	0·1762(1)	−0·0061(2)	0·2565(1)	*
Pt(2)	0·3148(1)	0·1345(2)	0·2406(1)	*
Cl(1)	0·1114(6)	−0·042(1)	0·359(1)	*
Cl(2)	0·1107(6)	−0·143(1)	0·146(1)	*
Cl(3)	0·2457(5)	0·136(1)	0·367(1)	*
Cl(4)	0·4060(5)	0·264(1)	0·331(1)	*
Cl(5)	0·3712(6)	−0·055(1)	0·307(1)	*
Cl(6)	0·2563(6)	0·314(1)	0·163(1)	*
N(1)	0·235(2)	0·033(3)	0·182(2)	6·4(9)
O(1)	0·227(2)	−0·009(3)	0·097(2)	9·7(9)
N(2)	0·364(2)	0·122(4)	0·141(3)	13·2(18)
O(2)	0·339(2)	0·098(4)	0·068(3)	13·0(14)

* Anisotropic thermal parameters ($\times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	62(1)	60(1)	76(1)	2(1)	20(1)	12(1)
Pt(2)	61(1)	56(1)	61(1)	3(1)	19(1)	3(1)
Cl(1)	98(9)	120(11)	102(10)	−3(8)	47(8)	26(9)
Cl(2)	92(9)	107(11)	102(9)	−35(9)	10(7)	9(9)
Cl(3)	68(6)	57(6)	61(6)	−2(6)	13(5)	6(6)
Cl(4)	81(8)	66(8)	88(8)	−29(7)	10(6)	−6(8)
Cl(5)	99(8)	63(7)	68(7)	20(6)	23(6)	9(6)
Cl(6)	80(7)	49(7)	91(8)	13(6)	23(6)	13(6)

TABLE 2

Interatomic distances (Å) and angles (deg.)

(*a*) Cation geometries *

(i) Cation (1): $i = 1$—$4, j > i$

⟨N(10)–C(*i*1)⟩	1·54(5)	⟨C(*i*1)–N(10)–C(*j*1]⟩	109(3)
⟨C(*i*1)–C(*i*2)⟩	1·53(6)	⟨N(10)–C(*i*1)–C(*i*2)⟩	113(3)

(ii) Cation (2): $i = 1$—$4, j > i$

⟨N(20)–C(*i*1)⟩	1·56(6)	⟨C(*i*1)–N(20)–C(*j*1)⟩	109(3)
⟨C(*i*1)–C(*i*2)⟩	1·53(8)	⟨N(20)–C(*i*1)–C(*i*2)⟩	111(4)

(*b*) Anion geometry

(i) Pt(1) co-ordination

Pt(1)–Cl(1)	2·30(1)	Cl(1)–Pt(1)–Cl(2)	90·6(5)
Pt(1)–Cl(2)	2·27(1)	Cl(1)–Pt(1)–Cl(3)	91·3(4)
Pt(1)–Cl(3)	2·34(1)	Cl(1)–Pt(1)–N(1)	174·1(10)
Pt(1)–N(1)	1·89(4)	Cl(2)–Pt(1)–Cl(3)	178·1(5)
		Cl(2)–Pt(1)–N(1)	95·2(10)
Pt(1) · · · Pt(2)	3·287(3)	Cl(3)–Pt(1)–B(1)	82·9(10)
Pt(1) · · · O(1)	2·79(4)	O(1)–N(1)–Pt(1)	123(3)
		Pt(1)–Cl(3)–Pt(2)	82·2(3)
N(1)–O(1)	1·27(5)	Pt(1)–N(1)–Pt(2)	119(2)

TABLE 2 (*Continued*)

(ii) Pt(2) co-ordination

Pt(2)–Cl(3)	2·62(1)	Cl(3)–Pt(2)–Cl(4)	96·0(4)
Pt(2)–Cl(4)	2·38(1)	Cl(3)–Pt(2)–Cl(5)	91·8(4)
Pt(2)–Cl(5)	2·35(1)	Cl(3)–Pt(2)–Cl(6)	92·0(4)
Pt(2)–Cl(6)	2·33(1)	Cl(3)–Pt(2)–N(1)	78·1(9)
Pt(2)–N(1)	1·93(3)	Cl(3)–Pt(2)–N(2)	174·7(12)
Pt(2)–N(2)	1·98(6)	Cl(4)–Pt(2)–Cl(5)	91·8(4)
		Cl(4)–Pt(2)–Cl(6)	91·6(4)
Pt(2) · · · O(1)	2·76(3)	Cl(4)–Pt(2)–N(1)	171·6(10)
Pt(2) · · · O(2)	2·69(5)	Cl(4)–Pt(2)–N(2)	86·9(13)
O(1) · · · O(2)	2·71(6)	Cl(5)–Pt(2)–Cl(6)	175·4(4)
		Cl(5)–Pt(2)–N(1)	88·9(9)
N(2)–O(2)	1·05(6)	Cl(5)–Pt(2)–N(2)	86·5(15)
		Cl(6)–Pt(2)–N(1)	88·2(9)
		Cl(6)–Pt(2)–N(2)	90·5(13)
		N(1)–Pt(2)–N(2)	101·5(18)
		Pt(2)–N(1)–O(1)	118(3)
		Pt(2)–N(2)–O(2)	122(5)

(*c*) Interspecies contacts (<3·5 Å) †

O(1) · · · C(22^{I})	3·39(6)	N(2) · · · C(12^{II})	3·38(8)

* Because of the high inaccuracy in the cation parameters, the geometry of which is well established, only mean values of the dimensions for each cation are given.

† Transformations of the asymmetric unit

I $x, 1 - y, z$ II $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$

TABLE 3

Selected least-squares planes through the anion, in the form, $lX + mY + nZ = p$ where the orthogonal (Å) frame (X, Y, Z) is given by $X = ax + cz \operatorname{Cos} \beta$, $Y = by$, $Z = cz \operatorname{Sin} \beta$. Distances (Å) of atoms from the planes are given in square brackets; σ is then the estimated standard deviation from the plane. Atoms defining the plane are italicized

	l	*m*	*n*	*p*	σ
Plane (i): Pt(1) environment	0·4916	−0·7609	0·4234	2·809	0·00
Plane (ii): Pt(2) environment, approx. coplanar with that of Pt(1)	−0·3670	0·8201	−0·4390	−2·340	0·02
Plane (iii): Pt(2) environment, through N(1), and approx. normal to plane (i)	−0·6344	0·1026	0·7661	−0·7738	0·11
Plane (iv): Pt(2) environment through Cl(3) and approx. normal to plane (i)	0·5696	0·5690	0·5931	5·836	0·03

Plane (i): *Cl* (1) −0·00, *Cl*(2) 0·00, *Cl*(3) 0·00, *Pt*(1) 0·00, *N*(1) −0·00, O(1) −0·06, Pt(2) 0·24, Cl(4) 0·49, N(2) 0·46, O(2) 0·12

Plane (ii): *Cl*(3) −0·04, *Cl*(4) 0·02, *Pt*(2) 0·03, *N*(1) 0·03, *N*(2) −0·04, O(1) 0·10, O(2) 0·30, Pt(1) −0·21, Cl(1) −0·48, Cl(2) −0·38, Cl(5) −2·32, Cl(6) 2·34

Plane (iii): *Cl*(4) 0·10, *Cl*(5) −0·10, *Cl*(6) −0·10, *Pt*(2) −0·03, N(1) 0·14, O(1) −0·93, Pt(1) 1·85, Cl(3) 2·55, N(2) −2·00

Plane (iv): *Cl*(3) −0·01, *Cl*(5) −0·01, *Cl*(6) −0·01, *Pt*(2) 0·06, *N*(2) −0·02

Angles (deg.) between the planes:

(i)–(ii)	8·0	(ii)–(iii)	88·9
(i)–(iii)	86·2	(ii)–(iv)	89·8
(i)–(iv)	84·3	(iii)–(iv)	81·3

[2·62(1) Å], so that the latter bridges in an asymmetric fashion. The nitrosyl bridge is not significantly asymmetric [Pt(1,2)–N(1) 1·89, 1·93(4) Å], neither does the Pt(2)–N(1) distance differ significantly from the non-bridging Pt(2)–N(2) distance [1·98(4) Å], *i.e.* none of the Pt(*i*)–N(*j*) distances differ significantly from the mean. The angular environment of Pt(2) is not as regular as that of Pt(1); in particular, some of the angles about the bridging atoms show a large deviation from 90° because of the elongation of Pt(2)–Cl(3).

A curious feature of the structure is the close approach of O(2) to O(1) [2·71(6) Å], a result of the bent Pt(2)–N(2)–O(2) sequence [122(5)°]; this distance is comparable to, or less than, the van der Waals contact of 2·8 Å. The possibility of a hyponitrite ONNO chelate as in the complex $[Co(NH_3)_5NO]_2^{2+}$ was considered but rejected on the grounds of bond length.[8] Moreover, there was no suggestion in the difference map that either of the species was a nitrite rather than a nitrosyl group. It is possible that the close approach of C(12) and C(32) to N(2)–O(2) [these C–N(2) distances are among the closest interspecies contacts found in the structure] may determine the disposition of O(2). A more likely reason for the effect, however, may be an attractive force between the nitrosyl by considering the bridging nitrosyl as NO^+ and the bent nitrosyl as NO^- (see Discussion section).

DISCUSSION

This is a remarkable example of a complex containing both bridging and terminal nitrosyl groups, as well as platinum in both square-planar and pseudo-octahedral co-ordination. Relatively few examples of nitrosyl bridging groups have been reported and this is only the second involving a platinum-containing species, the other example being the tetranuclear $Pt_4(AcO)_6(NO)_2$,2AcOH.[9]

As a result of a number of structural studies of nitrosyl complexes, it has been suggested that, where the metal–nitrogen bond is very short and the M–N–O angle *ca.* 180°, the ligand may be considered as NO^+, while in cases where the M–N bond is longer and the M–N–O angle *ca.* 120°, the ligand is better described as NO^-.[10,11] In the present complex, the observation that Pt(2)–N(2)–O(2) is 122(4)° strongly suggests that nitrosyl N(2)–O(2) is of the latter type; although no other platinum–terminal-nitrosyl distances have been reported, the bond length in this case is quite long. This is supported by consideration of the Cl(3)–Pt(2)–N(2) geometry. It has been suggested that in an $M(NO)X_5$ type of complex, shortening of an M–X σ bond *trans* to the nitrosyl is indicative of the relatively weakly σ-bonding NO^+ species,[12,13] as in $[Ru(NO)(OH)(NO_2)_4]^{2+}$ (ref. 14) and $[Ru(NO)Cl_5]^{2-}$ (ref. 12). The reverse phenomenon, exemplified by the species in Table 4,[15,16] is explained by considering the nitrosyl to be NO^-, a relatively strong σ donor. The present example appears to correspond more nearly to the latter, although the Pt(2)–Cl(3) distance lengthening may be as much as a consequence of the bridging nature of Cl(3) as the unusual *pseudo*-octahedral geometry of Pt(2) (if it is considered as a Pt^{II} species).

TABLE 4

Systems containing terminal NO^- species; distances in Å, angles in deg.

	Bond *trans* to NO	Normal bond distance	M–N–O	N–O
$[Co(NH_3)_5(NO)]Cl_2$ [a]	2·22	1·98 [b]	119	1·16
$[Coen_2(NO)Cl][ClO_4]$ [c]	2·58	2·27 [d]	121	1·14
$[Et_4N]_2^+[Pt_2(NO)_2Cl_6]^{2-}$	2·62	2·36 [b]	122	1·05

[a] Ref. 15. [b] Mean of *cis* bond lengths. [c] Ref. 16. [d] Co–Cl bond length for $[Co(NH_3)_5Cl]Cl_2$.

Two formulations are possible for the bridging nitrosyl group. It could be considered as NO^-, with the platinum atoms having a total valence of VI, a fact which best agrees with the square-planar co-ordination of Pt(1) (suggesting a Pt^{II} species) and the *pseudo*-octahedral co-ordination of Pt(2) which is usual for a Pt^{IV} species. However, O(2) is directed towards O(1), suggesting that the nitrosyl groups may have opposite charges and that if the terminal NO group is NO^-, then the bridging nitrosyl group in this complex is NO^+. Examples of bridging NO^+ species have been postulated elsewhere.[17,18] Mutual attraction of NO^- and NO^+ groups has been observed in $[RuCl(NO)_2(PPh_3)_2](PF_6)$ [11] and $[Os(OH)(NO)_2(PPh_3)_2][PF_6]$,[19] possibly as a result of a weak interaction between the NO^+ π^* orbital and a lone pair of the oxygen on the NO^- (ref. 20), and in these cases it is formally the NO^- which is bent rather than NO^+. If this formulation applies here, the platinum atoms have a total valence of IV, which would imply that both are Pt^{II} species, and the Pt(2) is a rare example of octahedral Pt^{II}, consistent with the observation that most octahedral Pt^{II} species so far defined involved nitrosyl ligands.

The present structure lends emphasis to the previous warning [9] concerning derivatives from platinum–nitrosyl mixtures, as the stoicheiometry of the crystal studied in this case is not consistent with the analysis of the apparently pure sample which gave rise to the solution from which the crystal was obtained.

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