

The Structure of *cis*-Dinitratobis(dimethyl sulphoxide)palladium(II)

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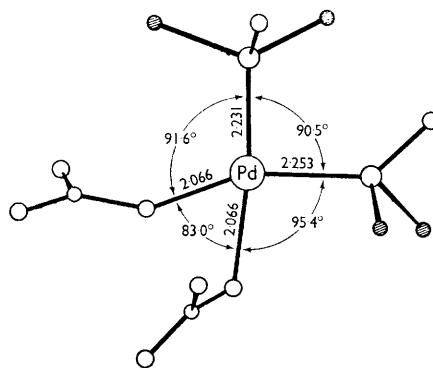
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INFORMATION concerning known, stable, non-chelate, palladous complexes of the *cis*-configuration is limited, in contrast to the analogous *cis*-platinous complexes.^{1,2} Bennett, Cotton, and Weaver³ have shown that the complex $\text{PdCl}_2(\text{Me}_2\text{SO})_2$ has a *trans*-configuration and that the dimethyl sulphoxide ligand co-ordinates *via* the sulphur atom. The structure of *cis*-($\text{C}_{15}\text{H}_{13}\text{O}$) $\text{Cl}_2\text{Ir}(\text{Me}_2\text{SO})_2$ has also recently been reported⁴ to be S-bonded and the metal-sulphur bond distances are shorter than those in *trans*- $\text{PdCl}_2(\text{Me}_2\text{SO})_2$. The short bond length has been attributed to $d\pi-d\pi$ back bonding. This hypothesis is confirmed in this study.

Crude *cis*- $\text{Pd}(\text{NO}_3)_2(\text{Me}_2\text{SO})_2$ was prepared from the reaction of $\text{Pd}(\text{NO}_3)_2$ with dimethyl sulphoxide. Recrystallization from nitromethane gave orange-yellow, monoclinic crystals, m.p. 143–145°. The unit-cell parameters $a = 8.981$, $b = 14.214$, $c = 10.824$ Å, $\beta = 117.6^\circ$, $Z = 4$, $M = 387$. The observed extinction conditions confirmed the space group $P2_1/c$ (No. 14). The intensities of 1069 nonzero reflections were measured with a G.E. XRD-5 diffractometer using Mo- K_α radiation. The least-squares refinement of the positional parameters obtained by Patterson and Fourier syntheses was terminated when the shifts in these parameters were less than their estimated standard deviations. The final residual stands at 0.050.

The structure of *cis*- $\text{Pd}(\text{NO}_3)_2(\text{Me}_2\text{SO})_2$ is given in the Figure. The Me_2SO ligands are S-bonded and the nitrate groups are monodentate in the distorted, square-planar complex. The planar nitrate ions are *trans* to the Me_2SO ligands and the co-ordinated oxygen atoms lie 0.08(1)† and

0.28(1) Å on either side of the plane described by the palladium and the two sulphur atoms. The related bond distances in both the nonequivalent nitrate and Me_2SO ligands were found to be the same within experimental errors. The average bond lengths in the Me_2SO ligands are S–O, 1.463(7) and S–C, 1.789(7) Å. In the nitrate



FIGURE

groups the co-ordinated N–O distance is 1.32(1) compared to 1.217(9) Å for the nonco-ordinated N–O bonds. The Pd–S bonds are nonequivalent with lengths of 2.231(3) and 2.253(3) Å, which are significantly shorter than the equivalent bond lengths of 2.300(4) Å observed in *trans*- $\text{PdCl}_2(\text{Me}_2\text{SO})_2$.

Messmer *et al.*^{5,6} found that the Pt–P bond lengths were larger in *trans*- $\text{PtCl}_2[\text{PEt}_3]_2$ than in *cis*- $\text{PtCl}_2[\text{PMe}_3]_2$. The Pt–P distances were

† The estimated standard deviation of the last significant figure is given in parentheses.

2.256(8) and 2.239(6) Å in the *cis*-complex compared to 2.30 Å in the *trans*. Furthermore, the larger ^{195}Pt – ^{31}P coupling constants for the *cis*-complexes have been explained by $d\pi$ – $d\pi$ bonding.⁷ Thus the shorter bond lengths in the *cis*-complexes are indicative of enhanced π -bonding.

Vaska and Bath⁸ have related an increase in the S–O stretching frequency to a decrease in the M–S $d\pi$ – $d\pi$ bonding for a series of SO_2 -containing complexes. The S–O stretching frequency for *trans*- $\text{PdCl}_2(\text{Me}_2\text{SO})_2$ is 1116 cm^{-1} , while the two

frequencies for *cis*- $\text{Pd}(\text{NO}_3)_2(\text{Me}_2\text{SO})_2$ are 1136 and 1157 cm^{-1} . Thus it would appear that the bond length and S–O frequency-shift criteria also support enhanced $d\pi$ – $d\pi$ bonding in the *cis*-complex. The related platinum complex, $\text{PtCl}_2(\text{Me}_2\text{SO})_2$ has two infrared bands at 1134 and 1157 cm^{-1} . On this basis and on the basis of its ultraviolet spectrum, we suggest that this compound is also *cis*. Its structure is at present under investigation.

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