

Five-co-ordinate Ethylene Complexes of Platinum(II). Part 2.¹ Synthesis and Reactivity of Some Five-co-ordinate Complexes of Platinum with Bis(hydrazones) and X-Ray Crystal Structure of [Butane-2,3-dione bis(methylhydrazone)]dichloro(η -ethylene)platinum(II)

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The reaction of bis(hydrazones) with Zeise's salt, $K[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]$, to give stable five-co-ordinate complexes of general formula $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{L})]$ is reported [$\text{L} = \text{Ph}(\text{H})\text{N}\cdot\text{N}\cdot\text{C}\cdot[\text{CH}_2]_4\cdot\text{C}\cdot\text{N}\cdot\text{N}(\text{H})\text{Ph}$ (L^1), $\text{Ph}(\text{H})\text{N}\cdot\text{N}\cdot\text{C}(\text{Me})\cdot\text{C}(\text{Me})\cdot\text{N}\cdot\text{N}(\text{H})\text{Ph}$ (L^2), $\text{Ph}(\text{Me})\text{N}\cdot\text{N}\cdot\text{C}(\text{Me})\cdot\text{C}(\text{Me})\cdot\text{N}\cdot\text{N}(\text{Me})\text{Ph}$ (L^3), $\text{Me}(\text{H})\text{N}\cdot\text{N}\cdot\text{C}(\text{Me})\cdot\text{C}(\text{Me})\cdot\text{N}\cdot\text{N}(\text{H})\text{Me}$ (L^4), or $\text{Me}_2\text{N}\cdot\text{N}\cdot\text{C}(\text{Me})\cdot\text{C}(\text{Me})\cdot\text{N}\cdot\text{NMe}_2$ (L^5)]. These have a trigonal bipyramidal structure with the chlorine atoms in the apical positions, and the bidentate ligand (which co-ordinates through its α -di-imine unit) and the ethylene in the equatorial plane. The five-co-ordinate species decompose in solution releasing ethylene and giving four-co-ordinate complexes of formula $[\text{PtCl}_2(\text{L})]$. The rate of decomposition in 1,2-dichloroethane has been measured and its relationship to ^1H n.m.r. data is discussed.

The crystal and molecular structure of the five-co-ordinate $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{L}^4)]$ has been determined at room temperature from three-dimensional X-ray data collected by counter methods. The structure has been refined by full-matrix least-squares techniques to a final R (on F) of 0.035 based on 712 reflections. The title compound crystallizes in the orthorhombic space group $Cmcm$, with four molecules in a cell of dimensions $a = 7.912(7)$, $b = 15.821(9)$, and $c = 10.718(8)$ Å. The co-ordination of the platinum atom is trigonal bipyramidal, assuming the ethylene molecule acts as a unidentate ligand. One symmetry plane contains the Cl-Pt-Cl group and bisects the bis(hydrazone) and the ethylene molecules, whilst the other contains the platinum atom and all the non-hydrogen atoms of the equatorial ligands. Significant bond distances are Pt-Cl = 2.304(3), Pt-N = 2.221(10), and Pt-C = 2.073(12) Å. The results suggest that the equatorial and axial covalent radii of five-co-ordinate platinum(II) resemble those of three-co-ordinate platinum(0) and four-co-ordinate platinum(II) respectively.

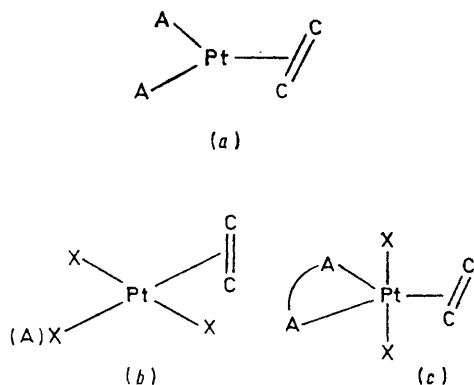
THE preparation of a series of five-co-ordinate η -ethylene complexes of platinum(II) of formula $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{L})]$

¹ Part 1, L. Maresca, G. Natile, and L. Cattalini, *Inorg. Chim. Acta*, 1975, **14**, 79.

with (L) a bidentate N-donor ligand has recently been reported.^{1,2} The structure of these complexes was

² L. Cattalini, F. Gasparrini, L. Maresca, and G. Natile, *J.C.S. Chem. Comm.*, 1973, 369.

deduced from n.m.r. and i.r. spectra to be trigonal bipyramidal with two chlorine atoms in the apical positions and the bidentate ligand and ethylene in the equatorial plane. We have extended this investigation and prepared a series of five-co-ordinate platinum(II) complexes in which a bis(hydrazone) molecule is co-ordinated to the metal through its α -di-imine unit. The rate of release of ethylene and formation of a four-co-ordinate complex, in this series of strictly related compounds, is found to be closely dependent on the nature of the substituents at the non-co-ordinating nitrogens. Three types of complexes are now known in which ethylene forms η -type bonds with platinum, involving (a), three-co-ordinate platinum(0), (b) four-co-ordinate platinum(II), and (c), five-co-ordinate platinum(II). Crystal data for compounds of type (a) and (b) have



A = donor atom of a neutral ligand, X = anionic ligand

already been reported; we have now determined the crystal structure of a compound of type (c) and compared these three different configurations. This is the first example of a (bidentate ligand)tris(unidentate ligand)-metal complex ever reported having trigonal bipyramidal structure.³

EXPERIMENTAL

Starting Materials.—The ligands cyclohexane-1,2-dione bis(phenylhydrazone) (L^1), butane-2,3-dione bis(phenylhydrazone) (L^2), butane-2,3-dione bis(methylphenylhydrazone) (L^3), butane-2,3-dione bis(methylhydrazone) (L^4), and butane-2,3-dione bis(dimethylhydrazone) (L^5) were prepared by literature methods.⁴ Their purity was established by t.l.c., elemental analyses, and i.r. spectroscopy. Zeise's salt was prepared according to the method of Cramer *et al.*⁵ from potassium platinite and ethylene gas. Zeise's dimer was prepared from the Zeise's salt by the method of Chatt and Searle.⁶

Preparation of Complexes.—The complexes were prepared by adding dropwise to a methanol solution of $K[Pt(C_6H_4)Cl_3] \cdot 3H_2O$ (ca. 1 mmol in a few cm³ of solvent) cooled at 0 °C (ice bath) the stoichiometric amount of the appropriate ligand (L) dissolved in the same solvent. Within a few minutes the product was precipitated from the solution; it was then filtered, washed twice with cold methanol, and dried. The yield was 40–70%, depending upon the solu-

bility of the product and the volume of solvent required to dissolve the ligand.

When (L) is butane-2,3-dione bis(phenylhydrazone), because of the insolubility of the free ligand in methanol, the above method could not be employed and the preparation was carried out in acetone. Thus to a vigorously stirred acetone solution of Zeise's dimer (ca. 0.5 mmol in the minimum amount of solvent), at 0 °C, the solid ligand (1 mmol) was added in small portions. An instantaneous reaction took place, the colour of the solution changing from yellow to light brown. The desired compound was precipitated by adding light petroleum to the acetone solution. Because of the instability of this compound no further purification was attempted but it proved to be sufficiently pure for our purposes.

Apparatus.—I.r. spectra in the range 4000–300 cm⁻¹ were recorded as KBr pellets with a Perkin-Elmer 457 spectrophotometer. ¹H n.m.r. spectra were obtained with a Varian NV14 spectrometer with CDCl₃ or (CD₃)₂CO as solvents and tetramethylsilane as internal standard. Conductivities (10⁻³ mol dm⁻³ solutions) of complexes in nitromethane at 0 °C were measured with an LKB conductolyzer. Visible and u.v. spectra were recorded on an Optica CF4R spectrophotometer.

Kinetic Data.—The rate of decomposition of the five-co-ordinate complexes to the four-co-ordinate species in 1,2-dichloroethane solution was determined spectrophotometrically by measuring changes of absorbance with time in the visible region of the spectrum. First-order rate constants were calculated from plots of $\log(A_\infty - A_t)$ against time, where A_t and A_∞ are absorbances at time t and after at least six half-lives respectively. From the values of rate constants at different temperatures the enthalpy and entropy of activation were calculated for the complexes with (L^2), (L^3), and (L^4); the complex with (L^5) is very stable and its half-life, at room temperature, was estimated to be about one month; the compound with (L^4) did not give sufficiently reproducible rate values to allow the determination of reliable activation parameters [the co-ordinated bis(hydrazone) is not very stable in solution].

Crystal Data.— $[Pt(C_6H_4)Cl_2\{Me(H)N \cdot N \cdot C(Me) \cdot C(Me) \cdot N \cdot N(H)Me\}]$, $M = 436.3$, Orthorhombic, $a = 7.912(7)$, $b = 15.821(9)$, $c = 10.718(8)$ Å, $U = 1341.6$ Å³, $D_c = 2.16$ g cm⁻³, $Z = 4$, $D_m = 2.3$ g cm⁻³; $\mu(Mo-K\alpha) = 114.4$ cm⁻¹. Space group $Cmcm$ from systematic absences and least-squares refinement. The dimensions of the crystal were $0.03 \times 0.02 \times 0.04$ cm.

The space group and the approximate cell unit dimensions were obtained from a preliminary photographic study. Final values of the cell parameters and the intensities were measured on a Siemens diffractometer by the θ – 2θ scan technique with Mo- $K\alpha$ radiation ($\lambda 0.7107$ Å) for a maximum 2θ angle of 54°. All reflections having $I_0 < 3\sigma(I_0)$ were rejected and a total of 712 independent reflections were corrected for the Lorentz and polarization factors and for absorption ($\mu_r = 1.71$).

Structure Solution and Refinement.—Three space groups, $Cmc2_1$, $C2mb$, and $Cmcm$ were allowed by the systematic absences. The Patterson map showed that all the peaks ascribable to Pt–N and Pt–C vectors were contained in the $(0, v, w)$ and $(\frac{1}{2}, v, w)$ sections, whereas the Pt–Cl vectors lay

³ J. C. Dewan and D. L. Kepert, *J. C. S. Dalton*, 1975, 959.

⁴ O. L. Chapman, R. W. King, and W. S. Welstead, *J. Amer. Chem. Soc.*, 1964, **86**, 4968.

⁵ R. D. Cramer, E. L. Jenner, R. V. Lindsey, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1963, **85**, 1961.

⁶ J. Chatt and M. L. Searle, *Inorg. Synth.*, 1957, **5**, 210.

TABLE 1

Fractional co-ordinates ($\times 10^4$) and temperature factors * ($\times 10^4$) with estimated standard deviations in parentheses

	X	Y	Z	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Pt	0	1 467(0)	2 500	91(1)	0	0	19(1)	0	53(1)
Cl	2 912(4)	1 439(2)	2 500	78(4)	14(4)	0	51(16)	0	130(4)
N(1)	0	2 603(6)	3 718(9)	150(14)	0	0	28(3)	-4(9)	69(8)
N(2)	0	2 559(8)	4 989(11)	489(42)	0	0	44(5)	-9(11)	49(7)
C(1)	0	3 337(7)	3 196(12)	150(17)	0	0	25(4)	-8(11)	81(11)
C(2)	0	4 143(9)	3 931(16)	431(47)	0	0	28(5)	-31(14)	106(14)
C(3)	0	1 786(10)	5 602(15)	481(53)	0	0	41(6)	36(15)	79(11)
C(4)	0	241(7)	3 183(14)	258(26)	0	0	20(4)	12(13)	109(13)

* In the form: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{13}hk + B_{13}hl + B_{23}kl)]$.

TABLE 2

Analytical(%)^a and i.r. data(cm⁻¹)

Compound	Colour	C	H	N	Cl	$\nu(\text{N-H})$	$\nu(\text{C=N})$	$\nu(\text{Pt-C-Cl})$	$\nu(\text{Pt-Cl})$
[Pt(C ₂ H ₄)Cl ₂ (L ¹)]	Yellow	41.3 (41.0)	4.3 (4.1)	9.6 (9.5)	12.1 (12.1)	3 260m	1 590vs 1 560vs	410s, br	325s
[Pt(C ₂ H ₄)Cl ₂ (L ²)]	Golden-yellow	39.0 (38.6)	4.2 (4.0)	9.9 (10.0)	12.4 (12.6)	3 270w	1 595vs 1 570vs	395s, br	345s
[Pt(C ₂ H ₄)Cl ₂ (L ³)]	Orange	40.4 (40.8)	4.3 (4.4)	9.4 (9.5)	12.0 (12.0)		1 595s 1 580s		340s
[Pt(C ₂ H ₄)Cl ₂ (L ⁴)]	Yellow	21.8 (22.0)	4.0 (4.2)	12.8 (12.8)	16.1 (16.2)	3 320m	1 580br	430s, br	335s
[Pt(C ₂ H ₄)Cl ₂ (L ⁵)]	Golden-yellow	25.8 (25.9)	4.7 (4.8)	12.3 (12.1)	15.6 (15.3)		1 620mw 1 540mw		340s

^a Calculated values are given in parentheses.

TABLE 3

Proton chemical shifts ^a (δ p.p.m. downfield from SiMe₄) of the five-co-ordinate complexes [Pt(C₂H₄)Cl₂(L)]

Ligand L	Solvent	$\theta_c/^\circ\text{C}$	C ₆ H ₅	N-CH ₃	C-CH ₃	CH ₂	C ₂ H ₄ ^b
Ph(H)N·N·C·[CH ₂] ₄ ·C·N·N(H)Ph	(CD ₃) ₂ CO	25	6.9—7.7			2.9, m 2.0m	2.98 (71)
Ph(H)N·N·C(Me)·C(Me)·N·N(H)Ph	(CD ₃) ₂ CO	-40	6.8—7.7		2.50		2.87 (70)
Ph(Me)N·N·C(Me)·C(Me)·N·N(Me)Ph	CDCl ₃	25	7.0—7.5	4.00	2.10		3.32 (70)
Me(H)N·N·C(Me)·C(Me)·N·N(H)Me	(CD ₃) ₂ CO	25		3.52d	2.23		3.21 (69)
Me ₂ N·N·C(Me)·C(Me)·N·NMe ₂	CDCl ₃	25		3.11	2.50		3.48 (69)

^a m = multiplet, d = doublet. ^b Values of $J(\text{Pt-H})$ in Hz are given in parentheses.

TABLE 4

Kinetic parameters for loss of ethylene from [Pt(C₂H₄)Cl₂(L)] complexes

Ligand (L)	$\theta_c/^\circ\text{C}$	$k_{\text{obs.}}/s^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$
Ph(H)N·N·C·[CH ₂] ₄ ·C·N·N(H)Ph	25.0	1.9×10^{-3}		
Ph(H)N·N·C(Me)·C(Me)·N·N(H)Ph	35.0	1.7×10^{-2}	75 ± 5	-33 ± 8
	25.0	5.8×10^{-3}		
	16.0	2.4×10^{-3}		
Ph(Me)N·N·C(Me)·C(Me)·N·N(Me)Ph	45.5	2.9×10^{-4}	91 ± 5	-25 ± 8
	35.0	8.5×10^{-5}		
	25.0	2.5×10^{-5}		
Me(H)N·N·C(Me)·C(Me)·N·N(H)Me	45.5	2.3×10^{-4}	95 ± 5	-17 ± 8
	35.0	7.0×10^{-5}		
	25.0	1.9×10^{-5}		
Me ₂ N·N·C(Me)·C(Me)·N·NMe ₂	25.0	$ca. 2.5 \times 10^{-7}$ ^a		

^a The half-life of this complex in 1,2-dichloroethane is *ca.* 4 weeks at 25 °C.

in the ($u, v, 0$) and ($u, v, \frac{1}{2}$) sections, suggesting an *mm* molecular symmetry. Hence the *Cmcm* space group was chosen and was then confirmed by successful refinement. All the non-hydrogen atomic parameters were refined with anisotropic thermal factors by the full-matrix least-squares method. The final refinement gave an *R* of 0.035.

All calculations were carried out on a CDC 6 200 computer using programmes described in ref. 7. Final atomic parameters are listed in Table 1. Atomic scattering factors were those of ref. 8. Observed and calculated structure factors, and r.m.s. displacements and orientations of thermal vibration ellipsoids, are listed in Supplementary Publication No. SUP 21870 (4 pp., 1 microfiche).*

* See Notice to Authors, No. 7 in *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

RESULTS AND DISCUSSION

The co-ordinating ability of bis(hydrazones) towards Pt^{II} is rather poor; neither Na[PtCl₄] nor [PtCl₂(benzocyanide)₂] react at room temperature with free bis(hydrazones) over a period of several days, and on heating only extensive decomposition of the starting materials occurs. However, these ligands react smoothly with Zeise's salt, K[Pt(C₂H₄)Cl₃], or its dimer [{Pt(C₂H₄)Cl₂]₂] forming five-co-ordinate complexes of formula [Pt(C₂H₄)Cl₂(L)]. These are stable in the solid state for a long time at room temperature and can be

⁷ V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, **96**, 922.

⁸ F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

stored almost indefinitely at 0 °C. However they decompose in solution in the common organic solvents releasing ethylene and giving the corresponding square-planar complexes $[\text{PtCl}_2(\text{L})]$; the decomposition can be repressed by lowering the temperature of the solution.

All complexes gave satisfactory elemental analyses (Table 2) and were non-conducting in nitromethane solution. Their i.r. and n.m.r. spectra indicated that they had a trigonal bipyramidal structure with the chlorine atoms in the apical positions and the bidentate ligand and the ethylene molecule in the equatorial plane. The more significant i.r. data are listed in Table 2. The overlap of the ligand absorptions with those for ethylene made spectral assignments impossible. In the region below 600 cm^{-1} the platinum-ethylene, the platinum-nitrogen, and the platinum-chlorine stretchings are expected to occur. A reliable assignment could be made only for the metal-halogen stretchings which appear as a single band as expected for two chlorine atoms mutually *trans* and occupying the apical positions of a trigonal bipyramid. The platinum-nitrogen and platinum-ethylene vibrations are expected to couple to each other; however, some bands which were present only in the five-co-ordinate complex, and not in the free ligand or in the four-co-ordinate $[\text{PtCl}_2(\text{L})]$ species, are tentatively assigned to $\nu[\text{Pt}-(\text{C}_2\text{H}_4)]$.

The n.m.r. data are collected in Table 3. The presence of a single sharp resonance for the C-methyl and N-methyl protons of ligands (L^2), (L^3), (L^4), and (L^5) clearly indicates that the ligands are bidentate and occupy equivalent positions of the trigonal bipyramid. The coupling constants of the C- CH_3 and N- CH_3 protons with platinum were found to be 4–4.5 and 5–6 Hz respectively. The ethylene protons always appeared as a triplet of relative intensity 1 : 4 : 1 due to coupling with ^{195}Pt ($I = 1/2$, 34% abundance). The upfield shift of the olefinic protons, on co-ordination, $\Delta\delta$, varies from 1.7–2.4 p.p.m. in the different complexes. Also the rate of release of ethylene varies from $2 \times 10^{-3}\text{ s}^{-1}$ for the more labile to *ca.* $2.5 \times 10^{-7}\text{ s}^{-1}$ for the more stable complex (Table 4). Tolman *et al.*⁹ have compared different types of spectroscopic data on a number of ethylene complexes and found a rough correlation between δ (H), δ (C), and other measures of back-bonding such as $\nu(\text{C}=\text{C})$ (cm^{-1}) and $d(\text{C}=\text{C})$ (Å). They concluded that all the factors which make for good π back-bonding to olefins (high metal electron density, low *trans* influence of the *trans* ligand) are expected to increase the shielding of the ethylene protons and strengthen the Pt- (C_2H_4) bond. In our series of complexes increasing the electron-releasing ability of the bis(hydrazone) ligand increases the stability of the five-co-ordinate species, but, contrary to all expectations, the upfield shift of the ethylene protons ($\Delta\delta$) decreases. It seems therefore that $\Delta\delta$ is not a good measure of the π back-bonding in this series of complexes with this particular geometry, but possibly other factors can cause an increase of $\Delta\delta$. As is apparent from Figure 1 the hydrazine substituents are fairly close to the co-

ordinated ethylene and when these substituents are phenyls (L^1 , L^2 , L^3) a ring current effect could also cause a high-field shift of the ethylene protons. It is also to be noted that in another series of five-co-ordinated η -ethylene platinum complexes of formula $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2(\text{L})]$ previously reported [$\text{L} = \text{NN}'$ -bis(cyclopropyl)-biacetyldi-imine, NN' -bis(*p*-tolyl)biacetyldi-imine, NN' -bis(*p*-tolyl)acenaphthenequinonedi-imine, 2,2'-bipyridyl, or 1,10-phenanthroline] no direct relationship between chemical shift of the ethylene protons and stability of the complex appeared to exist.

The coupling constant of the ethylene protons with platinum does not change significantly in this series of complexes, and only appears to be higher than that found in four-co-ordinate platinum-ethylene complexes.

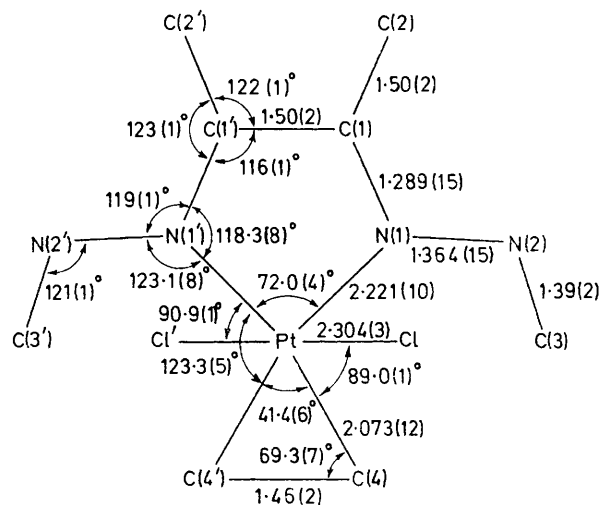


FIGURE 1. Numbering scheme for the atoms, and bond lengths and angles with estimated standard deviations in parentheses

X-Ray Structure.—The crystal consists of discrete molecules of $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2\{\text{Me}(\text{H})\text{N}\cdot\text{N}:\text{C}(\text{Me})\cdot\text{C}(\text{Me})\cdot\text{N}\cdot\text{N}(\text{H})\text{Me}\}]$, each with exact *mm* crystallographic symmetry. The geometry of the inner co-ordination sphere of platinum is trigonal bipyramidal, assuming the ethylene molecule is unidentate. The chlorine atoms occupy the axial positions, whereas ethylene and the bidentate bis(hydrazone) molecule occupy the equatorial positions. A view of the molecule is shown in Figure 2, together with some non-bonded distances. The symmetry planes of the molecule are also evident; one plane contains the Cl-Pt-Cl group and bisects the bis(hydrazone) and the ethylene molecules, the other plane containing the Pt atom and all the non-hydrogen atoms of the equatorial ligands. The C=C moiety is placed in the equatorial plane as expected on the basis of the steric interactions with the axial ligands.¹⁰

Bond lengths and angles are shown in Figure 1 together with the numbering scheme for the atoms. The Pt-N bond lengths are crystallographically equivalent [2.221(10) Å] and are significantly longer than the Pt-N(sp^2) values reported for square planar platinum(II) complexes, which range from 1.973(7) to 2.05(2) Å.¹¹

This lengthening may be due both to electronic and steric factors. However also in the other five-co-ordinate compound $[\text{Pt}(\text{AsMe}_3)_2(\text{F}_3\text{C}\cdot\text{C}\equiv\text{C}\cdot\text{CF}_3)(\text{CH}_3\text{Cl})]$ ¹² the equatorial Pt-As distances [mean value 2.434(4) Å] are significantly longer than those reported for four-co-ordinate complexes [2.308(2)¹³ and 2.376(4) Å].¹⁴ Moreover the platinum-ethylene and C=C distances of 2.073(12) and 1.46(2) Å respectively are in the ranges reported for $[\text{Pt}(\text{olefin})(\text{PPh}_3)_2]$ compounds.¹⁵

These results suggest that the equatorial covalent radius of five-co-ordinate Pt^{II} is larger than that of four-co-ordinate Pt^{II} . In contrast, the axial Pt-Cl bond lengths of 2.304(3) Å do not differ from those reported for a series of four-co-ordinate complexes [2.303(5) Å],¹⁶ indicating therefore that the axial covalent radius of five-co-ordinate Pt^{II} is shorter than the equatorial one.¹⁷

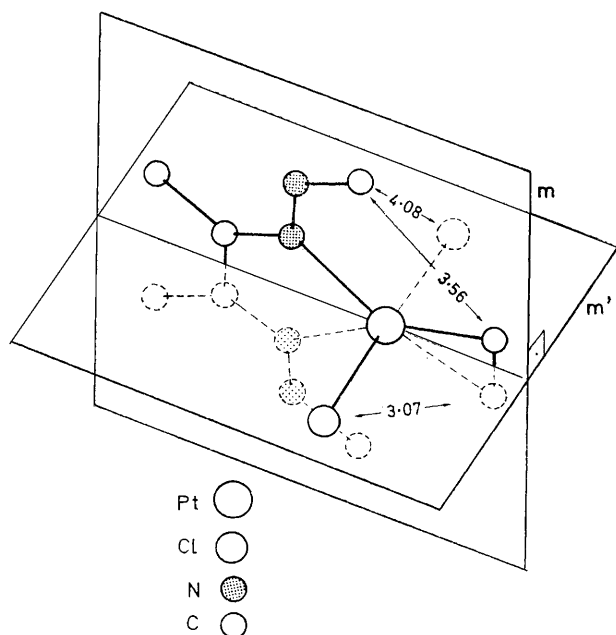


FIGURE 2 A view of the molecule together with some intramolecular non-bonded distances. The symmetry planes are also shown

The values of the Pt-Cl distances are significantly shorter than that of 2.47(1) Å found in $[\text{Pt}(\text{AsMe}_3)_2-$

⁹ C. A. Tolman, A. D. English, and L. E. Manzer, *Inorg. Chem.*, 1975, **14**, 2353.

¹⁰ Lj. Manojlović-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, 1969, **47**, 84.

¹¹ S. D. Ittel and J. A. Ibers, *J. Amer. Chem. Soc.*, 1974, **96**, 4804; P. Colamarino and P. L. Orioli, *J.C.S. Dalton*, 1975, 1956; N. Bresciani-Pahor, M. Calligaris, P. Delise, L. Randaccio, L. Maresca, and G. Natile, *Inorg. Chem. Acta*, 1976, **19**, 45.

$(\text{F}_3\text{C}\cdot\text{C}\equiv\text{C}\cdot\text{CF}_3)(\text{CH}_3\text{Cl})]$ where the axial chlorine atom occupies the *trans* position with respect to the methyl group. This result confirms that the lengthening of the

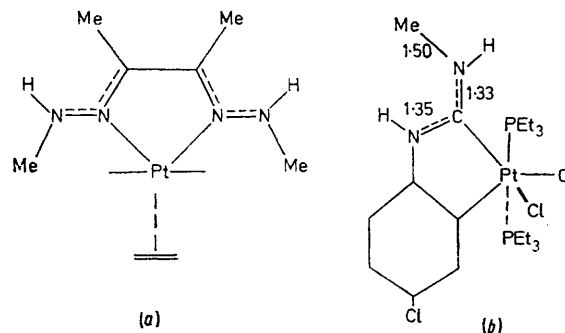


FIGURE 3 N-N-C and N-C-N bond scheme in two platinum complexes

Pt-Cl bond is ascribable to the greater *trans* influence of the methyl group as compared with that of Cl.¹² This appears to be the first example of evidence of *trans* influence in five-co-ordinate platinum compounds.

Bond lengths and angles of the bis(hydrazone) ligand (Figure 3) are in agreement with those expected for Figure 3(a); the N(1)-N(2) distance of 1.364(15) Å and the N(1)-N(2)-C(3) angle of 121(1)° suggests that the N-N bond has some double-bond character owing to the overlap of the N(*p*) orbitals normal to the ligand plane. This forces the N-methyl to be coplanar with the other ligand atoms. The π -electron delocalization is similar to, although not as great as, that found in the platinum(IV) complex shown in Figure 3(b), where the Me(H)-N \equiv C \equiv N grouping is also nearly planar.¹⁸

The value of 1.39(2) Å for the N(2)-C(3) bond length, however, appears to be particularly low for a single C(*sp*³)-N(*sp*²) bond, which would be expected to be ca. 1.50 Å.¹⁷ We attribute the shortening to the high thermal motion of the N(2) and C(3) atoms (see Supplementary Publication).

We thank Professor L. Cattalini for helpful discussion.

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¹² B. W. Davies, R. J. Puddephatt, and N. C. Payne, *Canad. J. Chem.*, 1972, **50**, 2276.

¹³ S. F. Watkins, *J. Chem. Soc. (A)*, 1970, 168.

¹⁴ N. C. Stephenson, *Acta Cryst.*, 1964, **17**, 1517.

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