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Evidence for both Sulphur and Oxygen Co-ordination Sites in the Tetrakis(dimethyl sulphoxide)palladium(II) Cation

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We report the complex $[Pd(DMSO)_4]^{2+}$ which has the novel property of containing two distinct types of co-ordinated dimethyl sulphoxide, one type bonded through sulphur and the other bonded through oxygen. Dimethyl sulphoxide (DMSO) is known to function as either a sulphur or oxygen donor toward metal-ion acceptors.[1] There are, however, no reported examples to date where DMSO acts as both a sulphur and oxygen donor in a metal-ion complex. We are unaware of any reported example where a neutral ligand exhibits well-defined mixed donor sites in a transition-metal ion complex. There are, however, several examples where anionic ligands co-ordinate through different donor atoms within a single complex. Some of the best examples of this occur in palladium(II) thiocyanate complexes,[2,3] several of which contain one sulphur-bonded and one nitrogen-bonded thiocyanate.

$[Pd(DMSO)_4](ClO_4)_2$ (I) was prepared by mixing palladium chloride and silver perchlorate in DMSO, filtering off the silver chloride and precipitating the complex with chloroform. The complexes $[Pd(DMSO)_4](BF_4)_2$ (II) and $[Pd([^2H_6]DMSO)_4](BF_4)_2$ (III) were easily obtained from the cationic acetonitrile complex[4] by metathesis reactions with DMSO and $[^2H_6]$DMSO respectively.† These complexes are diamagnetic and thus consistent with a roughly planar array of donor atoms. The i.r. spectral bands for (I) and (II) discussed here are independent of the choice of anion.

I.r. spectral studies of DMSO complexes have proved useful in distinguishing between co-ordination through the oxygen or sulphur donor site.[1] The *X*-ray structure determination of *trans*-$[Pd(DMSO)_2Cl_2]$[5] and *cis*-$[Pd(DMSO)_2(NO_3)_2]$ [6] have demonstrated that DMSO co-ordinates through the sulphur atom. The bands at 1116 cm.$^{-1}$ in the chloride complex[1] and at 1157 and 1136 cm.$^{-1}$ in the nitrate complex[6] were assigned to ν_{SO}. Examination of the i.r. spectra for the $[Pd(DMSO)_4]^{2+}$ complexes (Table) reveals strong bands at 1150 and 1140 cm.$^{-1}$ which shift only slightly on deuteriation, which can be attributed to ν_{SO}, and which demonstrate the

Sulphur–oxygen stretching frequencies in representative dimethylsulphoxide complexes

Complex	Donor atom	ν_{SO}
$[Pd(DMSO)_2Cl_2]$ ..	S	1116
$[Pd([^2H_6]DMSO)_2Cl_2]$ ..	S	1113
$[Pd(DMSO)_2(NO_3)_2]$ ..	S	1157, 1136
$[Fe(DMSO)_4Cl_2]\ [FeCl_4]$	O	933
$[SnCl_4,2DMSO]$	O	915
$[SnCl_4,2[^2H_6]DMSO]$ ..	O	929, 914
$[Pd(DMSO)_4]^{2+}$	S	1150, 1140
	O	920, 905
$[Pd([^2H_6]DMSO)_4]^{2+}$ ..	S	1146, 1141
	O	916, 904

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† Excellent C, H, and Pd analyses were obtained for these complexes.

presence of sulphur-co-ordinated DMSO. Co-ordination through the DMSO oxygen is characterized by a shift of ν_{SO} to lower energy as illustrated by the Fe^{III} (933 cm.$^{-1}$)[1] and Sn^{IV} (915 cm.$^{-1}$)[1] complexes in the Table. Examination of the $[Pd(DMSO)_4]^{2+}$ complex shows extra bands in the 900—1000 cm.$^{-1}$ region. The assignment of ν_{SO} is, however, complicated by the presence of methyl rocking bands in this region. The deuteriated complex was thus examined to aid in this assignment, for the methyl rocking modes shift to lower frequency by *ca* 200 cm.$^{-1}$. The strong bands at 920 and 905 cm.$^{-1}$ undergo only very slight shifts (916 and 904 cm.$^{-1}$) in the deuteriated complex and can thus be assigned to ν_{SO} for oxygen-bonded DMSO. Further evidence for a mixed donor site complex is found in the far i.r. which contains at least three strong absorptions (493, 437, and 420 cm.$^{-1}$) which can be assigned to "palladium-ligand" stretching frequencies.[7] Only one band would be expected for four equivalent donors in an idealized D_{4h} symmetry. Also, two or more bands are found in the regions where δ_s(CSO) and δ_a(CSO) occur. The vibrational spectra for $Pd(DMSO)^{+2}$ are thus consistent with a symmetry lower than D_{4h} caused by the presence of both sulphur and oxygen donor co-ordination sites.

Preliminary ^1H n.m.r. data for (III) are also consistent with the presence of two types of co-ordinated DMSO. The single, narrow proton-resonance obtained at 80° in nitromethane or perdeuterioacetonitrile separates into several resonances at $-30°$, indicating the presence of magnetically non-equivalent protons. Upon addition of an excess of DMSO one of the sets of resonances gains in intensity and shifts toward the resonance position for free DMSO, which thus indicates rapid ligand exchange. The other set of n.m.r. resonances is unaffected by addition of an excess of DMSO, and is thus consistent with the presence of two distinctly different types of co-ordinated DMSO.

I.r. spectral studies of (I) and (III) together with the n.m.r. data yield strong evidence for the presence of both sulphur- and oxygen-bonded DMSO in $[Pd(DMSO)_4]^{2+}$. Whether electronic or steric effects induce the mixed donor sites is not yet clear. An *X*-ray structure study now in progress is expected to lead to a better understanding of the bonding and non-bonding interactions in $[Pd(DMSO)_4]^{2+}$.

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