Isolation of Polynuclear Platinum Complexes in the Ammination Reaction of Activated Olefins. *X*-Ray Crystal Structure of a Diplatinum(II) Perchlorate Salt bridged by an Ammoniodiethylide Group †

By **Giuliano Annibale** and **Luciana Maresca,*** Istituto di Chimica Generale ed Inorganica, Università di Venezia, Italy
Giovanni Natile, Cattedra di Chimica Generale ed Inorganica, Università di Bari, Italy
Antonio Tiripicchio and **Marisa Tiripicchio-Camellini**, Istituto di Chimica Generale ed Inorganica e Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Università di Parma, Italy

By reaction of secondary and primary amines and ammonia with the cationic complex $[Pt(\eta^2\text{-}C_2H_4)Cl(Me_4en)]^+$, (1) ($Me_4en$ = *NNN'N'*-tetramethylethylenediamine), bi-, tri-, and tetra-metallated ammonium ions of formula $[\{Pt(C_2H_4)Cl(Me_4en)\}_n(NR_{4-n})]^+$ (n = 2, 3, and 4, respectively) have been obtained. The enhanced electrophilicity of η^2-ethene in (1), and the absence of a formal negative charge on platinum in the addition products, stabilizing the Pt–C σ bond, play a key role in the synthesis of such species. These compounds undergo acidolysis to give polyalkylated ammonium ions. The crystal and molecular structure of the salt $[\{Pt(C_2H_4)Cl(Me_4en)\}_2(NEt_2)][ClO_4]$ has been determined by *X*-ray diffraction. The compound crystallizes in the monoclinic space group *C*2/*c* with $Z = 8$ in a unit cell of dimensions $a = 30.38(2)$, $b = 8.55(1)$, $c = 25.26(2)$ Å, and $\beta = 111.0(1)°$. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.067$ for 2 817 independent reflections. In the cation the two Pt atoms are bridged by a 3,3-diethyl-3-azoniapentane, with a chlorine and two nitrogen atoms from a chelating Me_4en ligand completing the square-planar co-ordination around each metal atom.

ALTHOUGH polyalkylation of amines through their reaction with metal-activated olefins requires the formation of intermediate species containing several metal groups per aminic nitrogen,[1] so far only complexes possessing one metal residue have been isolated.[2-4] Moreover, in the case of platinum, these were rather unstable and zwitterionic in character, the nucleophilic addition having been performed on neutral substrates.[1,3,5-8]

Recently we have isolated a stable cationic complex of platinum(II) containing η^2-C_2H_4, namely $[Pt(\eta^2\text{-}C_2H_4)Cl(Me_4en)][ClO_4]$, (1) ($Me_4en$ = *NNN'N'*-tetramethylethylenediamine).[9] Its reactivity towards nucleophiles was greatly enhanced compared with that of neutral species such as *cis*- and *trans*-$[Pt(\eta^2\text{-}C_2H_4)Cl_2(L)]$ (L = amine or phosphine), and it reacted even with deactivated tertiary amines to give very stable σ-C_2H_4 complexes.[10] Therefore we believed that by reaction of the cation of (1) with less substituted amines it would be possible to isolate complexes having more than one platinum group per nitrogen atom. The results of this investigation together with the *X*-ray crystal structure of an addition product containing two platinum groups bonded to the same ammonium ion are reported in this paper.

EXPERIMENTAL

Commercial reagent-grade chemicals were used without further purification. Complex (1) was prepared as in ref. 10.

*Chloro(diethylammonioethylide)(*NNN'N'*-tetramethylethylenediamine)platinum*(II) *Perchlorate* (2).—This complex was prepared by adding the stoicheiometric amount of $NHEt_2$ (73 mg, 1 mmol, in 2 cm^3 of methanol) to a stirred suspension of (1) (474 mg, 1 mmol, in 5 cm^3 of solvent) in methanol. A fast reaction took place. The mixture was left stirring for 30 min, then filtered on a sintered glass filter {to separate a small amount of $[\{Pt(C_2H_4)Cl(Me_4en)\}_2(Me_4en)][ClO_4]_2$ which is always formed as by-product}[10] and the solution evaporated *in vacuo* to give an oily product which, on trituration with diethyl ether, afforded a white solid of (2), yield *ca.* 80% (Found: C, 26.3; H, 5.7; Cl, 13.3; N, 7.6. $[Pt(C_2H_4)Cl(Me_4en)(NHEt_2)][ClO_4]$ requires C, 26.3; H, 5.7; Cl, 12.9; N, 7.7%).

μ-[3,3-*Diethyl*-3-*azoniapentane*-1,5-*diyl*-C^1(Pt^1) : C^5(Pt^2)]-*bis*[*chloro*(NNN'N'-*tetramethylethylenediamine*)*platinum*(II)] *Perchlorate*, (3).—This compound was prepared in two different ways.

(*i*) A sample of compound (2) (0.2 g in a typical experiment) was kept in contact with water (2 cm^3) for about 24 h. During this time the original compound slowly dissolved while a colourless crystalline solid (3) separated out. The yield was less than 50% referred to platinum.

(*ii*) A suspension of (1) and (2) in equimolar amounts (1 mmol each) in methanol (5 cm^3) was treated with the stoicheiometric amount of $LiOH{\cdot}H_2O$ (1 mmol). A fast reaction took place with the formation of a white precipitate. This was separated by filtration of the mother-liquor, washed once with methanol, and dried in air, yield *ca.* 75% (Found: C, 25.9; H, 6.1; Cl, 12.0; N, 7.5. $[\{Pt(C_2H_4)Cl(Me_4en)\}_2(NEt_2)][ClO_4]$ requires C, 26.0; H, 5.5; Cl, 11.6; N, 7.6%).

Compound (4), $[\{Pt(C_2H_4)Cl(Me_4en)\}_3(NEt)][ClO_4]$.—The trinuclear compound was prepared by treating (1) (2 mmol) suspended in methanol (5 cm^3) with NH_2Et (0.66 mmol, 7.0% in water) and a total of 1.32 mmol of KOH (5.6% in water) added in two subsequent equivalent aliquots. The solution was filtered {to remove a small precipitate of $KClO_4$ and of the by-product $[\{Pt(C_2H_4)Cl(Me_4en)\}_2(Me_4en)][ClO_4]_2$} and evaporated *in vacuo* to give an oily product which was extracted with dichloromethane; by evaporation of the solvent a white microcrystalline solid of (4) was obtained, yield *ca.* 90% (Found: C, 24.1; H, 4.8; Cl, 11.3; N, 7.4. $[\{Pt(C_2H_4)Cl(Me_4en)\}_3(NEt)][ClO_4]$ requires C, 24.6; H, 5.2; Cl, 11.2; N, 7.7%).

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† μ-[3,3-Diethyl-3-azoniapentane-1,5-diyl-*C*^{1}(Pt^1):*C*^{5}(Pt^2)]-bis[chloro(*NNN'N'*-tetramethylethylenediamine)platinum(II)] perchlorate.

Compound (5), $[\{Pt(C_2H_4)Cl(Me_4en)\}_4N][ClO_4]$.—To the usual suspension of (1) (2 mmol) in methanol (5 cm^3) was added the stoicheiometric amount of ammonia (0.5 mmol, 1% in water) and then KOH (1.5 mmol, 5.6% in water) in three equivalent aliquots of 0.5 mmol each. The working up of the reaction mixture was carried out as described in the previous preparation. The yield was *ca.* 90% (Found: C, 23.1; H, 5.0; Cl, 11.1; N, 7.4. $[\{Pt(C_2H_4)Cl(Me_4en)\}_4N][ClO_4]$ requires C, 23.8; H, 5.0; Cl, 11.0; N, 7.8%).

X-*Ray Analysis*.—The colourless crystals of compound $[\{Pt(C_2H_4)Cl(Me_4en)\}_2(NEt_2)][ClO_4]$ were of poor quality and mostly twinned. A roughly prismatic fragment, having approximate dimensions 0.10 × 0.14 × 0.28 mm, was used for the structure determination. Preliminary rotation and Weissenberg photographs yielded the approximate cell dimensions and the monoclinic symmetry. The crystal was mounted and aligned on an on-line single-crystal automated Siemens AED diffractometer using niobium-filtered Mo-K_α radiation. The settings of 20 reflections with θ greater than 10.0° were determined and used to calculate the refined cell parameters.

Crystal data. $C_{20}H_{50}Cl_3N_5O_4Pt_2$, $M = 921.18$, monoclinic, $a = 30.38(2)$, $b = 8.55(1)$, $c = 25.26(2)$ Å, $\beta = 111.0(1)°$, $U = 6\,124(9)$ Å^3, $Z = 8$, $D_c = 1.998$ g cm^{-3}, $F(000) = 3\,552$, Mo-K_α radiation, $\bar{\lambda} = 0.710\,688$ Å, $\mu = 95.19$ cm^{-1}, space group $C2/c$ (from systematic absences and structure determination).

A complete set of intensity data was collected with θ within the angular range 3—25°, using the θ—2θ scan technique and a variable scan rate ranging from 2.5 to 10° min^{-1}. A standard reflection was periodically measured to check the stability of the sample and of the instrument. A total of 5 392 independent reflections was measured, of which 2 817 reflections having $I > 2\sigma(I)$ were used in the structure analysis. The structure amplitudes were obtained after the usual Lorentz and polarization corrections and the absolute scale was established by Wilson's method. No correction for absorption was applied in view of the small size and irregular shape of the crystal.

Structure determination and refinement. The structure was solved by the heavy-atom technique and the refinement was carried out by full-matrix least squares using the SHELX system of computer programs [11] with initially isotropic and then anisotropic thermal parameters for all the non-hydrogen atoms except the carbon atoms of the methyl or ethyl groups and the atoms of the perchlorate anion.

The perchlorate anion is disordered between two crystallographically independent sites, each with different site symmetry (C_2 and C_i respectively). No attempt was made to locate the hydrogen atoms. The final conventional R factor was 0.067 for the observed reflections only. Atomic scattering factors, corrected for the anomalous dispersion of the Pt and Cl atoms, were taken from ref. 12. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were used in the first cycles of refinement, while in the final cycles the weight used was calculated as $w = K/[\sigma^2(F_o) + gF_o^2]$, with $K = 0.8253$ and $g = 0.01$.

Final atomic co-ordinates are given in Table 1. A list of observed and calculated structure factors and thermal parameters is available from the authors on request or as Supplementary Publication No. SUP 23300 (20 pp.).[*]

Calculations were performed on the CYBER 7600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

TABLE 1

Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) and multiplicity factor for the non-hydrogen atoms

Atom	X/a	Y/b	Z/c	m
Pt(1)	4 227(0)	5 113(1)	5 266(0)	
Pt(2)	2 981(0)	7 275(1)	1 882(0)	
Cl(1)	4 235(3)	2 626(8)	4 929(3)	
Cl(2)	2 938(3)	4 647(9)	1 961(3)	
N(1)	4 021(6)	4 344(22)	5 942(6)	
N(2)	4 218(7)	7 281(20)	5 616(8)	
N(3)	2 976(5)	9 686(17)	1 826(6)	
N(4)	2 315(6)	7 461(28)	1 208(7)	
N(5)	4 100(6)	6 514(20)	3 542(7)	
C(1)	4 055(14)	5 633(29)	6 336(11)	
C(2)	4 008(15)	7 146(31)	6 059(13)	
C(7)	4 427(7)	5 851(36)	4 625(8)	
C(8)	4 013(7)	6 108(28)	4 084(7)	
C(13)	3 626(7)	6 789(29)	3 067(8)	
C(14)	3 633(6)	7 034(29)	2 496(8)	
C(15)	2 486(8)	10 137(35)	1 455(13)	
C(16)	2 255(12)	9 059(32)	985(13)	
C(3)	3 529(8)	3 690(37)	5 733(14)	
C(4)	4 297(11)	3 012(34)	6 299(13)	
C(5)	4 699(11)	8 053(54)	5 833(20)	
C(6)	3 886(13)	8 415(43)	5 190(15)	
C(9)	4 401(8)	7 995(24)	3 621(10)	
C(10)	4 183(12)	9 438(33)	3 763(14)	
C(11)	4 380(8)	5 248(23)	3 379(10)	
C(12)	4 136(10)	3 687(28)	3 271(13)	
C(17)	3 070(14)	10 515(44)	2 382(12)	
C(18)	3 293(12)	10 382(44)	1 546(16)	
C(19)	1 926(12)	7 025(48)	1 419(17)	
C(20)	2 246(14)	6 390(40)	715(14)	
Cl(3)	5 000	−477(17)	7 500	0.5
Cl(4)	2 500	2 500	0	0.5
O(1)	5 000	−2 163(59)	7 500	0.5
O(2)	4 840(29)	304(77)	6 980(29)	0.5
O(3)	5 300(30)	−530(95)	7 235(37)	0.5
O(4)	4 574(37)	75(111)	7 221(47)	0.5
O(5)	2 811(21)	922(68)	165(22)	0.5
O(6)	2 195(17)	2 408(57)	307(20)	0.5
O(7)	2 793(16)	2 927(57)	554(20)	0.5
O(8)	2 239(26)	1 376(84)	−69(30)	0.5

RESULTS AND DISCUSSION

Compound (3).—Pursuing our research in the field of nucleophilic addition of amines to co-ordinated olefins in platinum substrates,[10,13,14] we treated the cation of (1), $[Pt(\eta^2\text{-}C_2H_4)Cl(Me_4en)]^+$, with diethylamine in 1 : 1 molar ratio and obtained the complex $[Pt(C_2H_4)Cl(Me_4en)(NHEt_2)][ClO_4]$, (2), having one platinum ethylide group per amine molecule, in nearly quantitative yield. This complex dissolved in water to give a clear solution from which a crystalline solid slowly separated out in *ca.* 50% yield referred to platinum. Its elemental analysis pointed to the formation of an addition product containing 2 mol of cation (1) per mol of diethylamine. Moreover, on the basis of spectroscopic data showing the absence of N–H stretching bands and the presence of perchlorate as counter ion and of *C*-bonded platinum residues [bands characteristic of *cis*-chelated Me_4en (810 and 770 cm^{-1}), of Pt–Cl (320 cm^{-1}), and Pt–C (495 cm^{-1}) σ bonds], this compound could be formulated as $[\{Pt(C_2H_4)Cl(Me_4en)\}_2(NEt_2)][ClO_4]$, (3).

A possible reaction sequence for the formation of (3)

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[*] For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

under the above experimental conditions is as in equations (i)—(iii) and the driving force is, we believe, the low

$$[Pt(C_2H_4)Cl(Me_4en)(NHEt_2)]^+ \rightleftharpoons [Pt(C_2H_4)Cl(Me_4en)]^+ + NHEt_2 \quad \text{(i)}$$

$$[Pt(C_2H_4)Cl(Me_4en)(NHEt_2)]^+ + NHEt_2 \rightleftharpoons [Pt(C_2H_4)Cl(Me_4en)(NEt_2)] + NH_2Et_2^+ \quad \text{(ii)}$$

$$[Pt(C_2H_4)Cl(Me_4en)]^+ + [Pt(C_2H_4)Cl(Me_4en)(NEt_2)] \longrightarrow [\{Pt(C_2H_4)Cl(Me_4en)\}_2(NEt_2)]^+ \quad \text{(iii)}$$

solubility of (3) in water. This mechanism is fully supported by the observation that when treating (1) with $[Pt(C_2H_4)Cl(Me_4en)(NHEt_2)]^+$ in 1 : 1 molar ratio and in the presence of a stoicheiometric amount of base in order to deprotonate $[Pt(C_2H_4)Cl(Me_4en)(NHEt_2)]^+$, complex (3) is obtained in almost quantitative yield.

Compound (3) dissolves readily in chloroform from which, on standing, it reprecipitates incorporating one molecule of solvent. The chloroform of crystallization must interact rather strongly with the salt as indicated by the very sharp C–Cl bands, instead of the usual broad absorption, observed in its i.r. spectrum (at 725 and 738 cm^{-1} for the derivative with deuteriochloroform where net separation from other absorption bands occurs).[15]

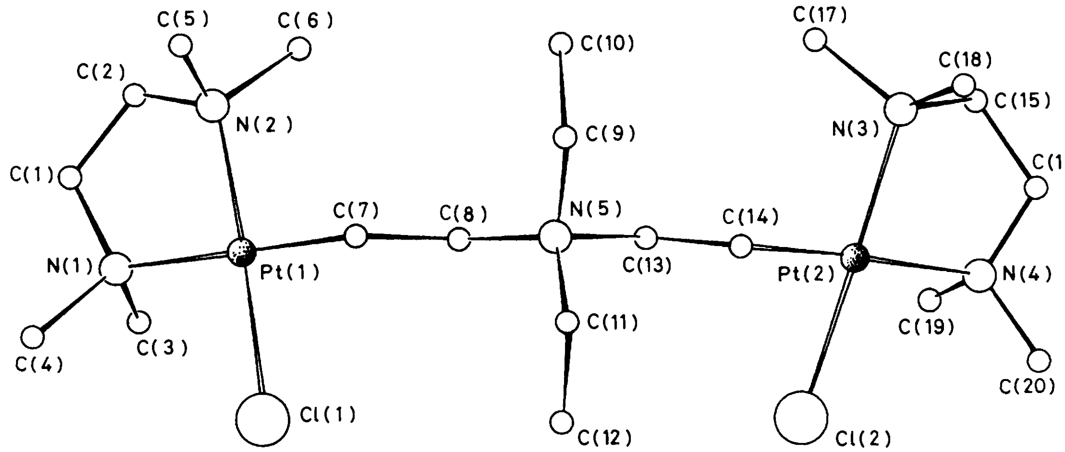
Compound (4).—The remarkable and quite unexpected results obtained in the reaction of (1) with $NHEt_2$ prompted us to explore the possibility of preparing a derivative with three platinum ethylide groups per nitrogen atom. In the light of previous results we treated one equivalent of ethylamine with a three-fold excess of (1), followed by 2 equivalents of base. By this procedure the quaternary ammonium ion initially formed in the reaction of the amine with (1) is deprotonated by the base and the novel amine formed therefrom can couple with a further molecule of cation (1); this process can be repeated as many times as there are hydrogens in the starting amine. The final product obtained was formulated as $[\{Pt(C_2H_4)Cl(Me_4en)\}_3(NEt)][ClO_4]$, (4), on the basis of elemental analysis and i.r. data {complete absence of bands due to aminic protons and presence of those due to perchlorate anion and *C*-bonded platinum moieties [*cis*-chelated Me_4en (810 and 770 cm^{-1}), Pt–Cl (330 cm^{-1}), and Pt–C (495 cm^{-1}) σ bonds]}.

Compound (5).—This compound completes the series of complexes reported in this paper. Its preparation was carried out, in analogy with (4), by treating 1 equivalent of ammonia with a four-fold excess of cation (1) followed by the addition of 3 equivalents of base. Also in this case the i.r. spectrum showed the complete absence of aminic protons and the presence of perchlorate anion, pointing to the formation of a tetrasubstituted ammonium perchlorate salt containing four platinum residues [bands of *cis*-chelated Me_4en at 810 and 770, ν(Pt–Cl) at 330, and ν(Pt–C) at 500 cm^{-1}].

This compound, which is characterized by thermal stability compared to the previous ones, can undergo in solution a further transformation with the expulsion of two chloride ions and formation of a chlorine bridge between each pair of platinum atoms; in this way the steric repulsion between the four platinum moieties is reduced.

The bi-, tri-, and tetra-nuclear compounds of types (3), (4), and (5) had already been postulated as intermediates in the reaction of nitrogen bases with *cis*- and *trans*-$[Pt(\eta^2\text{-olefin})X_2(L)]$ complexes (X = anionic and L = neutral ligand).[1] In fact, since cleavage of the Pt–C bond with transfer of an alkyl group to nitrogen occurred only in the final degradative step, the formation of polyalkylated amines and ammonium ions by this type of reaction implied the formation of intermediate polynuclear species containing at least as many Pt–C bonds as there are novel alkyl groups in the final product. We have now succeeded in preparing such polynuclear complexes and the reason for this is to be found, apart from some experimental details, in the enhanced electrophilicity of ethylene in cation (1) and in the absence of a formal negative charge on platinum in the addition product which, we believe, stabilizes the Pt–C bond.

We can also anticipate that the number of platinum residues in a given addition product can be even higher than the number of alkyl groups transferred to nitrogen after protolysis. For instance, it was believed that



View of the cationic binuclear complex (3) with the atomic numbering scheme secondary amines could only react with one molecule of olefin complex to give mononuclear addition products on the grounds that, after protolysis of the reaction mixture, only ammonium ions containing one more alkyl group than the original amine could be obtained.[5] We have performed the acidolysis reaction by bubbling gaseous HCl through a chloroform solution[16] of the binuclear complex (3) and, very surprisingly, we too obtained triethylammonium instead of the expected tetraethylammonium salt, indicating that a less-substituted ammonium ion can arise from a more substituted addition product. The different decomposition patterns of these polynuclear species under different protolysis conditions will be the subject of a forthcoming publication.

Crystal Structure of the Compound $[\{Pt(C_2H_4)Cl(Me_4en)\}_2(NEt_2)][ClO_4]$, (3).—The crystal structure consists of cationic binuclear platinum complexes and perchlorate anions. A view of the cation $[\{Pt(C_2H_4)Cl(Me_4en)\}_2(NEt_2)]^+$ with the atomic numbering scheme is given in the Figure and selected bond distances and angles are given in Table 2. The binuclear complex, having approximate *m* symmetry, contains a penta-atomic bridging chain, $-CH_2-CH_2-NEt_2-CH_2-CH_2-$, formed by the insertion of a NEt_2^- ion into two ethylene groups; each metal atom is square planar, co-ordinated by a carbon atom from the bridging ligand, a chlorine atom, and two nitrogen atoms from a chelating Me_4en ligand. The co-ordination geometry around Pt(1) is almost perfectly planar, while that of Pt(2) is slightly tetrahedrally distorted (Table 3). Both penta-atomic chelate rings are puckered, the torsion angles in these rings and in the bridging chain being given in Table 3.

TABLE 2

Selected bond distances (Å) and angles (°) in the cation $[\{(Me_4en)ClPt-CH_2-CH_2-\}_2NEt_2]^+$

Pt(1)–Cl(1)	2.294(7)	Pt(2)–Cl(2)	2.264(8)
Pt(1)–N(1)	2.12(1)	Pt(2)–N(4)	2.13(1)
Pt(1)–N(2)	2.06(1)	Pt(2)–N(3)	2.07(1)
Pt(1)–C(7)	2.02(2)	Pt(2)–C(14)	2.04(2)
N(1)–C(1)	1.46(3)	N(4)–C(16)	1.46(3)
N(2)–C(2)	1.48(3)	N(3)–C(15)	1.50(3)
C(1)–C(2)	1.45(3)	C(15)–C(16)	1.47(3)
N(1)–C(3)	1.50(3)	N(4)–C(19)	1.51(3)
N(1)–C(4)	1.51(3)	N(4)–C(20)	1.50(3)
N(2)–C(5)	1.52(4)	N(3)–C(17)	1.51(3)
N(2)–C(6)	1.53(4)	N(3)–C(18)	1.51(4)
C(7)–C(8)	1.50(3)	C(13)–C(14)	1.47(3)
N(5)–C(8)	1.52(3)	N(5)–C(13)	1.53(3)
N(5)–C(9)	1.53(3)	N(5)–C(11)	1.52(3)
C(9)–C(10)	1.50(3)	C(11)–C(12)	1.50(3)

Cl(1)–Pt(1)–N(1)	93.3(5)	Cl(2)–Pt(2)–N(4)	94.4(6)
Cl(1)–Pt(1)–C(7)	86.9(8)	Cl(2)–Pt(2)–C(14)	84.5(7)
N(1)–Pt(1)–N(2)	83.1(7)	N(4)–Pt(2)–N(3)	83.7(7)
N(2)–Pt(1)–C(7)	96.7(9)	N(3)–Pt(2)–C(14)	97.7(8)
Pt(1)–N(1)–C(1)	110(1)	Pt(2)–N(4)–C(16)	109(1)
N(1)–C(1)–C(2)	112(2)	N(4)–C(16)–C(15)	109(2)
C(1)–C(2)–N(2)	116(2)	C(16)–C(15)–N(3)	115(2)
C(2)–N(2)–Pt(1)	109(1)	C(15)–N(3)–Pt(2)	106(1)
Pt(1)–C(7)–C(8)	112(1)	Pt(2)–C(14)–C(13)	114(1)
C(7)–C(8)–N(5)	119(2)	C(14)–C(13)–N(5)	117(2)
C(8)–N(5)–C(13)	109(1)	C(13)–N(5)–C(9)	109(1)
C(8)–N(5)–C(9)	111(1)	C(13)–N(5)–C(11)	111(1)
C(8)–N(5)–C(11)	112(1)	C(9)–N(5)–C(11)	105(1)

TABLE 3

Least-squares planes through groups of atoms *

Plane (1): Cl(1), C(7), N(1), N(2)
$-0.8036X + 0.1007Y - 0.5866Z = -13.3441$
[Cl(1) −0.002(6), C(7) 0.01(1), N(1) 0.01(1), N(2) −0.01(1), Pt(1) 0.011(3)]

Plane (2): Cl(2), C(14), N(4), N(3)
$0.7216X - 0.1062Y - 0.6841Z = 1.6024$
[Cl(2) −0.028(6), C(14) 0.06(1), N(4) 0.06(1), N(3) −0.09(1), Pt(2) 0.007(3)]

Plane (3): Pt(1), N(1), C(1), C(2), N(2)
$-0.8114X + 0.0935Y - 0.5770Z = -13.3081$
[Pt(1) −0.001(3), N(1) 0.02(1), C(1) −0.20(3), C(2) 0.21(3), N(2) −0.02(1)]

Plane (4): Pt(2), N(3), C(15), C(16), N(4)
$0.7558X - 0.0363Y - 0.6538Z = 2.4308$
[Pt(2) −0.001(3), N(3) 0.04(1), C(15) −0.28(2), C(16) 0.27(3), N(4) −0.04(1)]

Torsion angles (°) in the chelate rings and in the bridging chain

Pt(1)–N(1)–C(1)–C(2)	−25.8
N(1)–C(1)–C(2)–N(2)	35.9
C(1)–C(2)–N(2)–Pt(1)	−27.1
C(2)–N(2)–Pt(1)–N(1)	9.0
N(2)–Pt(1)–N(1)–C(1)	9.0
N(1)–Pt(1)–C(7)–C(8)	156.5
Pt(1)–C(7)–C(8)–N(5)	174.2
C(7)–C(8)–N(5)–C(13)	177.3
Pt(2)–N(4)–C(16)–C(15)	33.7
N(4)–C(16)–C(15)–N(3)	−48.0
C(16)–C(15)–N(3)–Pt(2)	36.2
C(15)–N(3)–Pt(2)–N(4)	−11.9
N(3)–Pt(2)–N(4)–C(16)	−12.1
C(8)–N(5)–C(13)–C(14)	173.8
N(5)–C(13)–C(14)–Pt(2)	−176.9
C(13)–C(14)–Pt(2)–N(4)	146.0

* Displacements (Å) of relevant atoms are given in square brackets. *X*, *Y*, *Z* are orthogonalized co-ordinates obtained from the fractional co-ordinates by applying the matrix $\|a,0,c\cos\beta|0,b,0|0,0,c\sin\beta\|$.

The Pt–Cl [2.294(7) and 2.264(8) Å], Pt–C [2.02(2) and 2.04(2) Å], and Pt–N [2.12(1) and 2.06(1); and 2.13(1) and 2.07(1) Å] bond distances are comparable to those found in the binuclear cation $[\{Pt(C_2H_4)Cl(Me_4en)\}_2(Me_4en)]^{2+}$ [2.286(8), 2.006(19), and 2.112(16) and 2.064(15) Å respectively][17] in which the co-ordination around the metals is the same and the bridging organic chain is formed by a *NNN′N′*-tetramethylethylenediamine inserted into two ethylene groups.

The Pt–N bond distances, around each metal atom, are significantly different, the longer involving the nitrogen atoms *trans* to the carbon atoms. This feature has been observed not only in other complexes with platinum–carbon σ bonds[18-20] but also in the cation of (1), $[Pt(\eta^2\text{-}C_2H_4)Cl(Me_4en)]^+$, containing a π-bonded olefin, the structure of which we have already reported.[9] This indicates that a similar *trans* influence is exerted by either a η^2- or a σ-C_2H_4 group. Although in some cases this similarity has not been fully recognized, we believe that it has a real significance, allowing comparison of crystal data of two species which, apart from the η^2- or σ-ligand, are identical.

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