The Molecular Structure of Di-μ-chloro-[dichloro-*trans*-bis(trimethylarsine)]platinum(II)

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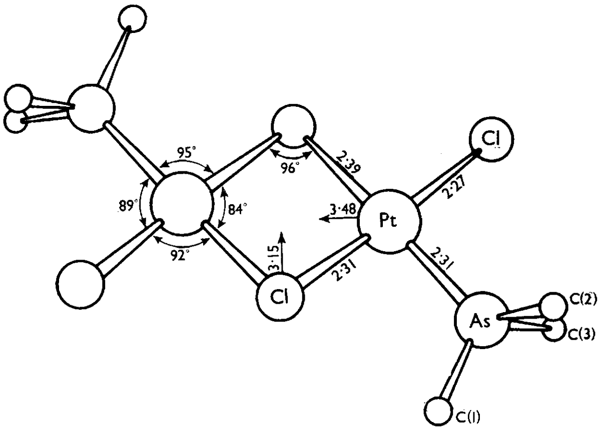
A recent i.r. study of bridged platinum and palladium chloro-complexes, $M_2Cl_4L_2$,[1] has shown that at least two of the three bands assigned to the M–Cl skeletal stretching modes in the region 500—200 cm.$^{-1}$ display extra structure when the central metal is platinum. The appearance of this splitting is independent of the nature of ligand L, and occurs both for solutions and for the solid state. It could therefore arise through some inherent structural feature of the Pt complexes. For this reason, and because the trimethylarsine derivative displays an apparently large *trans*-effect, the compound $Pt_2Cl_4(AsMe_3)_2$ was selected for single-crystal *X*-ray analysis.

Crystal data: $Pt_2Cl_4(AsMe_3)_2$, monoclinic, $P2_1n$ $a = 10{\cdot}386$, $b = 11{\cdot}841$, $c = 6{\cdot}744$ Å, $\beta = 94°20'$, $Z = 2$. The seven non-hydrogen atoms in the crystallographically independent unit were located by Patterson and difference Fourier techniques. Isotropic, full-matrix least-squares refinement of 1131 independent data has yielded a residual factor R of 6·5% for the model shown in the Figure.

The platinum atoms in this chlorine-bridged dimer display the approximately square-planar co-ordination expected for Pt^{II}. The terminal Cl and As are $+0{\cdot}02$ and $-0{\cdot}04$ Å respectively from the plane defined by the two platinum and two bridging chlorine atoms. The three As–C bonds and the two Pt–Cl bonds *trans* to one another have lengths comparable with reported values.[2] The terminal Pt–Cl bond may be slightly shorter than the Pt–Cl bond *trans* to it, but not significantly so at the present stage of refinement. However, the Pt–As bond length of 2·312 ± 0·003 Å is appreciably less than the sum of covalent radii (2·41),[3] or the average value reported for Pt(diars)$_2$Cl$_2$ (2·375 ± 0·004),[4] while the Pt–Cl distance *trans* to As is significantly longer than either of the other two Pt–Cl distances. These observations are consistent with calculations on a simple harmonic-oscillator model using the assigned stretching frequencies[1] to obtain force-constants relative to Pt–Cl (terminal): Pt–As, 2·0; Pt–Cl (terminal), 1·0; Pt–Cl(*cis*), 0·9; Pt–Cl(*trans*), 0·5, where *cis* and *trans* refer to the bridging chlorine positions relative to As.

While the elucidation of this structure has not provided an explanation for the i.r. band-splitting observed for such platinum complexes, the obviously considerable interaction between the As and the *trans*-bridged Cl is worthy of comment. I.r. and *X*-ray data together suggest that a mechanism like that proposed by Chatt and his co-workers[5] is strongly operative in Pt$_2$Cl$_4$(AsMe$_3$)$_2$; namely, that the formation of a Pt–As σ-bond polarizes the charge distribution about the metal atom in such a way as to repel the *trans*-co-ordinated chlorine. The d_π-d_π interaction between the As and Pt then tends to neutralize this charge separation and also leads to the formation of a short, strong Pt–As bond.



FIGURE

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[1] R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 1897.

[2] "Interatomic Distances", *Chem. Soc. Special Publ.*, No. 18, 1965.

[3] L. Pauling, "Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1948, 2nd edn.

[4] N. C. Stephenson, *Acta Cryst.*, 1964, **17**, 1517.

[5] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207.