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Crystal Structure of the Trichlorotris(1,3-dimethylimidazoline-2-thione)platinum(IV) Cation: the Product of a Novel Oxidation–Addition Reaction

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Reactions between platinum(II) salts and various heterocyclic thione molecules occur in neutral, acid and alkaline media [1]. With imidazolethiones complex formation occurs in acid and neutral media with the production, mostly, of compounds of stoichiometry: $[Pt(LH)_4]Cl_2$ and $[Pt(LH)_2Cl_2]$, (LH = benzimidazoline-2-thione [2], imidazoline-2-thione [2], 1-methylimidazoline-2-thione [3], 1,3-dimethylimidazoline-2-thione [2] and imidazolidine-2-thione [4]. Mixed valence complexes containing platinum(II) and (IV) have also been reported for imidazolidine-2-thione [5].

In alkaline media, deprotonation of the heterocyclic-thione occurs with the production of the corresponding thionate anion [1]. Polymeric complexes $[PtL_2]_n$, are reported for benzimidazole-2-thionate [6] and 1-methylimidazoline-2-thionate [7]. Bis-(pyrimidine-2-thionate)platinum(II) reacts with the tetraiodoplatinate(II) ion in methanol producing $[Pt(pyrimidine\text{-}2\text{-}thionate)_2I_2]_2$. This dimeric compound contains platinum(III), (Pt–Pt, 2.554(1) Å), four bridging pyrimidine-2-thionates and terminal iodide [8].

Stoichiometrically controlled reactions between platinum dichloride or potassium tetrachloroplatinate(II) and 1,3-dimethylimidazoline-2-thione (dmimt) in molar hydrochloric acid produce $Pt(dmimt)_4Cl_2{\cdot}4H_2O$ and $Pt(dmimt)_2Cl_2{\cdot}2H_2O$, respectively. Compound stoichiometries have been confirmed by chemical (C, H, N) and thermal analysis. Crystal structure analysis of the 4:1 (ligand: metal) complex revealed $[Pt(dmimt)_4]^{2+}$ cations, with sulphur donor ligands and square-planar PtS_4 coordination, together with ionic chlorides and lattice water molecules [2]. Upon turning our attention to the crystallography of the 2:1 (ligand: metal) complex we obtained surprising results. This report is largely concerned with the crystal structure analysis of a single crystal which was isolated from the preparation of $[Pt(dmimt)_2Cl_2]{\cdot}2H_2O$.

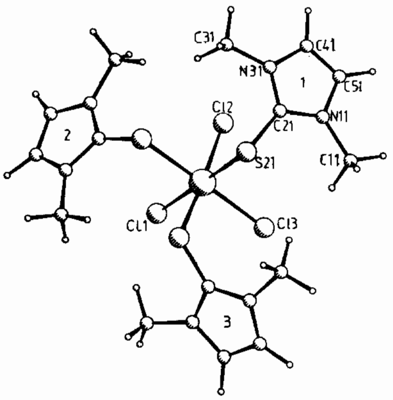

Fig. 1. Perspective diagram of the $[Pt(dmimt)_3Cl_3]^+$ cation. Bond lengths: Pt–S, range 2.356(2)–2.364(3), mean 2.361; Pt–Cl, range 2.356(4)–2.362(3), mean 2.359 Å; angles: Cl–Pt–Cl range 88.2(1)–89.7(1), mean 88.8; S–Pt–S range 84.0(1)–85.5(1), mean 84.7; Cl–Pt–S ranges 92.5(1)–93.7(1) and 125.9(1)–178.1(1), means 93.2 and 177.1°.

Crystal Data

$C_{15}H_{24}N_6S_3PtCl_4{\cdot}2H_2O$, $M_r = 757$ triclinic, $a = 8.858(4)$, $b = 13.577(2)$, $c = 13.576(3)$ Å, $\alpha = 117.08(2)$, $\beta = 94.92(3)$, $\gamma = 92.53(3)°$, $U = 1442.0$ Å^3, space group $P\bar{1}$, $Z = 2$. X-ray diffraction data was collected on an Enraf-Nonius diffractometer using a ω–2θ scan method with graphite monochromatised Mo Kα radiation ($\lambda = 0.71069$ Å). A total of 5065 independent reflections were measured of which 920 were suppressed. The structure was solved by Patterson and Fourier methods and refined with full-matrix least-squares methods with anisotropic temperature factors applied to the non-hydrogen atoms. All H atom positions were fixed by the program (C–H = 1.08 Å).

The R agreement index is currently 0.0404 with unit weights. All calculations were performed on the NUMAC IBM 370/168 computer at the University of Newcastle-upon-Tyne; SHELX [9] and related programs were used throughout the calculations.

The crystal structure revealed a complex of formula, $[Pt(dmimt)_3Cl_3]Cl{\cdot}2H_2O$, with the complex cation in the form of the confacial isomer. We suggest, in view of the analytical data obtained for the bulk product (see below), that *fac*-$[Pt(dmimt)_3Cl_3]Cl{\cdot}2H_2O$ is a by-product of the reaction between the tetrachloroplatinate(II) ion and dmimt in molar hydrochloric acid. *Anal.* Calc. (found) for $Pt(dmimt)_2Cl_2{\cdot}2H_2O$: C, 21.5(21.64); H, 2.9(3.11); N, 10.0(10.30); Pt, 34.9(36.0).

The production of *fac*-$[Pt(dmimt)_3Cl_3]Cl{\cdot}2H_2O$ may be envisaged to result from *trans* addition of chloride ion and dmimt to $[Pt(dmimt)_2Cl_2]$ coupled with aerial oxidation of the metal. Two possibilities

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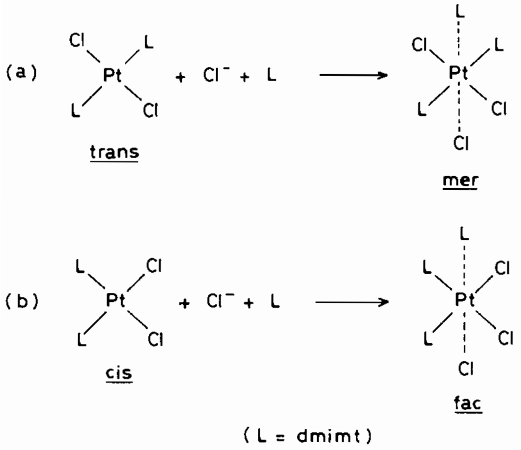

Scheme 1.

are illustrated in Scheme 1 where it can be seen that *trans* addition should produce the *mer*-isomer from *trans*-[Pt(dmimt)$_2$Cl$_2$] and the *fac*-isomer from *cis*-[Pt(dmimt)$_2$Cl$_2$] [10]. Alternatively, a five coordinate intermediate is possible which could rearrange to give the most thermodynamically favoured product.

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