Platinum(I) Complexes: Crystal Structure of Bis(tetra-n-propylammonium) Bis[carbonyldichloroplatinate(I)]

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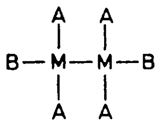
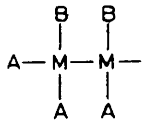
Crystals of the title compounds are monoclinic, space group $P2_1/a$, with $Z = 4$ in a unit cell of dimensions: $a = 19.727(6)$, $b = 9.176(3)$, $c = 21.481(10)$ Å, $\beta = 113.72(3)°$. The structure has been elucidated from 4 448 non-zero diffracted intensities, measured on a four-circle diffractometer, by conventional heavy-atom methods, and refined to R 0.109. The anion consists of two slightly distorted square planar $[PtCl_2(CO)]^-$ entities linked by an unbridged Pt–Pt bond such that the dihedral angle between the two planes is 60°. The carbonyl groups adopt a *transoid* configuration. The structure found is one of those predicted from spectroscopic observations. The Pt–Pt bond distance [2.584(2) Å] has a strong *trans*-influence on the Pt–Cl bond lengths.

THE isolation of binuclear carbonyl halide complexes of platinum(I) is of interest not only because of the rarity of such species, but also because the structures deduced from spectroscopic observation imply that an unusual form of isomerism may be present. Indeed, two isomers of the title compound have been isolated, and we present here our findings from a crystallographic determination of the structure of one of these. The result gives direct confirmation of the deductions of the original investigations [1] and provides interesting additional structural detail.

Any species $M_2A_4B_2$ containing a direct M–M bond, with M in a square-planar configuration, could in principle possess any of the structures (I)—(V). Goggin and Goodfellow,[1] from their i.r. and Raman studies, correctly deduce that $[Pt_2Cl_4(CO)_2]^{2-}$ belongs basically to type (II), but because the metal–metal bond does not provide a rigid constraint it is not necessary for the two square-planar ' halves ' of the molecule to be themselves coplanar. They point out that while an interplanar angle of 90° would minimise repulsions between ligands

(I) 

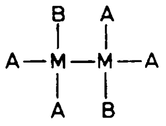
$$\begin{array}{ccccc} & A & & A & \\ & | & & | & \\ B- & M & - & M & -B \\ & | & & | & \\ & A & & A & \end{array}$$



$$\begin{array}{ccccc} & B & & B & \\ & | & & | & \\ A- & M & - & M & -A \\ & | & & | & \\ & A & & A & \end{array}$$

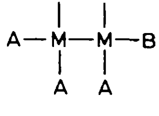
(IIa)

or

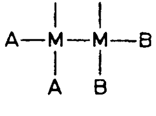


$$\begin{array}{ccccc} & B & & A & \\ & | & & | & \\ A- & M & - & M & -A \\ & | & & | & \\ & A & & B & \end{array}$$

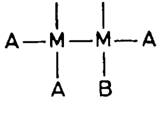
(IIb)

(III) 

$$\begin{array}{ccccc} & B & & A & \\ & | & & | & \\ A- & M & - & M & -B \\ & | & & | & \\ & A & & A & \end{array}$$

(IV) 

$$\begin{array}{ccccc} & A & & A & \\ & | & & | & \\ A- & M & - & M & -B \\ & | & & | & \\ & A & & B & \end{array}$$

(V) 

$$\begin{array}{ccccc} & A & & B & \\ & | & & | & \\ A- & M & - & M & -A \\ & | & & | & \\ & A & & B & \end{array}$$

on adjacent platinum atoms, an angle of 45° would enable the interaxial d orbitals to be as remote from one

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[1] P. L. Goggin and R. Goodfellow, *J.C.S. Dalton*, 1973, 2355.

another as possible, so minimising any antibonding interaction between them. Such an arrangement, however, would imply the existence of two forms of (II), namely, a *cisoid* form (IIa) in which the dihedral angle between the two Pt–Pt–CO planes is acute, and a *transoid* form (IIb) in which it is obtuse. We found that in the crystals studied the molecule was in fact *transoid* with a dihedral angle of *ca.* 120°.

EXPERIMENTAL

Crystals of $[Pr_4N]_2[Pt_2Cl_4(CO)_2]$ grow from nitromethane as large gold-yellow prisms. In view of the high X-ray absorption and high diffracting power of the crystals a small segment was cut with faces parallel to 100, $12\bar{1}$, and 001, of size $0.27 \times 0.40 \times 0.40$ mm. Diffraction intensities were collected, and lattice parameters measured, on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier [2] except that in this case, because the crystals decompose in the X-ray beam, all measurements were made at the fastest scan rate (0.997° s^{-1}), thereby reducing the total crystal exposure time to 8.5 h. Under these conditions the five check reflections (measured between every 55 intensities) varied by only -0.20 to 0.09%; no crystal-decay correction was applied, therefore. Reflections for which $I < 2.5\sigma(I)$ were regarded as 'unobserved' for the purposes of structure solution and preliminary refinement, but all non-zero intensities were included in the final refinement. Of the total 5 312 independent reflections (complete for $4.0° < 2\theta < 47.0°$), 2 524 were 'observed' and 4 448 had $I > 0$. The 100 measurements of each check reflection gave standard deviations 0.9—1.1 times those derived from counting statistics, indicating excellent constancy. Of the 391 systematic absences measured, two were above the 2.5σ threshold, and for one other the value of I/σ was < -2.5, the ratio $I : \sigma$ ranging from -2.60 to 2.68. Several strong low-angle reflections showed large negative ΔF: inclusion of an extinction parameter in the refinement gave a significant improvement in the agreement index. All intensities were corrected for X-ray absorption,[3] and for anomalous dispersion by the Pt atom.

Crystal Data.—$C_{26}H_{56}Cl_4N_2O_2Pt_2$, $M = 961$, Monoclinic, $a = 19.727(6)$, $b = 9.176(3)$, $c = 21.481(10)$ Å, $\beta = 113.72(3)°$ at 22 °C, $Z = 4$, $D_c = 1.76$ g cm^{-3} (D_m not measured), $F(000) = 1\,876$. Space group $P2_1/a$. Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.71069$ Å; μ(Mo-K_α) = 86.0 cm^{-1}.

Structure Solution and Refinement.—The positions of the two platinum and four chlorine atoms were located from a Patterson synthesis, and the remaining non-hydrogen atoms by electron-density difference syntheses. Least-squares full-matrix refinements, with isotropic thermal parameters and unit weights, gave R 0.074 (R' 0.084). Introduction of anisotropic thermal parameters for all atoms of the anion gave R 0.060 (R' 0.070). Of the 32 methylene hydrogen atoms, 20 were identified on an electron-density difference synthesis at this stage; all 32 were in fact introduced at calculated positions (C–H 1.02 Å, U_H 0.06 Å^2), and included in subsequent structure-factor calculations, but were not refined. No attempt was made to include methyl hydrogen atoms. Introduction of a more satisfactory weighting scheme, $1/w = (A/F)^2$ for

TABLE 1

Atomic positional (fractional co-ordinates) and thermal parameters, with estimated standard deviations in parentheses

Atom	x	y	z	$10^2U/$ Å^2 *
Anion				
Pt(1)	0.270 49(5)	0.076 84(12)	0.188 32(5)	†
Pt(2)	0.228 56(5)	0.064 64(12)	0.287 71(5)	†
Cl(1)	0.3047(4)	0.0978(9)	0.0943(4)	†
Cl(2)	0.2022(4)	0.0657(10)	0.3887(3)	†
Cl(3)	0.3822(4)	−0.0422(9)	0.2525(4)	†
Cl(4)	0.1233(3)	−0.0714(9)	0.2261(3)	†
C(1)	0.181(1)	0.157(3)	0.139(1)	†
O(1)	0.126(1)	0.204(3)	0.111(1)	†
C(2)	0.307(2)	0.178(3)	0.328(2)	†
O(2)	0.361(1)	0.242(3)	0.359(1)	†
Cation (1)				
N(1)	0.374(1)	0.569(2)	0.123(1)	3.7(3)
C(3)	0.295(1)	0.533(3)	0.112(1)	4.9(6)
C(31)	0.256(1)	0.642(3)	0.140(1)	5.3(6)
C(32)	0.187(2)	0.573(4)	0.140(1)	7.9(7)
C(4)	0.424(1)	0.583(3)	0.200(1)	4.7(5)
C(41)	0.418(1)	0.458(3)	0.241(1)	5.7(6)
C(42)	0.473(2)	0.473(4)	0.315(2)	7.5(8)
C(5)	0.379(1)	0.717(3)	0.093(1)	4.1(5)
C(51)	0.453(1)	0.761(3)	0.098(1)	6.5(7)
C(52)	0.447(1)	0.898(3)	0.052(1)	5.3(6)
C(6)	0.407(1)	0.452(3)	0.097(1)	4.9(5)
C(61)	0.378(2)	0.438(4)	0.020(1)	7.4(7)
C(62)	0.420(2)	0.323(3)	−0.002(1)	6.6(7)
H(301) ‡	0.265	0.524	0.061	
H(302)	0.296	0.435	0.135	
H(311)	0.291	0.671	0.188	
H(312)	0.243	0.733	0.110	
H(401)	0.478	0.590	0.206	
H(402)	0.410	0.676	0.218	
H(411)	0.366	0.456	0.240	
H(412)	0.428	0.364	0.222	
H(501)	0.345	0.715	0.043	
H(502)	0.362	0.794	0.117	
H(511)	0.485	0.785	0.147	
H(512)	0.476	0.677	0.082	
H(601)	0.463	0.471	0.115	
H(602)	0.398	0.355	0.116	
H(611)	0.324	0.409	0.002	
H(612)	0.383	0.537	0.001	
Cation (2)				
N(2)	0.135(1)	0.554(2)	0.380(1)	4.2(4)
C(7)	0.217(1)	0.557(3)	0.390(1)	5.1(5)
C(71)	0.236(2)	0.667(3)	0.348(1)	6.7(7)
C(72)	0.313(2)	0.644(4)	0.354(2)	7.9(8)
C(8)	0.084(1)	0.528(3)	0.305(1)	4.9(5)
C(81)	0.095(2)	0.382(3)	0.275(1)	7.0(7)
C(82)	0.042(2)	0.368(3)	0.203(1)	6.8(7)
C(9)	0.108(1)	0.703(3)	0.395(1)	5.1(6)
C(91)	0.143(2)	0.751(3)	0.467(1)	7.2(7)
C(92)	0.105(1)	0.886(3)	0.479(1)	5.7(6)
C(10)	0.127(1)	0.444(3)	0.425(1)	5.9(6)
C(11)	0.047(2)	0.419(4)	0.423(1)	7.8(7)
C(12)	0.047(2)	0.309(4)	0.476(2)	9.5(10)
H(701) ‡	0.248	0.578	0.440	
H(702)	0.230	0.457	0.377	
H(711)	0.200	0.657	0.298	
H(712)	0.231	0.769	0.365	
H(801)	0.031	0.533	0.301	
H(802)	0.093	0.610	0.277	
H(811)	0.147	0.376	0.278	
H(812)	0.086	0.299	0.303	
H(901)	0.119	0.781	0.366	
H(902)	0.053	0.697	0.382	
H(911)	0.140	0.669	0.498	
H(912)	0.198	0.775	0.479	
H(101)	0.144	0.347	0.414	
H(102)	0.161	0.472	0.474	
H(111)	0.028	0.516	0.433	
H(112)	0.014	0.382	0.376	

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[2] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

[3] Technical Report TR 192, Computer Science Center, University of Maryland, June 1972.

TABLE 1 (*Continued*)

* $B = 8\pi^2U$. † Anisotropic thermal parameters in the form $\exp\{-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]\}$, with parameters ($\times 10^2$):

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	3.96(6)	4.10(6)	4.91(6)	−0.37(5)	2.34(4)	−0.58(5)
Pt(2)	3.42(5)	3.77(6)	4.59(6)	−0.25(5)	1.72(4)	−0.14(5)
Cl(1)	6.3(4)	7.4(5)	7.6(4)	−1.1(4)	4.3(3)	−0.5(4)
Cl(2)	6.8(4)	7.6(4)	5.5(4)	−1.2(4)	3.6(3)	−0.0(4)
Cl(3)	4.3(3)	7.3(5)	7.2(4)	0.4(3)	1.8(3)	−1.0(3)
Cl(4)	4.5(3)	6.6(4)	6.7(4)	−1.5(4)	1.9(3)	−0.7(4)
C(1)	4.6(13)	6.6(16)	3.0(12)	2.5(12)	0.6(10)	2.5(11)
O(1)	5.0(11)	13.0(18)	6.1(11)	4.4(12)	1.4(9)	2.3(11)
C(2)	11.2(24)	6.0(17)	8.5(20)	−3.5(17)	7.8(19)	−1.9(15)
O(2)	8.4(14)	11.1(18)	12.0(17)	−8.2(14)	5.0(13)	−5.8(14)

‡ For H atoms 10^2U held constant at 6.0 Å^2.

$A \leqslant F$, $1/w = (F/A)^2$ for $A > F$ with $A = 140$, and inclusion of an extinction parameter in the refinement gave R 0.054 (R' 0.054), g 2.48 × 10^{-3}. Finally, because there is no justification for ignoring 'unobserved' reflections, all non-zero intensities were incorporated into the refinement (4 448) to give R 0.109 (R' 0.066), g 2.46 × 10^{-3}. In a final electron-density difference synthesis the maximum peaks (*ca.* 1.9 eÅ^{-3}) occurred in the neighbourhood of the platinum atoms, and in the last cycle the mean shift-to-error ratio was 0.015.

TABLE 2

Interatomic distances (Å) and bond angles (°)

(*a*) Distances

Anion			
Pt(1)–Pt(2)	2.584(2)		
Pt(1)–Cl(1)	2.382(10)	Pt(2)–Cl(2)	2.426(9)
Pt(1)–Cl(3)	2.347(7)	Pt(2)–Cl(4)	2.327(7)
Pt(1)–C(1)	1.81(2)	Pt(2)–C(2)	1.78(3)
C(1)–O(1)	1.10(3)	C(2)–O(2)	1.15(4)

Cation (1)		Cation (2)	
N(1)–C(3)	1.52(3)	N(2)–C(7)	1.54(3)
N(1)–C(4)	1.55(2)	N(2)–C(8)	1.54(3)
N(1)–C(5)	1.53(3)	N(2)–C(9)	1.55(4)
N(1)–C(6)	1.48(3)	N(2)–C(10)	1.46(4)
C(3)–C(31)	1.52(4)	C(7)–C(71)	1.50(4)
C(31)–C(32)	1.51(5)	C(71)–C(72)	1.50(5)
C(4)–C(41)	1.48(4)	C(8)–C(81)	1.54(4)
C(41)–C(42)	1.52(4)	C(81)–C(82)	1.49(4)
C(5)–C(51)	1.47(4)	C(9)–C(91)	1.49(4)
C(51)–C(52)	1.57(4)	C(91)–C(92)	1.53(4)
C(6)–C(61)	1.52(4)	C(10)–C(11)	1.57(5)
C(61)–C(62)	1.53(5)	C(11)–C(12)	1.52(5)

For both cations: mean N–C 1.52(3), mean C–C 1.52(3).

(*b*) Angles

Anion			
Pt(2)–Pt(1)–Cl(3)	91.8(2)	Pt(1)–Pt(2)–Cl(4)	93.6(2)
Cl(3)–Pt(1)–Cl(1)	90.9(3)	Cl(4)–Pt(2)–Cl(2)	92.7(3)
Cl(1)–Pt(1)–C(1)	90.9(9)	Cl(2)–Pt(2)–C(2)	91.1(13)
C(1)–Pt(1)–Pt(2)	86.4(9)	C(2)–Pt(2)–Pt(1)	82.7(13)
Pt(2)–Pt(1)–Cl(1)	177.1(2)	Pt(1)–Pt(2)–Cl(2)	173.7(2)
Cl(3)–Pt(1)–C(1)	176.0(9)	Cl(4)–Pt(2)–C(2)	175.0(11)
Pt(1)–C(1)–O(1)	177.8(28)	Pt(2)–C(2)–O(2)	173.8(29)

Cation (1)		Cation (2)	
C(3)–N(1)–C(4)	111(2)	C(7)–N(2)–C(8)	111(2)
C(3)–N(1)–C(5)	111(2)	C(7)–N(2)–C(9)	113(2)
C(3)–N(1)–C(6)	112(2)	C(7)–N(2)–C(10)	108(2)
C(4)–N(1)–C(5)	105(2)	C(8)–N(2)–C(9)	103(2)
C(4)–N(1)–C(6)	106(2)	C(8)–N(2)–C(10)	113(2)
C(5)–N(1)–C(6)	112(2)	C(9)–N(2)–C(10)	110(2)
N(1)–C(3)–C(31)	116(2)	N(2)–C(7)–C(71)	116(2)
C(3)–C(31)–C(32)	109(2)	C(7)–C(71)–C(72)	110(2)
N(1)–C(4)–C(41)	114(2)	N(2)–C(8)–C(81)	116(2)
C(4)–C(41)–C(42)	111(2)	C(8)–C(81)–C(82)	111(2)
N(1)–C(5)–C(51)	117(2)	N(2)–C(9)–C(91)	115(2)
C(5)–C(51)–C(52)	111(2)	C(9)–C(91)–C(92)	111(2)
N(1)–C(6)–C(61)	116(2)	N(2)–C(10)–C(11)	117(2)
C(6)–C(61)–C(62)	113(2)	C(10)–C(11)–C(12)	112(2)

For both cations: mean $>$C(α) 115(2), mean $>$C(β) 111(2).

TABLE 2 (*Continued*)

(*c*) Non-bonded distances

Cl(3) ··· C(2)	3.29(4)	Cl(4) ··· C(1)	3.30(3)
Pt(1) ··· Cl(4)	3.583(8)	Pt(2) ··· Cl(3)	3.545(8)
Pt(1) ··· C(2)	2.95(3)	Pt(2) ··· C(1)	3.06(2)
N(1) ··· Cl(1)	4.50(2)	N(2) ··· Cl(2)	4.66(2)
N(1^{I}) ··· Cl(3)	4.49(2)	N(2^{I}) ··· Cl(4)	4.71(2)
Cl(1) ··· H(602)	2.92	Cl(2) ··· H(101)	2.96
Cl(1) ··· H(502^{I})	2.97	Cl(2) ··· H(712)	2.87
Cl(3) ··· H(801^{II})	2.68	Cl(4^{II}) ··· H(401)	2.72
Cl(3) ··· H(402^{I})	2.81	Pt(2) ··· H(811)	3.24
O(1) ··· C(82)(Me)	3.40	Pt(2) ··· H(712^{I})	3.16

Roman numeral superscripts refer to the following symmetry operations: I $x, y - 1, z$; II $\frac{1}{2} + x, \frac{1}{2} - y, z$

TABLE 3

Equations of some least-squares planes and lines in the form $Ax + By + Cz = D$ where x,y,z are fractional co-ordinates: distances (Å) of relevant atoms from these planes or lines are given in square brackets

(*i*) Anion

Plane (1): Pt(1), Cl(1), Cl(3), C(1), Pt(2)

$$6.058x + 8.201y + 3.780z = 2.964$$

[Pt(1) 0.917, Cl(1) 0.040, Cl(3) −0.040, C(1) −0.055, Pt(2) 0.038]

Plane (2): Pt(2), Cl(2), Cl(4), C(2), Pt(1)

$$8.821x - 7.637y + 2.582z = 2.251$$

[Pt(2) 0.015, Cl(2) 0.035, Cl(4) −0.034, C(2) —0.050, Pt(1) 0.035]

Line (3): Pt(1), Pt(2)

$$x = 0.2495 - 0.0162t;\ y = 0.0707 - 0.0047t;\ z = 0.2380 + 0.0385t$$

[Cl(1) 0.121, Cl(2) 0.268]

(*ii*) Cation (2)

Plane (4): N(2), C(8), C(9)

$$16.588x + 4.248y - 12.780z = -0.266$$

[C(81) −0.060, C(82) −0.067, C(91) −0.138, C(92) −0.350]

Plane (5): N(2), C(7), C(10)

$$-1.932x + 6.288y + 15.038z = 8.944$$

[C(71) 0.027, C(72) −0.181, C(11) −0.032, C(12) 0.069]

(*iii*) Cation (1)

Plane (6): N(1), C(3), C(4)

$$-4.194x + 8.959y + 1.055z = 3.655$$

[C(31) 0.846, C(32) −1.046, C(41) −1.072, C(42) 1.275]

Plane (7): N(1), C(5), C(6)

$$12.600x + 1.478y + 9.280z = 6.701$$

[C(51) 1.033, C(52) 0.748, C(61) −1.099, C(62) −0.948]

Angles (°) between least-squares planes and lines:

(1)—(2) 60.0, (1)—(3) 89.5, (2)—(3) 89.6, (4)—(5) 88.1, (6)—(7) 89.5

Positional and thermal parameters are in Table 1, interatomic distances in Table 2, and some least-squares planes in Table 3. Atomic scattering factors were taken from ref. 4 for platinum, chlorine, carbon, oxygen, and nitrogen, and from ref. 5 for hydrogen. All computational work was carried out (on the CDC 7600 of the University of London) by use of the '*X*-Ray' system of programs.[3] Observed

[4] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[5] R. F. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

and calculated structure factors are listed in Supplementary Publication No. SUP 21277 (21 pp., 1 microfiche).*

RESULTS AND DISCUSSION

The crystal structure of the title compound (Figure 1) confirms the overall features deduced from spectroscopic investigations. Interest centres upon the strange twisted configuration of the anionic unit. Each platinum is in an essentially square planar environment and carries two chlorine atoms and one carbonyl group. Two such units are fused by a direct Pt–Pt bond of length 2.584(2) Å, but the mean planes of the ligands around each Pt atom are mutually rotated (around a direction close to that of the Pt–Pt bond) so that the angle between the two planes is *ca.* 60°. The carbonyl groups take up the *transoid* sites on the adjacent metal atoms. The 60° angle is a compromise between a situation in which the filled interaxial *d* orbitals are as remote from one another as possible (45°) and a situation in which the ligands are stereochemically as far apart as possible (90°).

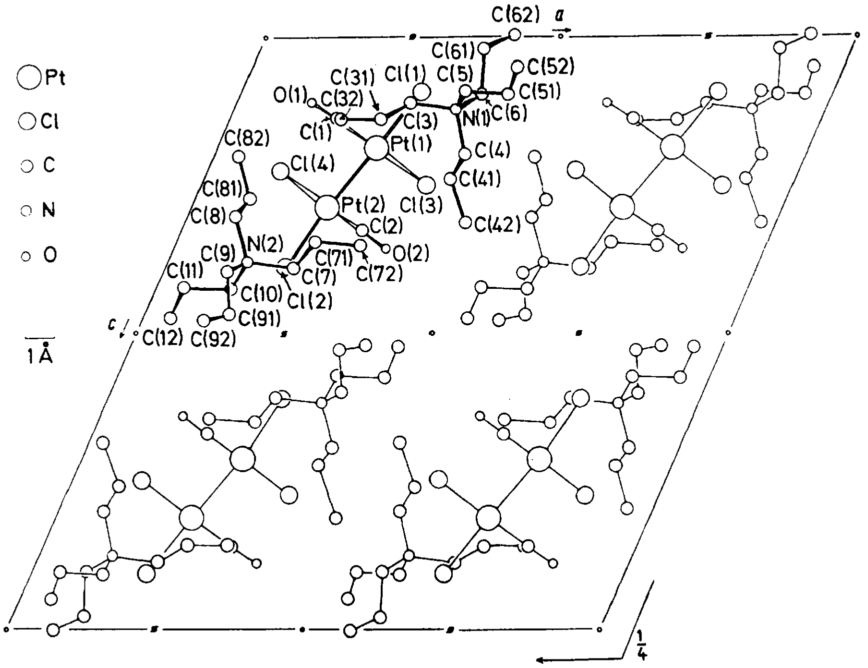

FIGURE 1 The contents of the monoclinic unit cell in projection down *b*. The atom numbering sequence is also shown

Some interesting details appear upon examination of the bond lengths and angles (Table 2). For both platinum atoms, the smallest interligand angle of the 'square' arrangement is Pt–Pt–CO; this introduces a significant non-linearity into the central Cl–Pt–Pt–Cl spine of the anion. Moreover, the 'square-planar' moieties, as well as being not square, are not planar either; each shows a slight tetrahedral distortion (Table 3) in such a manner that for Pt(1) the carbonyl group and the chlorine *trans* to it are below the local mean plane as viewed in Figure 1, whereas for Pt(2) the corresponding groups are above the local mean plane. If the interligand angles were undistorted, the planar deviations would have the effect of diminishing the C(1)–Cl(4) intramolecular distance and of increasing C(2)–Cl(3). In fact these distances are equal, the readjustment being accounted for by the bending of the central spine. Figure 2 shows a foreshortened view of the anion.

The Pt–Pt bond length [2.584(2) Å] is closely similar to that found in the remarkable compound μ-5-cyclopentadienylcyclopentadiene-bis(π-cyclopentadienylplatinum)(Pt–Pt),[6] though here the Pt–Pt bond [2.581(4) Å] is bridged by a cyclopentadiene moiety. It

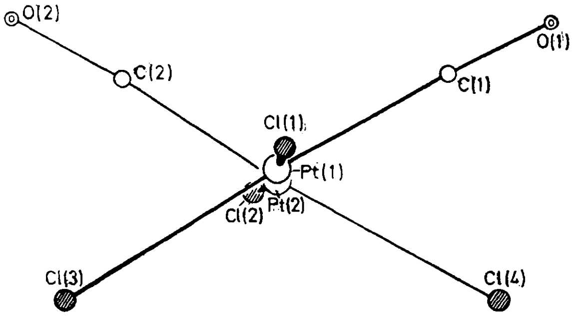

FIGURE 2 A view of the $[Pt_2Cl_4(CO)_2]^{2-}$ anion, showing the *transoid* relationship between the carbonyl groups of the two (essentially square-planar) halves of the unit

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[6] K. K. Cheung, R. J. Cross, K. P. Forrest, R. Wardle, and M. Mercer, *Chem. Comm.*, 1971, 875.

is one of the shortest Pt–Pt bonds on record.[7-11] Two other complexes of Pt^I seem to be well established: $[\{(Ph_3P)_2XPt\}_2]$, X = Cl or I;[12] and $[Pt_2Cl_2\{(Ph_2P)_2CH_2\}_2]$,[13] though neither has been examined crystallographically. A structure determination of $[(Ph_3P)_2\overline{Pt{\cdot}S{\cdot}Pt}(CO)(PPh_3)]$, arguably a compound of platinum(I), and in which the Pt–Pt bond is *S*-bridged, had Pt–Pt 2.647(2) Å.[14]

The Pt–Cl bond lengths show interesting variations. The two terminal ones of the central axis have a mean length of 2.404(22) Å, whereas the two *cis* to these are significantly shorter at 2.337(10) Å. These distances correlate well with the observed stretching frequencies in the vibrational spectra.[1] Comparison with data given in a discussion of the *trans*-influence of ligands upon the Pt–Cl bond in a series of square-planar platinum(II) complexes[15,16] would suggest that in the title compound the Pt–Cl bonds of the central axis of the anion are undergoing a strong *trans*-influence from the Pt–Pt bond; their length is near the upper end of the range commonly observed. The two terminal Pt–Cl bonds of the anion axis show a difference in length which, on the standard deviations given, may be just significant [Pt(1)–Cl(1) 2.382(10), and Pt(2)–Cl(2) 2.426(9) Å]. If this difference is real it can perhaps be ascribed to slightly different asymmetries of the two 'planar' moieties with respect to the Pt–Pt bond. The Pt–C and C–O bond lengths call for no special comment. The geometry of the tetrapropylammonium cations is likewise unexceptional, though oddly the atoms of the propyl ligands of cation (2) are constrained to lie on two mutually orthogonal planes defined by the tetrahedral valencies around the nitrogen atom. [The planes in question are those defined by C(7), N(2), C(10); and C(8), N(2), C(9); see Table 3.] Cation (1), on the other hand, has a different conformation: the overall symmetry is close to S_4, with the S_4 axis bisecting the C(3)–N(1)–C(4) angle. The nitrogen atom at the centre of each cation is positioned to be as closely related as possible to the electronegative ligands of the nearest half of the anion [N(1) with Cl(1) and Cl(3); N(2) with Cl(2) and Cl(4); see Figure 1]. Indeed, the shortest interionic contacts nearly all involve chlorine atoms (Table 2).

The structures of two formally similar nickel(I) compounds have been determined, namely $Rb_4[Ni_2(CN)_6]$ and $K_4[Ni_2(CN)_6]$, which each contain two 'square-planar' (but with distortions similar to those of the title compound) $Ni(CN)_3$ moieties joined by a Ni–Ni bond.[17] Here the two halves of the anion lie almost perpendicular to one another, but a quick inspection of van der Waals contact distances between CN groups on adjacent nickel atoms reveals that the cause is primarily steric interaction.

[4/2146 *Received*, 17*th October*, 1974]

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