Inorg. Chem. **1986**, *25*, 2207–2211

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Neutron Diffraction Analysis (T = 120 K) of $[Pt(C_2H_4)Cl(Me_2NCH_2CH_2NMe_2)](ClO_4)$

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Received August 30, 1985

The cationic complex of platinum(II) $[Pt(C_2H_4)Cl(Me_2NCH_2CH_2NMe_2)](ClO_4)$ proved to be a stable compound although very reactive toward nucleophilic agents. The structure has been established by neutron diffraction analysis (120 K); the compound crystallizes in the $Pna2_1$ orthorhombic space group with a = 11.550 (4) Å, b = 14.584 (5) Å, c = 8.504 (3) Å, and Z = 4. Refinement using 1781 reflections led to a final R value of 0.058. The coordination around platinum (one chlorine and two nitrogen atoms, and the midpoint of the ethylene ligand) is planar within the limits of experimental error. The ethylene ligand is perpendicular (88°) to the coordination plane with Pt–C bonds (2.184 (5) and 2.166 (5) Å) slightly longer than in Zeise's salt and a bending back of 16° ($\alpha/2$) of the four hydrogen atoms. The pentaatomic platinum diamine ring lies roughly on the coordination plane with the exception of a C atom, which shows a positional disorder between two nearly equivalent sites 0.6 Å above and below the coordination plane. The difference between the Pt–N distances (2.119 (2) and 2.084 (2) Å) reflects the trans influence of ethylene; the Pt–Cl bond (2.304 (2) Å) is similar to that of cis chlorine in Zeise's salt.

Introduction

The nature of the bond between olefins and transition metals is generally understood in terms of the description made by Dewar, Chatt and Duncanson in the early 1950s.[2] This bond can be safely described as in a "continuum" between two limiting situations represented respectively by pure donation of π electrons of the olefin into a vacant dp orbital of the metal and by back-donation from a filled dp orbital of the metal to the vacant π^* orbital of the olefin.[3]

Compounds of the first type would be characterized by a rather long metal–carbon distance accompanied by a relatively short C=C bond and small deviation from planarity of the olefinic moiety, the overall interaction being rather weak.

As one moves toward the opposite limiting case, both C=C distance and deviation from planarity would increase while the metal–carbon bonds would shorten. These effects are ascribed to the electron population of the π^* orbital, as a consequence of the charge donation from the metal, which reduces the C=C bond order, strengthens the interaction with the central metal, and puts the olefin in a cis bent excited state.[4]

Referring in particular to platinum, which is able to form olefin complexes in different oxidation states and coordination numbers and bear different total charges, the $[Pt(C_2H_4)Cl_3]^-$ and $[PtC_2(CN)_4(PPh_3)_2]$ complexes were considered to represent well the opposite limits outlined above.[5]

We have isolated a cationic platinum–olefin complex, $[Pt(C_2H_4)Cl(Me_2NCH_2CH_2NMe_2)]^+$, which should be closer than Zeise's anion $[Pt(C_2H_4)Cl_3]^-$ to the first limiting case: however, an X-ray analysis, performed on this complex to see the effect of the positive charge on the platinum–ethylene bonding, did not lead to conclusive results because of the intrinsic limits of the method.[6] Therefore, we have undertaken a neutron diffraction analysis, which allows a more precise determination of the light-atom positions.

Experimental Section

Data Collection. The values of the cell parameters and the main experimental conditions for the intensity measurements and structure analysis are reported in Table I. A suitable crystal of $[Pt(C_2H_4)Cl(Me_2NCH_2CH_2NMe_2)](ClO_4)$ was prepared by slow evaporation of a water solution at room temperature.

Table I. Crystal and Experimental Data for $[Pt(C_2H_4)Cl(Me_2NCH_2CH_2NMe_2)](ClO_4)$

space group	$Pna2_1$ (C_{2v}^9, No. 33)
a, Å	11.550 (4)
b, Å	14.584 (5)
c, Å	8.504 (3)
V, Å^3	1432.5 (8)
mol wt	474.25
Z	4
μ_{calcd}, cm^{-1}	2.21
approx cryst habit	parallelepiped
cryst vol, mm^3	9.3
cryst color	pale yellow
wavelength, Å	0.8449 (2)
monochromator	Cu (200)
temp, K	120
$2\theta_{max}$, deg	80
scan mode (ω:$x\theta$)	θ = 0.0, 12.5, 25.0, 37.5, 50.0°; x = 0.00, 0.35, 0.75, 1.15, 1.50
peak scan width (ω)	θ = 0, 15, 25, 35, 60°; ω = 1.40, 1.20, 1.40, 1.70, 4.50°
stds (hkl) (measd every 50 reflcns)	(6,6,0), (1,12,0)
collected reflcns	2071
unique reflcns	1781
rel transmission factors	0.652–0.768
R ($=\sum\lvert F_o\rvert - \lvert F_c\rvert/\sum\lvert F_o\rvert$)	0.058
R_w ($=\sum w^{1/2}(\lvert F_o\rvert - \lvert F_c\rvert)/\sum w^{1/2}\lvert F_o\rvert$)	0.045

No special precaution was taken in mounting the crystal owing to its good stability in air (although crystals kept for many months at room temperature turn black). Diffraction data were collected at low temperature (120 K) with use of the Displex cryorefrigerator[7] on the single-crystal four-circle neutron diffractometer D9, on the hot source of the high-flux beam reactor of the Institut Laue-Langevin in Grenoble. The unit cell parameters were obtained at 120 K with use of 26 accurately centered reflections.

For the intensity measurements, each peak was scanned in 25 steps with 6 additional background steps of either 0.1 or 0.15°. Throughout the data collection two reflections were periodically monitored for any changes in intensity. No significant change was observed.

Background corrections were made with the method of ref 8. An analytical absorption correction was applied with the crystal faces approximated by 12 rational boundary planes;[9] the 12 crystal faces belong to the forms {110}, {$\bar{1}$10}, {111}, {$\bar{1}\bar{1}$1}, {1$\bar{1}$1}, and {$\bar{1}$11}. A total of 2071 intensities were accessible with the restrictions imposed on the four-circle

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(1) (a) University of Turin. (b) ILL, Grenoble. (c) University of Venice. (d) University of Bari.

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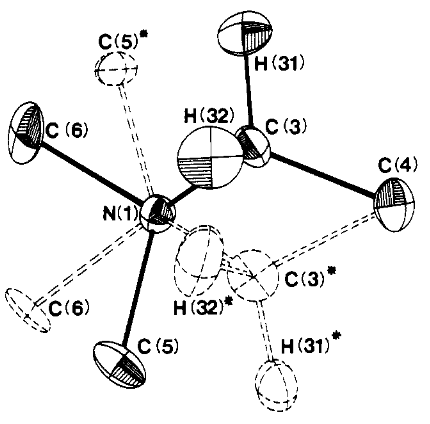

Figure 1. ORTEP drawing of the disordered portion of the cation. The dashed part corresponds to the form with occupancy 0.47. The coordination plane (passing through C(4) and N(1)) is perpendicular to the figure.

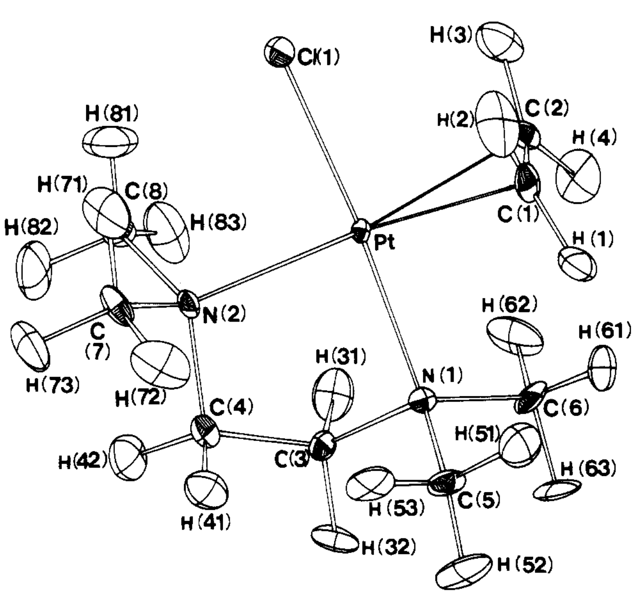

Figure 2. ORTEP projection of the $[Pt(C_2H_4)Cl(CH_3)_2NCH_2CH_2N(CH_3)_2]^+$ cation, with the atom labeling scheme. The view is slightly inclined with respect to the coordination plane. The thermal ellipsoids are scaled to enclose 30% probability.

geometry by the Displex mount; after the equivalent *hkl*'s were averaged, (internal consistency *R* index as defined in ref 14 equal to 0.02), 1781 reflections were obtained, including those with $F_o^2 \leq 0$. No secondary extinction correction was applied.

Structure Analysis. A first difference-Fourier map, calculated by using coordinates from the X-ray analysis,[6] with non-hydrogen atoms only, revealed the positions of the H atoms and the presence of disorder in the pentaatomic ring of the cation. In fact the C(3) atom, which lies out of the plane of coordination, is nearly equally partitioned above and below this plane (Figure 1); consequently the $CH_3(5)$ and $CH_3(6)$ groups and the H(41) and H(42) atoms also follow this behavior; an image with coordinates x, ,y, $-z$ is created and a noncrystallographic plane perpendicular to the c axis coinciding with the coordination plane is simulated.

At this stage two types of refinement were tried:

(i) In the Acentric Space Group *Pna*2$_1$. To each image created by disorder (the $CH_2(3)$, $CH_3(5)$, $CH_3(6)$ groups and the H(41) and H(42) atoms with and without asterisks in Figure 1) was assigned a different occupation factor, and these were allowed to vary subject to obvious chemical constraints (their sum equals unity). Some distances were constrained to vary together as well. Occupation factors of the two images were refined to 0.53 and 0.47. The H(51) and H(62) atoms are equally shared by the two images.

(ii) In the Centric Space Group *Pnam* with the Ions Exactly Bisected by the Mirror Planes. Occupancy factors of atoms lying on the mirror planes and those belonging to the two disordered moieties were fixed at 0.5.

All refinements (anisotropic for all the atoms) were performed, including reflections with $F_o^2 < 0$, as suggested by some authors,[10] but with F^2 set to 0.01 for convenience; the final values of *R* were 0.058 (R_w = 0.045) and 0.038 (R_w = 0.032) (for all reflections included and for 1450 reflections with $I > 2\sigma(I)$, respectively) for refinement i. The corresponding values of *R* for refinement ii were 0.064 (R_w = 0.053) and 0.043 (R_w = 0.036).

Table II. Fractional Atomic Coordinates for the Compound $[Pt(C_2H_4)Cl(Me_2NCH_2CH_2NMe_2)](ClO_4)$[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*
Pt	0.5886 (1)	0.4563 (1)	0.0
C(1)	0.5025 (5)	0.5811 (4)	0.0803 (7)
C(2)	0.5002 (4)	0.5784 (3)	−0.0814 (7)
C(3)′	0.8285 (3)	0.4386 (2)	−0.0721 (6)
C(4)	0.8037 (2)	0.3481 (1)	0.0001 (2)
C(5)′	0.7918 (4)	0.5341 (3)	0.1644 (4)
C(6)′	0.7703 (4)	0.5966 (3)	−0.0966 (6)
C(7)	0.6443 (6)	0.2739 (5)	0.1408 (9)
C(8)	0.6481 (5)	0.2733 (4)	−0.1424 (8)
H(1)	0.5645 (7)	0.6215 (6)	0.1462 (14)
H(2)	0.4298 (9)	0.5574 (9)	0.1490 (15)
H(3)	0.4228 (6)	0.5535 (7)	−0.1390 (11)
H(4)	0.5562 (9)	0.6224 (8)	−0.1501 (10)
H(31)′	0.8098 (10)	0.4455 (8)	−0.1981 (6)
H(32)′	0.9211 (4)	0.4542 (8)	−0.0612 (14)
H(41)′	0.8305 (9)	0.3527 (7)	0.1237 (6)
H(42)′	0.8507 (7)	0.2898 (4)	−0.0493 (12)
H(51)	0.7339 (8)	0.5870 (6)	0.2092 (11)
H(52)′	0.8833 (5)	0.5521 (10)	0.1605 (13)
H(53)′	0.7768 (10)	0.4751 (6)	0.2403 (11)
H(61)′	0.7183 (9)	0.6487 (6)	−0.0327 (15)
H(62)	0.7479 (8)	0.5830 (7)	−0.2199 (7)
H(63)′	0.8609 (5)	0.6198 (8)	−0.0820 (13)
H(71)	0.5492 (13)	0.2592 (10)	0.1440 (16)
H(72)	0.6716 (11)	0.3058 (9)	0.2456 (13)
H(73)	0.6953 (10)	0.2082 (9)	0.1352 (15)
H(81)	0.5555 (8)	0.2629 (9)	−0.1447 (16)
H(82)	0.6909 (14)	0.2090 (8)	−0.1373 (17)
H(83)	0.6737 (14)	0.3135 (9)	−0.2520 (14)
Cl(1)	0.4103 (1)	0.3854 (1)	0.0004 (7)
Cl(2)	0.3836 (1)	0.1484 (1)	0.4971 (7)
N(1)	0.7548 (1)	0.5120 (1)	0.0005 (2)
N(2)	0.6760 (1)	0.3286 (1)	0.0004 (7)
O(1)	0.4288 (7)	0.1893 (7)	0.6358 (9)
O(2)	0.2612 (3)	0.1471 (4)	0.5049 (16)
O(3)	0.4222 (10)	0.1971 (6)	0.3629 (11)
O(4)	0.4207 (5)	0.0556 (3)	0.5044 (16)
C(3)*	0.8295 (4)	0.4383 (4)	0.0704 (7)
C(5)*	0.7947 (4)	0.5324 (3)	−0.1630 (6)
C(6)*	0.7705 (4)	0.5955 (3)	0.1001 (6)
H(31)*	0.8093 (9)	0.4270 (7)	0.1946 (13)
H(32)*	0.9213 (10)	0.4616 (8)	0.0526 (14)
H(41)*	0.8270 (11)	0.3440 (9)	−0.1401 (15)
H(42)*	0.8508 (13)	0.2954 (11)	0.0499 (16)
H(52)*	0.8835 (10)	0.5561 (12)	−0.1683 (18)
H(53)*	0.7874 (15)	0.4734 (11)	−0.2413 (15)
H(61)*	0.7257 (11)	0.6580 (6)	0.0535 (13)
H(63)*	0.8657 (11)	0.6074 (10)	0.1197 (13)

[a] Atoms marked with primes and asterisks correspond to occupation factors 0.53 and 0.47, respectively.

Hamilton's test[11] on the validity of the two models (R_G = 0.052 (i) and R_G = 0.064 (ii)) and a positive test of piezoelectricity led to the choice of the acentric space group.

The function minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was $w = 1/(\sigma^2(F) + aF^2)$, where $a = 0.003$ was chosen in order to maintain $\sum w\Delta^2$ satisfactorily constant for the amplitudes batched in various ranges of $|F_o|$ and $(\sin \theta)/\lambda$.

All reported results correspond to $R = 0.058$. Neutron-scattering lengths were taken to be $b_{Pt} = 9.5$, $b_C = 6.6484$, $b_H = -3.7409$, $b_{Cl} = 9.5792$, $b_N = 9.21$, and $b_O = 5.805$ (in units of 10^{-13} cm).[12]

Listings of observed and calculated structure factors and of the anisotropic thermal parameters are available.[13]

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Table III. Interatomic Distances (Å) and Angles (deg)[a]

Around the Pt Atom							
Pt–C(1)	2.184 (5)	Pt–N(1) (cis)	2.084 (2)	Pt–N(2) (trans)	2.119 (2)	Pt–Cl(1)	2.304 (2)
Pt–C(2)	2.166 (5)						
C(1)–Pt–C(2)	36.9 (1)	C(1)–Pt–Cl(1)	88.1 (2)	C(2)–Pt–Cl(1)	87.0 (1)	N(1)Pt–Cl(1)	176.3 (1)
C(1)–Pt–N(1)	95.4 (2)	C(2)–Pt–N(1)	96.5 (1)	N(1)–Pt–N(2)	84.5 (1)	N(2)–Pt–Cl(1)	91.8 (1)
C(1)–Pt–N(2)	161.7 (3)	C(2)–Pt–N(2)	161.4 (2)				
In the Ethylene Ligand							
C(1)–C(2)	1.376 (3)	C(1)–H(2)	1.083 (3)^c	C(2)–H(3)	1.083 (3)^c	C(2)–H(4)	1.083 (3)^c
C(1)–H(1)	1.083 (3)^c						
C(2)–C(1)–H(1)	123.0 (9)	H(1)–C(1)–H(2)	113.9 (1.2)	C(1)–C(2)–H(3)	118.5 (8)	H(3)–C(2)–H(4)	116.6 (9)
C(2)–C(1)–H(2)	121.3 (1.0)	H(1)–C(1)–Pt	108.3 (6)	C(1)–C(2)–H(4)	120.8 (8)	H(3)–C(2)–Pt	104.9 (7)
C(2)–C(1)–Pt	70.9 (4)	H(2)–C(1)–Pt	104.9 (8)	C(1)–C(2)–Pt	72.3 (4)	H(4)–C(2)–Pt	112.2 (7)
In the Tetramethylethylenediamine Ligand							
C(3)–C(4)	1.482 (3)^c	C(4)–H(42)	1.093 (2)^c	C(6)–H(61)	1.107 (2)^c	C(7)–H(73)	1.126 (13)
C(3)–N(1)	1.501 (2)^c	C(5)–N(1)	1.493 (2)^c	C(6)–H(62)	1.106 (2)^c	C(8)–N(2)	1.492 (7)
C(3)–H(31)	1.097 (2)^c	C(5)–H(51)	1.090 (2)^c	C(6)–H(63)	1.107 (2)^c	C(8)–H(81)	1.081 (11)
C(3)–H(32)	1.097 (2)^c	C(5)–H(52)	1.090 (2)^c	C(7)–N(2)	1.482 (8)	C(8)–H(82)	1.061 (14)
C(4)–N(2)	1.503 (3)	C(5)–H(53)	1.090 (2)^c	C(7)–H(71)	1.120 (17)	C(8)–H(83)	1.140 (15)
C(4)–H(41)	1.098 (2)^c	C(6)–N(1)	1.490 (3)^c	C(7)–H(72)	1.054 (14)		
C(4)–C(3)–N(1)	110.9 (2)	N(1)–C(5)–H(51)	107.7 (6)	N(2)–C(7)–H(71)	111.5 (8)	Pt–N(1)–C(3)	104.1 (2)
C(4)–C(3)–H(31)	116.6 (7)	N(1)–C(5)–H(52)	107.5 (6)	N(2)–C(7)–H(72)	111.8 (1.0)	Pt–N(1)–C(5)	110.5 (2)
C(4)–C(3)–H(32)	109.7 (7)	N(1)–C(5)–H(53)	109.7 (6)	N(2)–C(7)–H(73)	107.2 (8)	Pt–N(1)–C(6)	115.6 (2)
N(1)–C(3)–H(31)	103.0 (6)	H(51)–C(5)–H(52)	115.8 (1.1)	H(71)–C(7)–H(72)	110.9 (1.2)	C(3)–N(1)–C(5)	112.0 (3)
N(1)–C(3)–H(32)	111.7 (7)	H(51)–C(5)–H(53)	104.7 (1.0)	H(71)–C(7)–H(73)	110.5 (1.2)	C(3)–N(1)–C(6)	107.3 (3)
H(31)–C(3)–H(32)	104.7 (9)	H(52)–C(5)–H(53)	111.2 (1.0)	H(72)–C(7)–H(73)	104.8 (1.1)	C(5)–N(1)–C(6)	107.4 (3)
C(3)–C(4)–N(2)	111.0 (2)	N(1)–C(6)–H(61)	103.7 (6)	N(2)–C(8)–H(81)	107.7 (8)	Pt–N(2)–C(4)	107.5 (1)
C(3)–C(4)–H(41)	106.7 (6)	N(1)–C(6)–H(62)	110.3 (6)	N(2)–C(8)–H(82)	110.1 (8)	Pt–N(2)–C(7)	110.9 (3)
C(3)–C(4)–H(42)	116.0 (6)	N(1)–C(6)–H(63)	108.0 (7)	N(2)–C(8)–H(83)	109.4 (8)	Pt–N(2)–C(8)	111.7 (3)
N(2)–C(4)–H(41)	106.6 (6)	H(61)–C(6)–H(62)	117.3 (1.0)	H(81)–C(8)–H(82)	109.8 (1.2)	C(4)–N(2)–C(7)	110.2 (4)
N(2)–C(4)–H(42)	109.9 (5)	H(61)–C(6)–H(63)	104.7 (9)	H(81)–C(8)–H(83)	108.3 (1.1)	C(4)–N(2)–C(8)	108.3 (4)
H(41)–C(4)–H(42)	106.0 (8)	H(62)–C(6)–H(63)	112.1 (9)	H(82)–C(8)–H(83)	111.5 (1.2)	C(7)–N(2)–C(8)	108.2 (2)
In the Perchlorate Anion							
Cl(2)–O(1)	1.422 (8)	Cl(2)–O(2)	1.416 (4)	Cl(2)–O(3)	1.416 (9)	Cl(2)–O(4)	1.420 (4)
O(1)–Cl(2)–O(2)	109.5 (7)	O(1)–Cl(2)–O(4)	104.7 (7)	O(2)–Cl(2)–O(4)	106.6 (3)	O(3)–Cl(2)–O(4)	114.7 (7)
O(1)–Cl(2)–O(3)	110.0 (3)	O(2)–Cl(2)–O(3)	111.0 (7)				

[a] Constrained distances are labeled with a superscript "c".

Table IV. Structural Parameters Involving the Metal Atoms and the Ethylene Ligand for Selected Complexes

compd	M–C (M = Pt, Ta), Å	$H_2C{=}CH_2$, Å	α, deg	β, deg	ref
$[Pt(C_2H_4)Cl_3]^-$	2.128 (3)	1.375 (4)	32	74	19
	2.135 (3)				
$[Pt(C_2H_4)_3]$	2.176 (2)	1.402 (7)	31	74	20
$[Pt(C_2H_4)_2(C_2F_4)]$	2.191 (6)	1.365 (8)	32	74	20
	2.272 (6)				
	2.195 (6)	1.378 (8)			
	2.258 (6)				
$[Pt(C_2H_4)Cl(CH_3)_2NC_2H_4N(CH_3)_2]^+$	2.184 (5)	1.376 (3)	32	77	this work
	2.166 (5)			71	
$Ta(C_2H_4)[C_5(CH_3)_5][CHC(CH_3)_3][P(CH_3)_3]$	2.228 (3)	1.477 (4)	68	56	21
	2.285 (3)				

Owing to the disorder and to the high correlation factors caused by the symmetry of the ions with respect to 001 planes, high esd's were obtained; in order to reduce the consequent variation of the C–H distances of the ethylene molecule, these four C–H distances also were constrained to vary together. The geometry of ethylene was not perturbed by this approach.

For the solution and refinement of the structure the programs of SHELX 76[14] were used. The calculation of the best planes passing through the atoms was made as in ref 15.

Final fractional atomic coordinates are listed in Table II.

Description of the Structure and Discussion

The molecular structure is shown in Figure 2, and bond lengths and angles are listed in Table III.

The coordination around the Pt atom is roughly square-planar, considering the middle point of the ethylene ligand, the chlorine atom Cl(1), and the nitrogen atoms of the tetramethylethylenediamine ligand; the Pt atom lies in the plane.[16]

The pentaatomic ring resulting from the coordination of tetramethylethylenediamine to platinum is, as expected, not planar owing to the tetrahedral geometry of the nitrogen and carbon atoms involved (see Table III); in fact, the ring lies roughly in the *ab* plane with the exception of the C(3) atom responsible for the observed disorder (see above) (Figure 3).

The C=C bond of the ethylene ligand is perpendicular (88°) to the coordination plane. The two ethylenic carbon atoms are,

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(16) The best plane passing through these points, C(4), and Pt is $-0.001X - 0.010Y + 8.504Z + 0.003 = 0$ for fractional coordinates: $\chi^2 = 2.00$. The distances of M (middle point), N(1), N(2), Cl(1), C(4), and Pt from the plane are 0.00 (1), 0.001 (3), 0.002 (6), 0.002 (6), −0.001 (3), and −0.002 (2) Å, respectively.

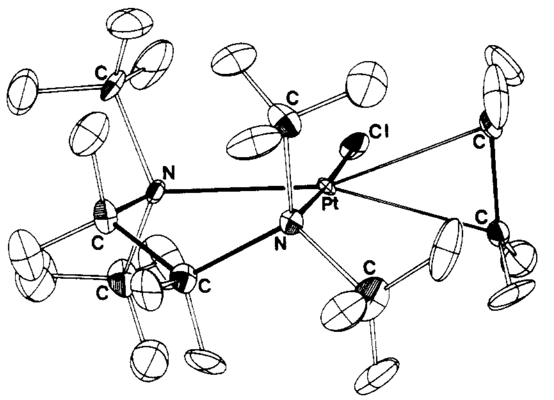

Figure 3. ORTEP projection of the cation, showing the puckering of the pentaatomic ring and the deformation of the ethylene molecule.

within the limits of experimental accuracy, equidistant (2.184 (5) and 2.166 (5) Å) from the platinum atom.

The Ethylene Ligand. The geometry of the ethylene ligand should be, according to the Dewar–Chatt–Duncanson model,[2] strongly influenced by its coordination. Examination of a large number of complexes has confirmed this distortion and suggested[17] some parameters used for quantifying it. In Table IV the α and β angles[18] are compared for the present complex (32 and 74° (mean), respectively), for Zeise's salt,[19] and for the $[Pt(C_2H_4)_3]$ and $[Pt(C_2H_4)_2(C_2F_4)]$[20] and the $[Ta(C_2H_4)(C_5Me_5)(CHCMe_3)(PMe_3)]$ complexes,[21] whose structures were determined by neutron diffraction. Comparison has been restricted to neutron diffraction studies of unsubstituted ethylene complexes in order to deal with homogeneous data.

The following points are noteworthy: (i) No significant change in the mean ethylene deformation is observed in comparisons of an anionic and a cationic square-planar platinum(II) complex and three-coordinate platinum(0) species.

(ii) The metal–carbon distances are not directly correlated to the deformation of the ethylene plane. In Zeise's anion the Pt–C distances are shorter than in the other three platinum species, but the α and β angles have nearly the same values. Moreover, in the neutron analyses of the $[Pt(C_2H_4)_2(C_2F_4)]$ and $[Ta(C_2H_4)(C_5Me_5)(CHCMe_3)(PMe_3)]$ complexes,[20,21] the difference in the two M–C bond lengths is not reflected by any asymmetry in the bending back of the ethylene hydrogens ($\beta = \beta' = 70°$ and $\beta = \beta' = 56°$, respectively). On the other hand, in the cationic complex the asymmetry of β ($\beta = 71°$, $\beta' = 77°$) cannot be correlated to a highly significant asymmetry of the Pt–C bonds; this fact can support the hypothesis already suggested[20] that the bending of hydrogens is most susceptible to intermolecular influences. A conclusive discussion however should be made on data not affected by disorder and consequently by high esd's.

(iii) On the other hand, the elongation of the C=C bond appears to be correlated with the deformation of the ethylene plane; therefore as the C=C bond becomes longer, the deviation from planarity increases and the α angle becomes larger.

The Other Ligands. The trans influence of ethylene gives rise to the most remarkable feature of the puckered ring of tetramethylenediamine, that is, a difference of about 0.04 Å (corresponding to ca. 18σ) in the Pt–N bond lengths (2.119 (2) and 2.084 (2) Å), the longest distance being that trans to ethylene. This difference is comparable to that observed in cis and trans chlorine atoms of Zeise's salt, indicating that the trans influences exerted by ethylene toward the chlorine and nitrogen donor atoms are comparable.

The other parameters of the chelate diamine are quite close, within the experimental errors, to those observed in some analogous complexes, where the coordination around platinum differs only in the replacement of the η^2-ethylene by a η^1-alkyl group.[22-24] In these latter complexes the platinum–nitrogen bond trans to carbon was ca. 0.06 Å (corresponding to ca. 6σ), larger than that trans to chlorine, indicating that a similar trans influence is exerted by either a η^2- or a σ-C_2H_4R group. Although in some cases this similarity has not been fully recognized, we believe it has real significance, on the basis of comparison of species which, apart from the η^2- or σ-carbon ligand, are identical.

The Pt–Cl(1) bond length cis to ethylene (2.304 (2) Å) agrees well with that of the two cis Pt–Cl bonds of Zeise's anion (2.302 (2) and 2.303 (2) Å) and with that of other similar compounds.[25-28]

In the perchlorate anion the oxygen atoms are arranged tetrahedrally about the chlorine atom at an average distance of 1.418 (3) Å.

Conclusions. It is apparent from the above discussion that the presence of a net positive charge on the complex, as opposed to the negative charge of Zeise's anion, does not cause any appreciable structural change in the ethylene moiety; moreover, the ethylene geometry is also similar to that found in the tricoordinate platinum(0) complex $[Pt(C_2H_4)_3]$. In contrast with the very strict structural analogy the reactivities of ethylene in the three complexes are very different and the cationic species under discussion is far more reactive toward nucleophiles than the neutral or anionic species[22,29] and behaves like other cationic complexes of the platinum-group metals such as iron, ruthenium, and rhodium.[30] This leads to the following considerations: First, the electrostatic attraction between the organometallic complex and the nucleophile is important in promoting the reaction. Second, the extent of electron donation from the metal to the π^* orbital of the olefin must be as small as possible in order to leave the π^* orbital free to accept an extra electron pair from the nucleophile. Such an electron donation appears to be rather small in four-coordinate platinum(II) complexes, as indicated not only by the structural data, showing a rather small elongation of the C=C bond and small deviation from planarity of the olefin moiety, but also by a recent ligand field analysis of Zeise's anion, showing the ethylene to be a strong σ donor and a very weak π acceptor toward platinum(II).[31] A third source of activation of metal-bonded olefins comes from a slipping of the metal–ligand fragment along the ethylene axis while the nucleophile is attacking. Indeed, it turns out that the less deactivated the olefin in the symmetrical η^2 complex, the more activated it is as an η^1 slipped olefin.[32]

In contrast with four-coordinate platinum(II) complexes, both experimental and theoretical evidence point to a largely deactivated[2] olefin in five-coordinate Pt^{II} species, which could represent the limiting case of a strong metal to olefin electron donation.[26,32]

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It would therefore be of some interest to study such a complex by neutron diffraction to see the extent of the elongation and of the deviation from planarity of the ethylene moiety.

Safety Notes. Perchlorate salts of metal complexes with organic ligands are potentially explosive. In general, when noncoordinating agents are required, every attempt should be made to substitute anions such as the fluoro sulfonates for the perchlorates. If a perchlorate must be used, only small amounts of material should be prepared and this should be handled with great caution.

Acknowledgment. We thank Dr. M. S. Lehmann and J. Archer for advice during the experiment and Prof. G. Ferraris for useful discussion. We are indebted to the CSI Piemonte, Torino, Italy, for financial support to carry out the computer calculations.

Registry No. $[Pt(C_2H_4)Cl(Me_2NCH_2CH_2NMe_2)](ClO_4)$, 71639-56-0.

Supplementary Material Available: A listing of anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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Anisotropic Exchange in Transition-Metal Dinuclear Complexes. 8.[1] Bis(μ-pyridine *N*-oxide)bis[dichloro(dimethyl sulfoxide)copper(II)]

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Received October 28, 1985

Single-crystal EPR spectra of bis(μ-pyridine *N*-oxide)bis[dichloro(dimethyl sulfoxide)copper(II)], $[Cu(pyO)Cl_2(Me_2SO)]_2$, were recorded at room temperature at both X- and Q-band frequencies. They are typical of a triplet with $g_{xx} = 2.069$ (2), $g_{yy} = 2.077$ (2), $g_{zz} = 2.337$ (2), $D_{x'x'} = 0.0898$ (6), $D_{yy} = 0.0373$ (5), and $D_{z'z'} = -0.1271$. The z and z' axes make an angle of 28.7 (5)°, while the x' direction makes an angle of 82.0 (2)° with the copper–copper direction. The overall appearance of the **D** tensor is indicative of a relevant exchange contribution, and the observed deviation of the z' axis from the z direction suggests a sizable, essentially exchange-determined D_{yz} component of the zero-field-splitting tensor. The polycrystalline-powder EPR spectra of the manganese(II)-doped compound show the presence of exchange-coupled copper(II)–manganese(II) pairs and are characteristic of a quintet state.

Introduction

In the course of a systematic study on the relationships between anisotropic exchange and structural parameters in dinuclear copper(II) complexes,[3–9] we have shown that for bis(μ-oxo)-bridged complexes that have magnetic orbitals lying on the same plane, the interaction between the ground xy and the excited $x^2 - y^2$ orbital is dominant and ferromagnetic in nature.[1,3–5] This result found an independent check from Russian authors.[10]

We also found that, for this class of complexes, the intensity of the interaction tends to decrease as the metal–metal distance increases.[1,5] These data were interpreted within the scheme of the ferromagnetic interactions between the xy and $x^2 - y^2$ orbitals.

Looking for systems at the long edge of available copper–copper distances, we found in the literature bis(μ-pyridine *N*-oxide)bis[dichloro(dimethyl sulfoxide)copper(II)], $[Cu(pyO)Cl_2(Me_2SO)]_2$,[11] which contains the usual dinuclear units, with a copper–copper distance of 3.342 (3) Å, which, to our knowledge, is the largest reported thus far for bis(μ-oxo)-bridged complexes. Since no EPR spectra were available, we decided to characterize this complex in order to compare its spectromagnetic properties to those of structurally similar systems.

We obtained also manganese(II)-doped samples, whose polycrystalline-powder EPR spectra show evidence of a substantial copper(II)–manganese(II) coupling.

Experimental Section

The title compound, $[Cu(pyO)Cl_2(Me_2SO)]_2$, was prepared by recrystallizing the anhydrous pyridine *N*-oxide complex $[Cu(pyO)Cl_2]_2$ in dimethyl sulfoxide, according to the reported procedure.[11] EPR suitable single crystals were oriented with a Philips PW 1100 diffractometer. They were found to correspond to the reported structure with prominent (100) and ($\bar{1}$00) faces.

Mixtures of $[Cu(pyO)Cl_2]_2$ and its manganese(II) analogue in a molar ratio of 2:1 in favor of copper were dissolved in dimethyl sulfoxide, yielding single crystals of the doped complex. The analysis of the metals was in agreement with the calculated value for the copper (calcd, 20.65%; found, 20.40%), and indicated a manganese percent rate of 2%. The crystals were revealed to have the same lattice parameters as for the copper(II) pure dimer, having well-developed (011) and (0$\bar{1}\bar{1}$) faces, but the crystal had a very unusual appearance, with two zones of different color, without showing any evidence of gemination.

Polycrystalline-powder and single-crystal EPR spectra were recorded with a Varian E9 spectrometer equipped with standard X- and Q-band facilities. The symmetry properties of the crystals were used to check the alignment of the magnetic field.

Results and Discussion

Polycrystalline-powder EPR spectra of $[Cu(pyO)Cl_2(Me_2SO)]_2$ at both X- and Q-band frequencies at room temperature are shown in Figure 1. They are typical of a triplet state split in the zero field by about 0.10–0.15 cm^{-1}. When the sample is cooled down to liquid-nitrogen temperature the spectrum disappears, and only

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