A Revised Structure for Chugaev's Salt $[PtC_8H_{15}N_6]_xCl_x$

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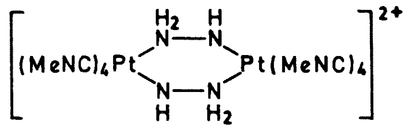
Summary The previous formulation $[Pt_2(N_2H_3)_2(MeNC)_8]Cl_2$ for Chugaev's salt is shown to be wrong and a structure involving a chelating carbene ligand is suggested.

THE bright-orange salt, $[PtC_8H_{15}N_6]_xCl_x$, which separates when an excess of methyl isocyanide, followed by hydrazine, is added to aqueous tetrachloroplatinate(II) was formulated by Chugaev[1] as the chloride of cation (I) and is sometimes cited as an example of six-co-ordinate platinum(II). We show this structure to be wrong and tentatively suggest an alternative structure (II). The conductivity of the chloride salt in methanol or of the tetraphenylborate in nitromethane gives values of Kohlrausch's constant within the range expected for univalent electrolytes.[2] The chloride $[PtC_8H_{15}N_6]Cl$ shows an intense broad i.r. absorption band at 2250 cm^{-1}, assigned to $C\equiv N$ stretch(es). When treated with bis(diphenylphosphino)ethane (diphos) it gives a yellow salt $[Pt(C_4H_9N_4)(diphos)]Cl$ and two moles of methyl isocyanide per g. atom of Pt are displaced. The complex $[Pt(C_4H_9N_4)(diphos)]Cl$ has no bands assignable to co-ordinated methyl isocyanide. Thus, Chugaev's salt can be reformulated as $[Pt(C_4H_9N_4)(MeNC)_2]Cl$. When the salt is treated with potassium cyanide, methyl isocyanide is displaced giving $[Pt(C_4H_9N_4)(CN)_2]^-$, isolated as the $AsPh_4^+$ salt.

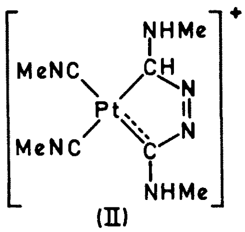
Aqueous solutions of $[Pt(C_4H_9N_4)(MeNC)_2]Cl$ and $[Pt(C_4H_9N_4)(diphos)]Cl$ are respectively weakly and strongly alkaline and the diphos complex reacts reversibly with one mole of hydrochloric acid to give a colourless cation $[Pt(C_4H_{10}N_4)diphos]^{2+}$; $[Pt(C_4H_9N_4)(CN)_2]^-$ similarly gives the non-ionic $Pt(C_4H_{10}N_4)(CN)_2$.

The almost colourless compound obtained by heating Chugaev's salt with aqueous hydrochloric acid had been assigned structure (III).[1] However, we find it non-conducting in dimethylformamide and it has no bands assignable to co-ordinated methyl isocyanide. The stoicheiometry $Pt(C_4H_{10}N_4)Cl_2$ suggests an analogous structure to $Pt(C_4H_{10}N_4)(CN)_2$. We find that methylamine hydrochloride is the other product of heating Chugaev's salt with dilute hydrochloric acid. $Pt(C_4H_{10}N_4)Cl_2$ gives a soluble ammine on being treated with ethanolic ammonia and the ammonia can be readily displaced by other ligands. In this way we have made $[Pt(C_4H_9N_4)(dipy)]^+$ and the neutral species $Pt(C_4H_9N_4)L^1L^2$ where L^1L^2H = dimethylglyoxime, 8-hydroxyquinoline, or salicylaldoxime; these last three species are monomeric in methanol and non-conducting.

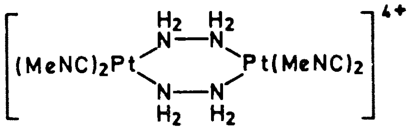
The ^1H n.m.r. spectrum of $[Pt(C_4H_9N_4)(MeNC)_2]BPh_4$ in nitrobenzene shows phenyl resonances, a 1 : 1 doublet at τ 7·08 (with ^{195}Pt satellites) due to 6H, and a singlet at τ 6·50, with ^{195}Pt satellites, also due to 6H. The resonances of the other three hydrogens are presumably too broad to be observed. The resonance at τ 6·50 is due to co-ordinated methyl isocyanide and is absent from the resonance pattern of the diphos complex or the oxinate. The doublet at τ 7·08 collapsed to a singlet after deuteriation with an excess of D_2O. This suggests that the ligand $C_4H_9N_4$ contains two MeNH– moieties. The resonance appears as a doublet in $Pt(C_4H_9N_4)$(oxinate). With $[Pt(C_4H_9N_4)diphos]BPh_4$ the resonance is a broad singlet but on adding CF_3CO_2H a doublet is obtained; the trifluoroacetic acid presumably inhibits the exchange of the NH protons. When a known excess of D_2O was added to a pyridine solution of $Pt(C_4H_9N_4)$(oxine) the doublet at τ 6·90 collapsed to a singlet and a sharp resonance appeared at τ 4·9 due to HDO. The intensity of this sharp resonance shows that only two protons in $C_4H_9N_4$ exchange; these are clearly the two NH protons.



(I)



(II)



(III)

It has recently been reported[3] that the complex $PtCl_2(MeNC)PEt_3$ adds primary amines to give carbene complexes of type $PtCl_2[C(NHMe)(NHR)]PEt_3$. We think that a similar reaction occurs during the formation of Chugaev's salt, and tentatively suggest structure (II). The methyls of the –NHMe groups presumably do not have sufficiently different chemical shifts for their resonances to be resolved (the resonances are rather broad because of the nitrogens). The resonance of the methine hydrogen is probably broadened by the nitrogens and not observed. The insoluble complex $PtCl_2(C_4H_{10}N_4)$ could have the extra hydrogen either on one of the nitrogens or on the carbene carbon atom [*i.e.*, $PtCl_2(C_4H_{10}N_4)$ is possibly a polynuclear derivative of Pt^{IV} with bridging chlorines].

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