

PS-07.04.14 CIS/TRANS-INFLUENCE IN PLATINUM(II) COMPLEXES. CRYSTAL STRUCTURE OF CIS-[Pt(dimethylsulfoxide)(dimethylsulfide)Cl₂].

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Comparable Pt-S bond distances in sulfoxide complexes are shorter than in thioether ones. For example, in [PtLCl₃], the Pt-S distances are 2.19 and 2.25 Å for L=dms ((CH₃)₂SO) (Melanson, R., Hubert, J. and Rochon, F.D. *Acta Cryst. B32* (1976)1914) and L=dms ((CH₃)₂S) (Kukushkin, V., Löqvist, K. and Oskarsson, Å., to be published), respectively. If the cis-influences are changed from Cl/Cl to S/Cl as in *cis*-[PtL₂Cl₂] the Pt-S distances will increase to 2.24 and 2.27 Å for L=dms (Melanson, R. and Rochon, F., *Can. J. Chem.* 53(1975)2371) and L=dms (Horn, G., Kumar, K., Maverick, A., Fronczek, F. and Watkins, S., *Acta Cryst. C46*(1990)135.), respectively. By using the Pt-S distance in [PtLCl₃] as a reference value the cis-influence Cl/S(dms) on the Pt-S(dms) distance is thus much more drastic than for Cl/S(dms) on the Pt-S(dms) distance. In order to study the cis-influence of dms on dms and *vice versa* we have synthesized and determined the crystal structure of the title compound.

Cis-[Pt(dms)(dms)Cl₂] crystallizes in *P2₁/c* with *a*=8.377(1), *b*=8.496(2), *c*=14.747(3) Å, *β*=90.34(2)°, *Z*=4 and *R*=5.2%. Pt-S(dms)=2.212(4) and Pt-S(dms)=2.272(1) Å. These results indicate a significant difference in the cis-influence of dms compared to dms. This will be further discussed in connection with other platinum complexes containing sulfur bonded dms or dms.

PS-07.04.15 Cis/trans-Influences in Pt(II)-complexes. Crystal Structure of tetrakis (tetrahydrothiophene) platinum(II) bis(trifluoromethanesulfonate).

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Recently a new definition of the *cis/trans* influences in square-planar complexes has been proposed (Bugarcic, Z., Norén, B., Oskarsson, Å., Stålhandske, C. and Elding, L.I., *Acta Chem. Scand.* 45(1991)361). The difference between the bond length M-L in [MLXYZ] and in [ML₄] is used as a quantitative measure of the combined influences of X, Y and Z on the bond M-L. In certain cases it is also possible to discriminate between the *cis*- and the *trans*-influences *i.e.* bond length determinations of *trans*-[ML₂X₂] will give the *cis*-influence of X/X on the M-L bond while corresponding determinations of [ML₃X] give the *trans*-influence of X on M-L. Our studies have been centered on platinum(II) complexes with L as the thioethers dimethylsulfide (dms) and 1,4-thioxane (tx), both coordinating *via* their sulfur atoms. The other ligands have mainly been halides or sulfoxides. An average value 2.319(2) Å, of the Pt-S distance, was found from X-ray diffraction determinations of the crystal structures of [Pt(dms)₄](CF₃SO₃)₂ and [Pt(tx)₄](CF₃SO₃)₂·H₂O. As this value is used as a reference for the Pt-S bond length it was found desirable to investigate other tetrakis(thioether) complexes of Pt(II) with different packing properties. More-

over the mentioned *cis/trans* influences are often small, even if they have dramatic effects on rates and mechanisms for ligand substitution reactions in solution. To improve the reliability of the Pt-S reference value the crystal structure of [Pt(tht)₄](CF₃SO₃)₂ (tht=tetrahydrothiophene) was determined.

The title compound consists of well separated [Pt(tht)₄]²⁺ and CF₃SO₃²⁻ ions (minimum Pt-Pt distance is 8.62 Å) and crystallizes in the space group *P2₁/c* with *a*=8.6172(6), *b*=14.174(1), *c*=12.019(1) Å, *β*=98.30(1)°, *Z*=2 and *R*=4.3 %.

According to the space group symmetry the coordination geometry is perfectly planar with Pt-S distances 2.305(3) and 2.307(3) Å. These results are not significantly different from previously reported ones. However a new reference distance 2.316(6) Å is found for Pt-S(thioether) bonds. Thus the *cis*-influence of I/I on S is -0.007(6) Å in *trans*-[Pt(tht)₂I₂] (Oskarsson, Å., Norén, B., Svensson, C. and Elding, L.I., *Acta Cryst. B46*(1990)748). The corresponding value for Cl/Cl is -0.011(7) Å in *trans*-[Pt(tht)₂Cl₂] (Norén, B., Oskarsson, Å. and Svensson, C., to be published). Evidently the *cis*-influence of halides on the Pt-S(thioether) bond is very small and can be neglected.

PS-07.04.16 VANADIUM(III) AND OXO-VANADIUM(IV)-AMIDE BINDING. A. Terzis*, T.A. Kabanos¹, A.D. Keramidas¹, and A.B. Papaioannou¹

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In contrast to other biologically important transition metals (Fe, Cu, Zn etc.) the role of Vanadium in biochemical processes is still poorly understood. The discovery of Vanadium in biomolecules such as marine algal bromoperoxidase, nitrogenase from *Azotobacter vinelandii*, marine ascidians and in crude oils has led to considerable interest in its biological activity. Although there is a large body of work on the interactions of Vanadium with oxygen and sulphur atoms, little is known about the coordination of nitrogenous ligands to Vanadium, in particular Vanadium-amide binding [Kabanos, T.A., Keramidas, A.D., Mentzafos, D. and Terzis A., *J. Chem. Soc., Chem. Comm.*, 1664 (1990)].

Here we report the synthesis of [VOL] and Na[VOL'], rare examples of a VO²⁺ complex and [VCl₂L*], the first structural characterization of a V(III) complex, all containing a V-amide bond. Their structures are in Figs A, B and C. Cyclic voltametry of [VOL] and Na[VOL'] in acetonitrile reveals a reversible one-electron redox process at +0.09V and -1.60V and at -0.07V and +0.56V (vs NHE) respectively. CV of [VCl₂L*] reveals a cathodic peak at 0.61V and an anodic peak at 2.04V (vs NHE).