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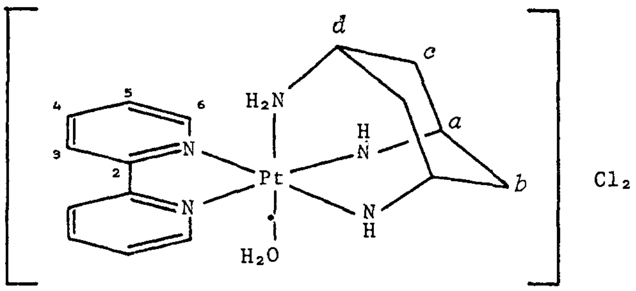
Structural Characterization of a Novel Platinum(IV) Complex Produced by Deprotonation of Coordinated Amino Groups of the Rigid Ligand *cis,cis*-1,3,5-Triaminocyclohexane

Sir:

We describe herein details of the preparation and structural characterization of a novel octahedral platinum(IV) complex, **1**, which resulted from the aqueous solution reaction of *cis,cis*-1,3,5-triaminocyclohexane (tach) with dichloro(bipy)platinum(II), where bipy = 2,2′-bipyridyl. This complex is unique in two respects. First, the platinum(II) to platinum(IV) oxidation occurred under mild conditions (probably air oxidation) in contrast to the normal requirements of strong oxidants to effect this conversion.[1] Secondly, deprotonation of two amine donors occurred readily in aqueous solution. Such an acidity of coordinated amino groups is unusual in that, where similar deprotonation reactions are known to occur, a strong base is generally found to be necessary to effect proton removal.[2,3] A discussion of the evidence leading to structure **1**, derived from mutually complementary information from NMR and ESCA spectroscopy and an x-ray crystal structure analysis, is presented.



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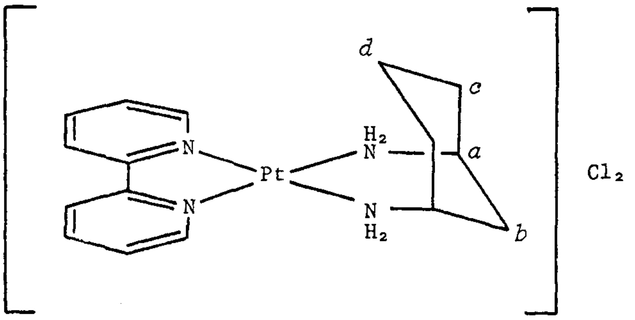

2

Table I. ^{13}C NMR Chemical Shifts[a] and ^{195}Pt-^{13}C Coupling Constants[b]

	1	2
	A. bipy	
C(2)	154.95 (NO)	157.57 (34)
C(6)	147.73 (9)	148.36 (27)
C(4)	144.91 (<5)	143.05 (6)
C(5)	129.63 (21)	128.68 (32)
C(3)	126.78 (17)	125.35 (28)
	B. Aliphatic Amine Ligand[c]	
CH(a)	45.19 (20)	44.24 (24)
CH_2(b)	37.33 (8)	35.11 (52)
CH_2(c)	33.60 (16	29.40 (<6)
CH(d)	42.17 (19)	14.60 (<6)

[a] In parts per million vs. TMS external standard. [b] In hertz, given in parentheses after chemical shifts; NO, not observed owing to signal saturation. [c] Relative intensity of a:b:c:d, 2:1:2:1.

Complex **1** was prepared by reacting a stoichiometric quantity of the tach ligand with dichloro(bipy)platinum(II) in aqueous solution by a synthetic procedure analogous to that employed to produce a wide variety of square-planar platinum(II) complexes of bipy and aliphatic ligands.[4] Elemental analysis[5] for the yellow crystalline product was consistent with the formulation of one bipy, one tach, two chlorine atoms, and four water molecules per platinum atom. This formulation is in accord with the 100-MHz ^{1}H NMR spectrum in aqueous (D_2O) solution. Moreover, the excellent resolution and lack of contact shifts in this spectrum attest to the diamagnetic nature of the complex.

Data from the 25.2-MHz ^{13}C NMR spectrum of **1** and an analogous square-planar platinum(II) complex, **2**, of bipy and *cis*-1,3-diaminocyclohexane (dach) are presented in Table I. The multiplicity and relative intensities of the resonances are indicative of symmetrical binding arrangements for the bipy and tach moieties in **1**. The tridentate nature of the coordinated tach in **1** can be discerned from the similarity of the 19-Hz

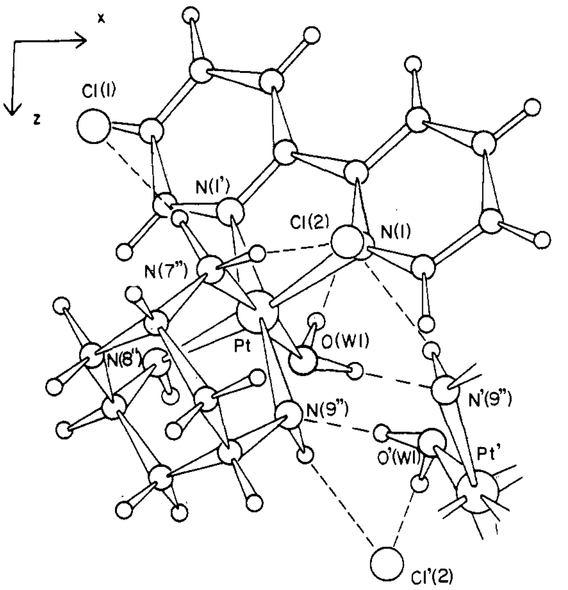

Figure 1. Structure of $[\mathrm{Pt(bipy)(tach\text{-}2H)(H_2O)}]\mathrm{Cl_2}$ with the hydrogen bonding indicated by the broken lines; small circles denote hydrogen atoms. Bond lengths at platinum follow: Pt-N(1), 2.135 (9); Pt-N(1′), 2.044 (8); Pt-N(7″), 2.070 (9); Pt-N(8″), 2.013 (8); Pt-N(9″), 2.044 (8), Pt-O(W1), 2.001 (7) Å.

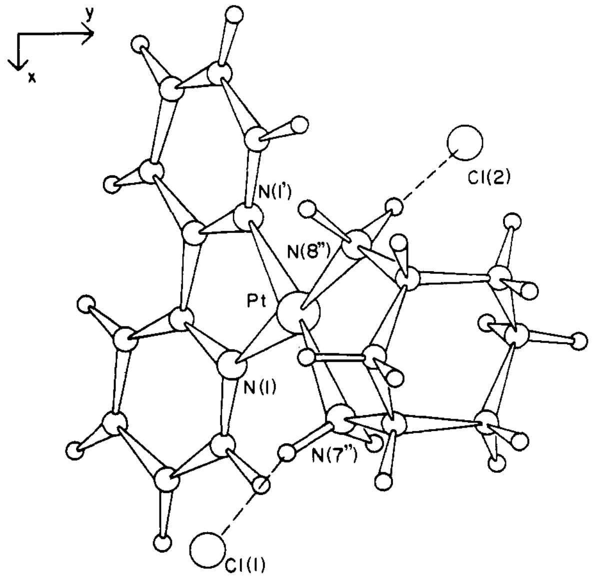

Figure 2. Structure of $[\mathrm{Pt(bipy)(dach)}]\mathrm{Cl_2}$; small circles denote hydrogen atoms and broken lines represent N-H···Cl⁻ hydrogen bonds. Bond lengths at platinum follow: Pt-N(1), 1.988 (11); Pt-N(1′) 2.029 (11); Pt-N(7″), 2.036 (12); Pt-N(8″), 2.041 (11) Å.

platinum-carbon coupling constants exhibited by the apical carbon atom (d) and the $^{2}J_{\mathrm{PtC}}$ coupling of 20 Hz experienced by the methine (a) carbon atoms. In the square-planar dach complex **2**, the platinum-carbon coupling to the analogous carbon atom (d), now four bonds removed from the metal nucleus, is negligible in accord with all $^{4}J_{\mathrm{PtC}}$ situations involving coordinated aliphatic diamines.[4] Thus, the ^{13}C NMR spectra provide evidence for at least five coordination at the platinum center and they are in agreement with structure **1** found by x-ray analysis of the solid.

Structural details for **1** and **2** were obtained by single-crystal x-ray analyses. Monoclinic crystals of trihydrate **1**, $\mathrm{C_{16}H_{29}Cl_2N_5O_4Pt}$, belong to space group $C2/c$, with a = 25.099 (10), b = 7.771 (4), c = 21.834 (8) Å; β = 93.78 (5)°; Z = 8. Complex **2** crystallizes as the dihydrate, $\mathrm{C_{16}H_{26}Cl_2N_4O_2Pt}$, in the orthorhombic system, space group $Pbca$, with a = 13.424 (6), b = 22.038 (8), c = 13.301 (6) Å; Z = 8. Intensity data for all unique reflections to θ 67° for **1** and **2** were recorded on an Enraf-Nonius CAD-3 automated diffractometer (Ni-filtered Cu Kα radiation (λ = 1.5418 Å), θ-2θ scans) and the structures solved by the heavy-atom method. Atomic positional and thermal parameters (anisotropic C, Cl, N, O, Pt; fixed H contributions) were refined to R = 0.049 over 2721 observed reflections for **1** and R = 0.042 over 1875 observed reflections for **2**. Views of the coordination geometries in **1** and **2** are shown in Figures 1 and 2, respectively. In **1**, one water molecule, and the nitrogen atoms of the bidentate bipy ligand and of the tridentate tach ligand are arranged in a distorted octahedral manner around the platinum atom. In **2**, the platinum atom lies only 0.041 Å from the least-squares plane through the bipy and dach nitrogen atoms and thus has a slightly distorted square-planar coordination geometry. Bond lengths in both complexes all lie in the normal ranges.

Although the original intent of this work was to attempt to force platinum(II) into a situation of greater than four coordination,[6] the diamagnetic nature of the octahedral platinum complex **1** presents a dilemma. By analogy with numerous d^8 octahedral nickel(II) examples which are available,[7] if octahedral platinum(II) were present, then a paramagnetic complex would be expected. This apparent contradiction may be resolved, however, if the complex contains d^6 platinum(IV), which prefers octahedral coordination, is generally diamagnetic and is consistent with all the physico-chemical information presented above but with the additional constraint that, besides the two chloride ions, two other negatively charged centers per platinum atom must be present. Loss of two hydrogen ions to produce these centers would, of course, have little influence on the elemental analysis and could give the necessary charge balance. Feasible sources for the loss of acidic protons are the four water molecules and the three tach amino ($-\mathrm{NH_2}$) groups of which a maximum of any two would be, respectively, $\mathrm{OH^-}$ ions or deprotonated amino ($-\mathrm{NH^-}$) groups in the crystalline complex.

The oxidation level of platinum is most readily investigated by use of ESCA techniques where the $4f_{5/2,7/2}$ binding energies of the platinum atoms in these two states are known to differ by 2 eV.[8] ESCA spectra of **1**, as well as model platinum(II) and platinum(IV) complexes, presented in Figure 3, confirm the presence of platinum(IV) in **1**. Furthermore, when **1** was subjected to x-ray bombardment in the ESCA spectrometer, spectral changes indicative of a surface reduction of platinum(IV) to platinum(II) were observed; such x-ray damage of platinum(IV) compounds is well documented in the literature.[9]

With the platinum oxidation level established beyond doubt, there still remained to be defined the identity of the two negatively charged centers in addition to the chloride ions. Lack of any pronounced basicity of aqueous solutions of the isolated crystalline complex argues against the presence of $\mathrm{OH^-}$ in the solid. Although complexes containing deprotonated amino groups ($-\mathrm{NH^-}$) are known, the acidity of the parent coordinated amine groups is generally low. In fact, complexes with coordinated $-\mathrm{NH^-}$ groups must generally be stored in anhydrous conditions because water readily hydrolyzes this group back to the $-\mathrm{NH_2}$ form.[2] With **1**, however, aqueous solutions are only slightly basic and the deprotonated amino groups appear to be very weakly basic ($\mathrm{p}K_\mathrm{b} > 11$). These observations may be reconciled with the aid of the x-ray structural data for **1** and the hydrogen bonding scheme in the crystal.

Owing to the presence of the platinum atom, hydrogen atom positions could not be located unambiguously in a difference electron-density map but their positions were calculated assuming geometries appropriate to the states of hybridization at their bonded carbon atoms and, in addition, to maximize

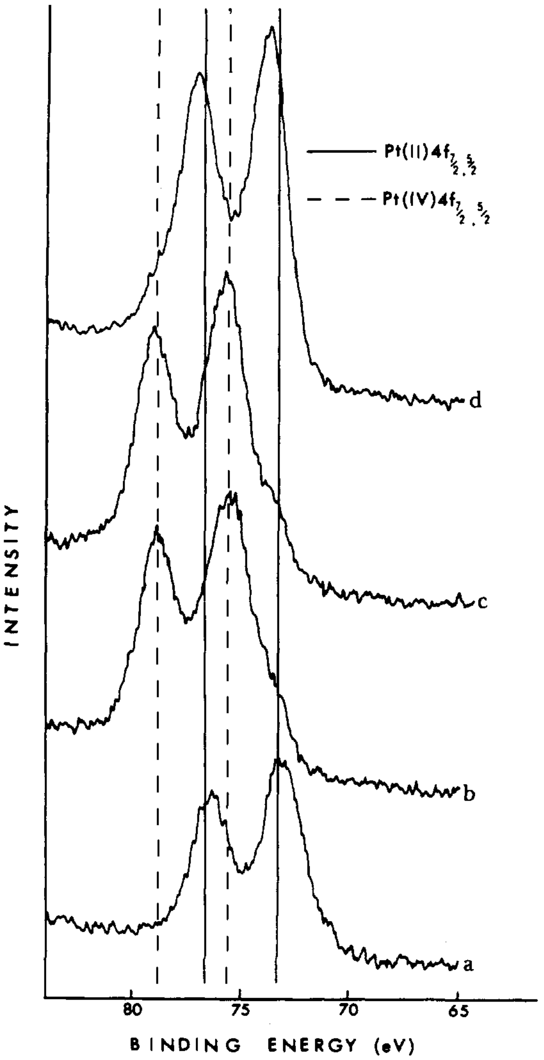

Figure 3. ESCA spectra of various solid platinum complexes: (a) [Pt(bipy)(dach)]Cl_2; (b) [Pt(bipy)[$CH_3CH(NH_2)CH_2CH(NH_2)$-CH_3]]Cl_4; (c) [Pt(bipy)(tach-2H)(H_2O)]Cl_2 (**1**), initial spectrum; (d) **1**, after 15 min of x-ray bombardment.

hydrogen bonding interactions at the nitrogen and oxygen atoms. The results of these calculations showed that the axial amino group participates in two N(7″)-H···Cl^- hydrogen bonds. Moreover, if the in-plane tach nitrogen atoms (N(8″) and N(9″)) remain tetrahedral, then a pair of unfavorably short H···H interactions would occur between the bipy hydrogen atoms on C(6) and C(6′) and the pseudoequatorial amino protons on N(8″) and on N(9″).[10] This interaction is relieved by ionization of these two protons, thus leaving only one hydrogen atom on each of these nitrogen atoms as shown in Figure 1. The pseudoequatorial lone pair on deprotonated amine nitrogen N(9″) is involved in O(W1)-H···N(9″) hydrogen bonds between complex ions related by the crystallographic 2_1 screw axis while the hydrogen atom on this same nitrogen atom participates in an N(9″)-H···Cl^- hydrogen bond. Neither the pseudoequatorial lone pair nor the pseudoaxial hydrogen atom at N(8″) is involved in any hydrogen bonding. All of the water molecules fully utilize their hydrogen bonding capabilities. In addition to the O(W1)-H···N(9″) interaction, the coordinated water molecule is involved in an O(W1)-H···Cl^- hydrogen bond. The three water molecules of solvation in the asymmetric crystal unit are not only associated through O-H···O hydrogen bonds but two of them serve to bridge chloride ions through O-H···Cl^- hydrogen bonds.

A closer examination of the ^{13}C-^{195}Pt coupling constants for the bipy carbon atoms in complex **1** and the analogous square-planar platinum(II) complex **2** provides further support for the platinum(IV) state in **1**. For the C(3) and C(5) bipy carbon atoms, J_{PtC} in **2** is 1.5 times as large as that found for **1**. Simple valence bond theory predicts dsp^2 hybridization at the platinum in the former complex and d^2sp^3 hybridization in the latter. Since the magnitudes of nuclear spin-spin coupling interactions are thought to be dependent on the individual character of the hybridizations of the coupled nuclei,[11] the higher s character of platinum bonds in the square-planar complexes might be expected to lead to a larger coupling than in a similar platinum(IV) moiety. Indeed, for identically bound amine ligands $^3J_{PtH}$ was found to be ~1.5-1.6 times larger in square-planar platinum(II) complexes than in octahedral molecules.[12] Venanzi et al.[13] observed similar behavior for $^1J_{^{195}Pt-^{15}N}$ in platinum(II) and platinum(IV) amine complexes. Interestingly, J_{PtC} for the bipy C(6) in **1** is three times smaller than is normally found in square-planar complexes like **2**. This may be a manifestation of electronic perturbation due to the close proximity of the lone pair on the deprotonated in-plane amino group with H(6) of the bipy ligand.

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