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Selenium Chelates. Preparation and X-ray Structure Determination of Methyl(diethyldiselenocarbamato)-(triphosphine)platinum(II), $Pt(Se_2CNEt_2)(CH_3)(PPh_3)$

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Recently we have extended our studies of sulphur chelates to the preparation and characterization of diselenocarbamate complexes, both to compare the ligating properties of sulphur and selenium, and as an adjunct to the development of ^{77}Se n.m.r. in these laboratories [1, 2]. In this latter regard, the wide chemical shift range and extreme sensitivity of the n.m.r. parameters to the selenium environment necessitate the study of a variety of model compounds of accurately known structure before the technique can be interpolatively applied to the determination of solution structures and reaction mechanisms of unknowns; an obvious target of course being the elucidation of the environment and role of selenium in biological processes [3].

Accordingly, we have initiated a comparative X-ray crystallographic study of several diselenocarbamates to complement the ^{77}Se n.m.r. work, and report here the preparation and single crystal X-ray analysis of the title compound $Pt(Se_2CNEt_2)(CH_3)(PPh_3)$. It is the first structural report of a platinum (II) organometallic compound containing co-ordinated selenium atoms, and moreover, is formally a selenium analog of compounds derived from ring opening reactions of cyclobutenylpalladium complexes [4]. The present study correlates the ^{77}Se n.m.r. shielding with the metal–ligand distance, consistent with the large ^{77}Se shielding deriving from magnetic anisotropy of the metal [2].

The reaction of $Pt(Se_2CNEt_2)_2$ with $Pt(CH_3)_2(PPh_3)_2$ in benzene under reflux in a nitrogen atmosphere produces $Pt(Se_2CNEt_2)(CH_3)(PPh_3)$ in high yield. A cyclic methyl bridged intermediate has been suggested in related symmetrization reactions of PtR_2L_2 and PtX_2L_2 species [5]. Such a simple mechanism is obviously not completely appropriate in the present case. The reaction is currently under investigation and will be described completely elsewhere. After removal of the solvent, and recrystallization from acetone/heptane, $Pt(Se_2CNEt_2)(CH_3)(PPh_3)$ is obtained as pale yellow crystals. It was characterized by elemental analysis, supported by ^{1}H, ^{13}C, ^{31}P and ^{77}Se n.m.r. data. The solid, m.p. 167–9 °C, is indefinitely stable in air. The compound is soluble in the usual polar organic solvents (acetone, dichloromethane, *etc.*) wherein we have observed no decomposition.

N.m.r. spectra were obtained in $CDCl_3$ at 303 K. The ^{1}H n.m.r. spectrum shows the ethyl groups to be inequivalent (CH_3; two overlapping triplets $\delta = 1.23$ and 1.33 ppm relative to TMS: CH_2; two overlapping quartets $\delta = 3.63$ and 3.71 ppm. $J_{CH_3-CH_2} = 7.0$ Hz). The methyl bound to the platinum is observed at 0.57 ppm with the following coupling constants: $^2J_{Pt-H} = 74.0$ Hz, $^3J_{P-H} = 4.5$ Hz, $^3J_{Se-H} = 8.0$ Hz. We have previously shown [6] that inequivalence of the dithiocarbamate alkyl groups in related compounds is a consequence of the large barrier to C⩦N bond rotation and the same conclusion would seem to apply here. ^{77}Se n.m.r. parameters have been reported previously [2]. The ^{13}C n.m.r. spectrum exhibits, in addition to peaks due to triphenylphosphine, a 1:4:1 triplet due to $Pt-CH_3$ ($\delta = -13.09$ ppm, $J_{P-C} = 7.2$ Hz, $J_{Pt-C} = 629$ Hz for ^{195}Pt, I = 1/2 33% abundant), a singlet ($\delta = 12.23$ ppm) due to the methyls on the diselenocarbamate and two peaks ($\delta = 46.42$ ppm, $\delta = 47.77$ ppm multiplet) due to the methylene carbons. *Crystal data:* $C_{24}H_{28}NPPtSe_2$: M = 714.5 crystal dimensions *ca.* 0.3 × 0.25 × 0.2 mm, monoclinic, space group $P2_{1/C}$. $a = 16.124(2)$, $b = 9.239(2)$, $c = 19.291(3)$ Å, $\beta = 119.76(1)°$, V = 2494.8(7) Å^3, $D_c = 1.90$ g cm^{-3}, $Z = 4$, μ_c(Mo-Kα) = 91.2 cm^{-1}. Intensity data ($0.0 \leqslant 2\theta \leqslant 55°$) were recorded on a Syntex $P2_1$ four-circle diffractometer at 25 °C, with graphite monochromated Mo-Kα radiation. The 3334 unique observed intensities [$I > 3.0\sigma(I)$] were translated and reduced and the structure solved by heavy-atom methods. Instrumentation, programs, *etc.* have been reported previously [7]. Least squares refinement with anisotropic thermal parameters for the Pt, Se, P and methyl C atoms gave residuals $R = \{\Sigma\Delta/\Sigma|F_0|\} = 6.5$, $R_w = \{\Sigma w\Delta^2/\Sigma w|F_0|^2\}^{1/2} = 10.0$. The hydrogen atoms were not located.

The molecular geometry is shown in Fig. 1, which includes some important bond parameters. $Pt(Se_2CNEt_2)(CH_3)(PPh_3)$ exists as discrete monomers with no significant intermolecular contacts. The $PtSe_2PC$ core is essentially planar (rms deviation of fitted atoms from the plane 0.0039 Å) and makes an angle of 2.5° with the Se_2CN plane at Se....Se. The C⩦N bond distance (1.34(4) Å) is consistent with the interpretation of the ^{1}H and ^{13}C n.m.r. non-equivalence of the diselenocarbamate alkyl groups given above, and agrees well with values in analogous structures determined in these and other laboratories [8]. An asymmetry in the Pt–Se bonding is observed, with

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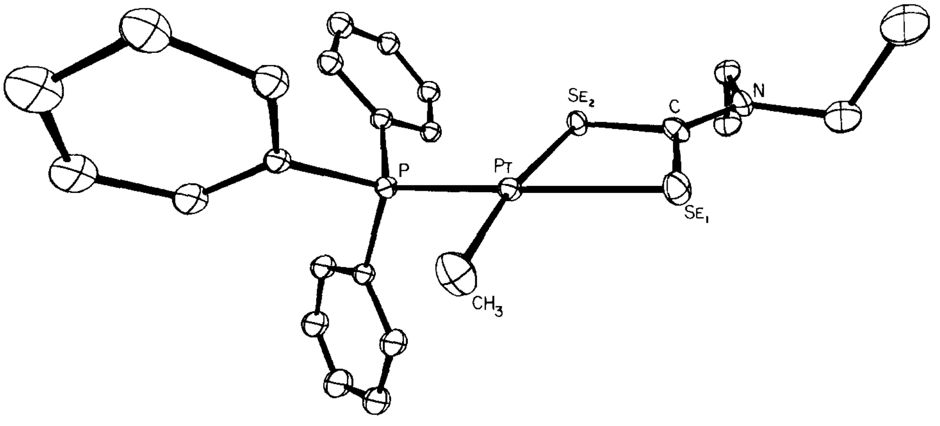

Fig. 1. The molecular structure of Pt(Se$_2$CNEt$_2$)(CH$_3$)(PPh$_3$). Bond lengths: Pt–Se(1) 2.462(4); Pt–Se(2) 2.491(3); Pt–P 2.224(8); Pt–CH$_3$ 2.113(25); Se(1)–C 1.89(2); Se(2)–C 1.86(3); C–N 1.34(4); ave. P–C$_{ring}$ 1.86(2) Å. Bond angles: Se(1)–Pt–Se(2) 76.9(2); P–Pt–CH$_3$ 91.0 (1.0); Se(1)–Pt–CH$_3$ 91.0(1.0); Se(2)–Pt–P 101.1(3); Se(1)–C–Se(2) 110.5 (1.4)°.

Pt–Se *trans* to P being significantly shorter (2.462(4) Å), than the Pt–Se bond *trans* to the methyl group (2.492(3) Å). The Pt–Se bond *trans* to the methyl group is lengthened relative [9] to the Pt–Se bonds in Pt(Se$_2$CNibu$_2$)$_2$ (2.43 Å). Any corresponding asymmetry in the C–Se bonding is below the limits of statistical significance. The Pt–P distance (2.224(8) Å) is in good agreement with [9] that of the analogous Pt(S$_2$CNEt$_2$)Cl(PPh$_3$) (2.26(1) Å) and the Pt–CH$_3$ distance is within the range [10, 11] of Pt–CH$_3$ distances. No unusual distortions of the phosphine are noted nor is there any apparent severe steric crowding about the metal.

The most striking feature of the structure, and the one of greatest relevance to the ^{77}Se n.m.r. study is the asymmetric Pt–Se bonding. In the analogous dithio-and diselenocarbamato chloro complexes [9], the *trans* influence of the phosphine is greater than that of the chloride, whereas in the present case, the methyl group exerts a larger *trans* influence than does the phosphine. This structural *trans* influence is reflected in the ordering [2] of the ^{77}Se n.m.r. resonance positions, δ *trans* Cl < δ *trans* P < δ *trans* CH$_3$ and $^1J_{Pt-Se}$ *trans* CH$_3$ < $^1J_{Pt-Se}$ *trans* P. The structural results are, therefore, reflected in the n.m.r. spectra. Although both steric and electronic effects can produce asymmetry in the Pt–Se bonding, ascribing the asymmetry solely to phosphine steric pressure does not explain the observation that in the analogous chloride derivative, Pt–Se *trans* Cl (2.397(3)) < Pt–Se *trans* P (2.457(2)) [9].

We have previously noted the likely dependence of the ^{77}Se n.m.r. resonance positions on molecular dimensions [2]. Further structural studies which relate to this question are in progress.

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