Reactions of Hydrazines with Platinum–Nitrile Complexes; *X*-Ray Structural Characterization and Electrochemistry of *trans*-Bis-1-acetyl-3-t-butyl-1,2,4-triaza-butadieneplatinum

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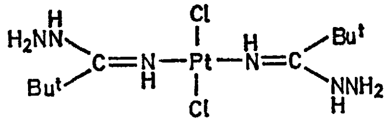
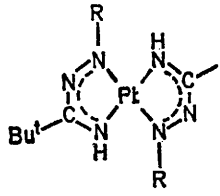
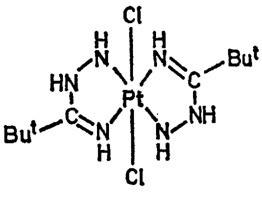
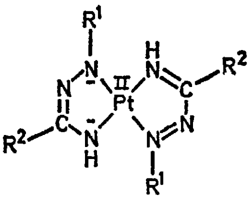
Summary Mono- and bi-dentate platinum complexes of ligands derived from $R^1N{=}NCR^2{=}NR^3$ are described: *X*-ray crystal structure analysis and E.S.C.A. data indicate that the intensely green $[Pt\{HNC(Bu^t)N_2Ac\}_2]$ has extensive delocalization of electrons within the chelate ring; the complex undergoes a reversible one-electron reduction to a paramagnetic species.

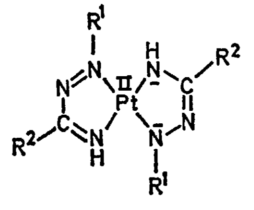
ADDITION of hydrazine hydrate to an ethanolic solution of *trans*-[$PtCl_2(Bu^tCN)_2$] yields a white air-sensitive compound which we formulate as (**a**) by analogy with the reactions[1] of hydrazines with nitriles to provide didehydroamidrazones. Furthermore, amines react with metal nitrile complexes to form amidine complexes.[2] Oxidation of compound (**a**) in air (preferably under alkaline conditions) causes chelation and provides a red compound, formulated as (**b**; R = H) on the basis of analytical and spectroscopic data (Table) and the *X*-ray structural analysis of the related acetate derivative (**b**; R = Ac). Compound (**b**; R = H) is converted into the green compound (**b**, R = Ac) by treatment with acetic anhydride. Treatment of (**b**; R = H) with concentrated HCl in EtOH gives the white, air-stable complex, $C_{10}H_{24}Cl_2N_6Pt$, which is tentatively formulated as (**c**), on the basis of spectroscopic evidence (see Table) and its ready reconversion into (**b**; R = H) under alkaline conditions.


(**a**)


(**b**)


(**c**)


(**d**) .


(**e**)

TABLE

Spectroscopic data (*i.r. data in* cm^{-1})

	Colour	ν(N–H)	ν(C–N)	ν(N–H)	ν(C–O)	ν(Pt–Cl)	λ_{max}/nm
$C_{10}H_{26}Cl_2N_6Pt$ (**a**)	White	3319s 3298s 3260vs	1664vs†			333vs	
$C_{10}H_{22}N_6Pt$ (**b**; R = H)	Red purple	3310vs 3224s	1488s†	1419s†			524 (ε 25,600) (in EtOH)
$C_{14}H_{26}N_6O_2Pt$ (**b**; R = Ac)	Green	3357vs	1492s†	1364s†	1684vs		713 (ε 21,900) (in $CHCl_3$)
$C_{10}H_{24}Cl_2N_6Pt$	White	3318vs 3096s	1579†			332vs	

†Tentative assignments.

The acetate (**b**; R = Ac) crystallizes from acetone in the space group *C*2/*m* with $a = 11{\cdot}580(2)$, $b = 7{\cdot}118(1)$, $c = 11{\cdot}414(3)$ Å, $\beta = 93{\cdot}09(1)°$; $Z = 2$, $D_c = 1{\cdot}78$ g cm^{-3}, $D_m = 1{\cdot}78$ g cm^{-3}. 1281 reflections having $F^2_{obs} \geqslant 3{\cdot}0\ \sigma(F^2_{obs})$ and $4° \leqslant 2\theta \leqslant 56°$ were observed with automatic four-circle diffractometer methods (Mo-K_α; graphite monochromator, ω–2θ scan routine). The structure analysis was achieved by standard heavy-atom methods, full-matrix least-squares refinement of the absorption-corrected data and of all atom positional parameters with isotropic temperature factors for the light atoms but with an anisotropic temperature factor for the platinum atom, has converged to $R_1 = 0{\cdot}042$. E.s.d.'s in the bond lengths shown in the Figure average 0·008 (Pt–N) and 0·014 Å (C–C, C–N, N–N, and C–O).

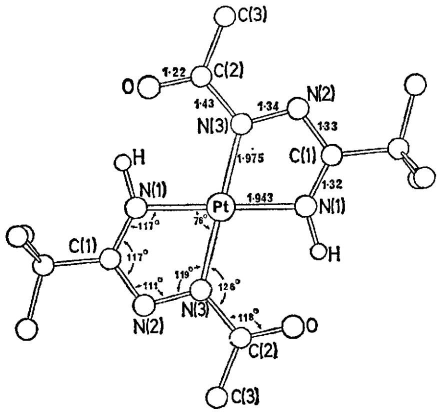


FIGURE. *Structure of the acetate* (**b**)

The rigorous C_{2h} symmetry of the complex shows that two supposedly neutral ligands can impose strictly planar co-ordination on the platinum and that early proposals[3] of tetrahedral co-ordination geometries in platinum–1-phenylthiosemicarbazide complexes may well be incorrect (*cf.* Holm *et al.*[4]). The co-planarity of the acetate group with the platinum heterocycle suggests that the N(1)(H) · · · · O bond length of 2·80(1) Å corresponds to an intramolecular hydrogen bond; the hydrogen atom is detectable in a difference electron density synthesis and lies close to the N(1) · · · · O direction (see Figure). The sharpness of the N–H stretching vibration (3357vs cm^{-1}; hexachlorobutadiene mull) is unexpected. E.S.C.A. measurements give the Pt $4f_{7/2}$ binding energy as 74·3(3) eV [relative to C (1*s*) at 285·0 eV]; this is somewhat greater than those observed for platinum(II) complexes such as $PtCl_4^{2-}$ and $Pt(CN)_4^{2-}$,[5] whereas formal platinum(0) complexes have bonding energies which vary from 71·7 to 73·2 eV.[6] Taken with the bond lengths within the platinum–ligand heterocycle, it is obvious that there is extensive π-electron delocalization.

In valence-bond terms the most important canonical forms are (**d**) and (**e**).

The complexes (**b**) are therefore analogous to the dithiolene complexes which are remarkable for their ability to undergo one- and two-electron reversible reductions without structural degradation.[7] The electrochemical behaviour of the platinum(II) complex (**b**; R = Ac) was examined at 20 °C under argon in a CH_2Cl_2–MeOH electrolyte, 0·1M in Et_4NBF_4. Polarograms displayed two reduction waves ($E_{1/2}$ −0·25 and −0·56 V *vs.* SCE), the ratio of the diffusion currents being 2:1 respectively. Analysis of the wave at −0·25 V met the criteria for a reversible one-electron charge-transfer step ($Pt^{II} + e \rightleftharpoons Pt^{I}$).[8] This result suggests that the wave at −0·56 V is due to the reduction of a dimeric species.

Cyclic voltamograms of (**b**; R = Ac) on a vitreous carbon electrode (VCE) between −0·05 and −0·45 V exhibited a quasi-reversible reduction wave ($Ep_c - Ep_a$ = *ca.* 100 mV, α = *ca.* 0·8). The departure from reversibility was attributed to a chemical reaction occurring subsequent to the charge-transfer step. A further irreversible reduction corresponding to the second polarographic wave was observed at more negative potentials. Also an irreversible oxidation of (**b**; R = Ac) was observed by cyclic voltametry at +1·1 V on the VCE at 90 mV/s.

Controlled-potential electrolysis of the platinum(II) complex (**b**; R = Ac) at −0·40 V on a platinum gauze electrode produced an indigo-blue solution which exhibited a polarographic reduction wave ($E_{1/2}$ − 0·56 V) with a diffusion current equal to one half of the diffusion current, measured at −0·40 V, of the starting solution. Integration of the total electrolysis current indicated that only 50% of the starting material had received an electron. Thus the binuclear species with $E_{1/2}$ −0·56 V must be a mono-anion ($Pt^{II} + e^- \rightleftharpoons Pt^{I}$; $Pt^{I} + Pt^{II} \rightarrow [Pt^{I} - Pt^{II}]^-$). The reduction of the isolated Et_4N^+ salt was found to be irreversible and produced a reduced species having the same peak potentials and redox behaviour as the reduced form observed during cyclic voltammetry of the starting platinum(II) complex (**b**; R = Ac). Preliminary characterization of the binuclear species shows it to be a paramagnetic, 1:1 electrolyte (Λ_H = *ca.* 20 $^{-1}$ cm^{-2} in nitrobenzene). Molecular-weight determinations support this formulation. Controlled-potential oxidation of the complex (**2**; R = Ac) at +1·2 V on VCE leads to the formation of a brown precipitate and the loss of all colour from the solution.

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