Mode of Binding of Dimethyl Sulphoxide in Platinum(II) and Palladium(II) Cationic Complexes containing a Chelated Diamine. *X*-Ray Crystal Structures of (2,2′-Bipyridyl)chloro(dimethyl sulphoxide-*O*)palladium(II) Tetrafluoroborate and Chloro(dimethyl sulphoxide-*S*)(ethylenediamine)palladium(II) Perchlorate†

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The mode of binding of dimethyl sulphoxide (dmso) in cations of the type $[M(N-N)(dmso)Cl]^+$ [M = Pd or Pt; N–N = 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), or ethylenediamine (en)] has been examined by i.r. and ^1H n.m.r. spectroscopy. Infrared spectra of the complexes in the solid state indicate that dmso binds through oxygen in the palladium(II) adducts containing bipy and phen, and through sulphur in the other cases. Proton n.m.r. spectra in CD_3NO_2 solution show that the complexes in which dmso is S-bonded in the solid state retain their structure in solution, while those containing O-bonded dmso equilibrate to a mixture of O- and S-bonded isomers whose composition depends upon the nature of the chelated diamine. Interconversion between the two isomers is slow on the n.m.r. time-scale, while exchange of S- and O-bonded dmso is fast. The crystal and molecular structures of $[Pd(bipy)(dmso)Cl][BF_4]$, (**1**), and $[Pd(en)(dmso)Cl][ClO_4]$, (**2**), have been determined by *X*-ray diffraction: (**1**) crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, $a = 10.318(1)$, $b = 12.503(1)$, $c = 7.436(1)$ Å, and $\alpha = 95.40(1)$, $\beta = 109.10(1)$, $\gamma = 109.75(1)^\circ$; (**2**) crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$, $a = 9.960(1)$, $b = 8.652(1)$, $c = 14.152(2)$ Å, and $\beta = 92.25(1)^\circ$. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.026$ and 0.024 for (**1**) and (**2**), respectively. The co-ordination geometry of the metal atom is square planar in both cases; in complex (**1**) the dmso ligand is oxygen bonded, while in (**2**) it is sulphur bonded. The geometries of O- and S-bonded dmso differ considerably: in (**2**) the S=O distance, O–S–C and C–S–C angles correspond to the geometry of free dmso; in (**1**) the S=O distance is intermediate between single and double bond lengths, the two O–S–C angles increase by some 7° with respect to S-bonded dmso, while the C–S–C angle increases only by 3.6°.

The co-ordinating properties of sulphoxides present many problems of widepsread interest[1] including those arising from the ambidentate nature of these ligands. In general sulphoxides co-ordinate *via* oxygen to 'hard' metals and *via* sulphur to 'soft' metals unless the complex is crowded. Steric factors, however, are not the sole cause of departure from simple 'hard–soft' rules since, as Davies and Hartley[2] point out, $[Pd(Me_2SO)_4]^{2+}$ would have the *trans*-$[Pd(OSMe_2)_2\{S(O)Me_2\}_2]^{2+}$ configuration rather than the *cis* form observed,[3,4] but there are no reported examples of the d^8 metal ions binding sulphoxide through oxygen in the absence of steric effects.

In this paper we report the mode of binding of dimethyl sulphoxide (dmso) in cations of the type $[M(N-N)(dmso)Cl]^+$ [M = Pd or Pt; N–N = 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), or ethylenediamine (en)] in the solid state and in solution. *X*-Ray structures of $[Pd(bipy)(dmso)Cl][BF_4]$ and $[Pd(en)(dmso)Cl][ClO_4]$, determined in the course of this investigation, are also included.

Experimental

Dipotassium tetrachloroplatinate (II) and palladium(II) chloride were obtained from Johnson Matthey plc; dimethyl sulphoxide, 2,2′-bipyridyl, 1,10-phenanthroline, ethylenediamine, the inorganic salts, and solvents were reagent-grade products. Nitromethane was dried with sodium sulphate and fractionally distilled (conductivity 7×10^{-7} ohm^{-1} cm^{-1} at 25 °C).

Preparation of Complexes.—The complexes $[Pd(N-N)Cl_2]$ (N–N = bipy, phen, or en)[5] and $[Pt(N-N)Cl_2]$ (N–N = bipy or phen)[6] were prepared according to published methods and characterized by their elemental analysis and i.r. spectra. The complexes $[M(N-N)(dmso)Cl][X]$ (M = Pd or Pt; X = BF_4, ClO_4, or PF_6) were obtained by the following procedure: to a suspension of $[M(N-N)Cl_2]$ (typically 0.5 g) in dmso (5 cm^3) a solution of the stoicheiometric amount of Ag[X] in the same solvent (2 cm^3) was added dropwise, with stirring, keeping the mixture in the dark. After 1 d the precipitated AgCl was filtered off and the crude product precipitated with nitromethane–diethyl ether (2:1, v/v). It was recrystallized from a filtered nitromethane solution (10 cm^3) by careful addition of diethyl

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Analytical and conductivity data

Complex	Analysis (%)^a C	H	N	Cl	B^b
$[Pt(bipy)(dmso)Cl][BF_4]$	26.1	2.45	5.10	6.40	184
	(26.1)	(2.55)	(5.10)	(6.45)	
$[Pt(bipy)(dmso)Cl][PF_6]$	23.5	2.35	4.60	5.75	
	(23.6)	(2.30)	(4.60)	(5.80)	
$[Pt(phen)(dmso)Cl][BF_4]$	29.2	2.40	4.85	6.10	207
	(29.2)	(2.45)	(4.85)	(6.15)	
$[Pt(phen)(dmso)Cl][PF_6]$	26.6	2.25	4.40	5.55	
	(26.5)	(2.25)	(4.40)	(5.60)	
$[Pd(bipy)(dmso)Cl][BF_4]$	30.8	2.90	6.10	7.75	160
	(31.1)	(3.05)	(6.05)	(7.65)	
$[Pd(bipy)(dmso)Cl][PF_6]$	27.7	2.45	5.55	6.80	
	(27.7)	(2.70)	(5.40)	(6.80)	
$[Pd(phen)(dmso)Cl][BF_4]$	34.5	2.85	5.75	7.25	165
	(34.5)	(2.90)	(5.75)	(7.30)	
$[Pd(phen)(dmso)Cl][PF_6]$	30.8	2.55	5.10	6.55	
	(30.8)	(2.60)	(5.15)	(6.50)	
$[Pd(en)(dmso)Cl][BF_4]$	13.1	3.85	7.65	9.65	190
	(13.1)	(3.85)	(7.65)	(9.65)	
$[Pd(en)(dmso)Cl][PF_6]$	11.2	3.30	6.60	8.30	
	(11.3)	(3.30)	(6.60)	(8.35)	
$[Pd(en)(dmso)Cl][ClO_4]$	12.5	3.65	7.45	18.8	
	(12.7)	(3.70)	(7.40)	(18.7)	

^{a} Calculated values are given in parentheses. ^{b} From $\Lambda_e = \Lambda_0 - Bc^{\frac{1}{2}}$ with linear regression having $r > 0.99$, $B\ \Omega^{-1}$ dm$^{\frac{3}{2}}$ equiv.$^{-\frac{3}{2}}$, determined in nitromethane solution ($10^{-2} - 10^{-4}$ equiv. dm^{-3}) at 25 °C.

Table 2. Infrared^a and n.m.r.^{b} data

Cation	ν(S=O)/ cm^{-1}	ν(M–Cl)/ cm^{-1}	$\delta(CH_3)$	J(Pt–H)/ Hz
$[Pt(bipy)(dmso)Cl]^+$	1 135	350	3.76	22.8
$[Pt(phen)(dmso)Cl]^+$	1 140	360	3.80	23.3
$[Pd(bipy)(dmso)Cl]^+$	925	366	3.03, 3.69	
$[Pd(phen)(dmso)Cl]^+$	920	364	3.08, 3.78	
$[Pd(en)(dmso)Cl]^+$	1 130	350	3.37	

^{a} Nujol mulls of complexes as hexafluorophosphate salts. ^{b} Solutions in CD_3NO_2 of complexes as tetrafluoroborate salts; internal standard $SiMe_4$, 35 °C.

Table 3. Crystal data^a

Compound	(1)	(2)
Formula	$C_{12}H_{14}BClF_4N_2OPdS$	$C_4H_{14}Cl_2N_2O_5PdS$
M	462.98	379.54
Crystal size (mm)	0.12 × 0.17 × 0.38	0.12 × 0.21 × 0.33
Space group	$P\bar{1}$	$P2_1/n$
a/Å	10.318(1)	9.960(1)
b/Å	12.503(1)	8.652(1)
c/Å	7.436(1)	14.152(2)
α/°	95.40(1)	90
β/°	109.10(1)	92.25(1)
γ/°	109.75(1)	90
U/Å^3	830.2(2)	1 218.6(2)
$F(000)$	456	752
Z	2	4
D_c/g cm^{-3}	1.85	1.87
D_m/g cm^{-3}	1.80	1.82
μ(Mo-K_α)/cm^{-1}	14.3	18.9
Independent reflections	3 618	2 645
Reflections with $I > 3\sigma(I)$	3 018	2 381
Variables (last cycle)	300	192
Final R,R'^b	0.026, 0.035	0.024, 0.036
Final maximum shift/error	0.3	0.1
Largest peak (e Å^{-3}) in the final difference map	0.41	0.3
Weighting scheme (w)	$4F_o^2/[\sigma^2(F_o^2) + (0.03F_o^2)^2]$	$4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
Error in an observation of unit weight, S	1.5	1.4

^{a} Data common to both determinations: graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å; 22 °C; $\theta_{min.}$—$\theta_{max.}$ = 2—27°. ^{b} $R = \Sigma|\Delta F_o|/\Sigma|F_o|$, $R' = (\Sigma w|\Delta F_o|^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$.

ether, washed twice with diethyl ether, and dried *in vacuo* over P_2O_5. The yield was typically 80%. Analytical data are reported in Table 1. Crystals of $[Pd(bipy)(dmso)Cl][BF_4]$, **(1)**, and of $[Pd(en)(dmso)Cl][ClO_4]$, **(2)**, suitable for *X*-ray analysis, were obtained by adding diethyl ether to a concentrated (0.1 mol dm^{-3}) nitromethane solution of the complex until incipient clouding occurred, and the resulting solution was left overnight at room temperature.

Apparatus.—Infrared spectra of Nujol mulls between NaCl or polyethylene (below 600 cm^{-1}) plates were recorded with a Perkin-Elmer 683 spectrophotometer. Proton n.m.r. spectra of CD_3NO_2 solutions, using $SiMe_4$ as internal standard, were recorded with a Varian EM390 spectrometer. Conductance measurements were carried out with a CDM 83 Radiometer Copenhagen conductivity meter and a CDC 334 immersion electrode. Conductivity data are collected in Table 1, i.r. and n.m.r. data in Table 2.

Crystal Structure Determination of Compound (**1**).—Intensity data were collected on a Enraf-Nonius CAD4 diffractometer with monochromated Mo-K_α radiation and ω–2θ scan technique. Cell parameters were obtained from least-squares refinement of the setting angles of 25 centred reflections in the range $7 < \theta < 14°$. Crystal data are reported in Table 3. Intensities were corrected for Lorentz, polarization and absorption (minimum transmission factor, 0.948). Scattering factors and anomalous dispersion parameters were taken from ref. 7. The position of the Pd atom was found by Patterson synthesis and all other non-hydrogen atoms were located in the subsequent Fourier map. All hydrogen atoms were located in the difference Fourier maps carried out after a few cycles of isotropic refinement. Finally, the structure was refined by full-matrix least squares using anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogens. The BF_4^- group was disordered and was treated as a B atom surrounded by two interlocking tetrahedra of F atoms, whose positions were determined from the difference Fourier maps. The occupancy of each F atom was fixed at a value of 0.5. Weights for the last cycle were applied according to the scheme given in Table 3. All calculations were performed by SDP[8] and PARST[9] systems of programs. Final positional parameters[10] are given in Table 4.

Crystal Structure Determination of Compound (**2**).—Intensity data and cell parameters (25 reflections in the range $9 < \theta < 13°$) were obtained by the procedure given for compound (**1**). Intensities were corrected for Lorentz polarization and absorption (minimum transmission factor, 0.872). Crystal data are reported in Table 3.

Table 4. Positional ($\times 10^4$ for non-H, $\times 10^3$ for H atoms) parameters with estimated standard deviations (e.s.d.s) in parentheses for compound (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	4 260.7(2)	3 665.7(2)	1 736.0(2)	F(3)*	718(5)	−1 128(4)	2 805(8)
Cl	6 261.4(7)	3 338.3(8)	1 532(1)	F(4)*	2 793(6)	−591(5)	5 361(8)
S	3 246.3(8)	995.4(6)	−159(1)	F(11)*	380(5)	−2 599(5)	3 490(10)
O	2 960(2)	1 938(2)	949(3)	F(21)*	2 170(9)	−1 385(8)	5 780(10)
N(1)	5 307(2)	5 395(2)	2 725(3)	F(31)*	2 632(4)	−1 672(3)	3 532(7)
N(2)	2 563(2)	4 035(2)	1 951(3)	F(41)*	1 031(6)	−651(3)	4 015(8)
C(1)	4 468(3)	5 939(2)	3 105(3)	H(2)	444(3)	742(2)	407(4)
C(2)	5 050(3)	7 129(3)	3 835(4)	H(3)	693(4)	856(3)	474(5)
C(3)	6 525(4)	7 766(3)	4 164(4)	H(4)	830(3)	743(3)	401(5)
C(4)	7 352(3)	7 229(3)	3 770(5)	H(5)	719(2)	571(2)	272(3)
C(5)	6 741(3)	6 038(3)	3 055(4)	H(7)	217(3)	630(2)	354(4)
C(6)	2 912(3)	5 173(2)	2 688(3)	H(8)	−17(3)	493(2)	267(4)
C(7)	1 877(3)	5 532(2)	3 013(4)	H(9)	−93(3)	295(3)	122(4)
C(8)	447(3)	4 723(3)	2 539(5)	H(10)	102(3)	251(2)	104(4)
C(9)	91(3)	3 587(3)	1 754(5)	H(111)	508(3)	97(3)	230(5)
C(10)	1 177(3)	3 267(2)	1 485(5)	H(112)	413(3)	−28(3)	100(5)
C(11)	4 171(4)	409(3)	1 690(6)	H(113)	372(3)	33(3)	242(5)
C(12)	1 449(4)	−155(3)	−1 112(6)	H(121)	111(3)	−32(3)	−1(4)
B	1 556(4)	−1 516(3)	4 009(5)	H(122)	149(4)	−81(3)	−164(5)
F(1)*	1 829(7)	−1 821(4)	2 492(7)	H(123)	91(3)	7(2)	−197(4)
F(2)*	1 038(4)	−2 295(3)	4 908(5)				

* Occupancy: 0.5.

Table 5. Positional ($\times 10^4$ for non-H, $\times 10^3$ for H atoms) parameters with e.s.d.s in parentheses for compound (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	1 758.6(2)	−2 661.7(2)	238.4(1)	H1(N1)	161(3)	−505(4)	61(2)
Cl(1)	723.9(7)	−4 361.0(9)	−1 282.1(5)	H2(N1)	303(3)	−491(4)	34(2)
S	1 077.4(6)	−688.9(8)	−1 183.9(4)	H1(N2)	334(3)	−64(4)	45(2)
O(1)	−398(2)	−476(3)	−1 247(1)	H2(N2)	221(3)	−87(4)	103(2)
N(1)	2 311(2)	−4 445(3)	636(2)	H(11)	446(3)	−269(3)	123(2)
N(2)	2 722(2)	−1 356(3)	787(2)	H(12)	350(3)	−177(4)	213(2)
C(1)	3 435(4)	−2 400(4)	1 467(2)	H(21)	319(3)	−459(4)	197(2)
C(2)	2 685(4)	−3 843(4)	1 580(2)	H(22)	142(4)	−370(6)	180(3)
C(3)	1 824(3)	1 115(4)	−877(2)	H(31)	156(2)	193(3)	−126(2)
C(4)	1 658(3)	−984(4)	−2 330(2)	H(32)	268(3)	104(3)	−89(2)
Cl(2)	4 649.1(7)	2 335.4(7)	1 194.4(5)	H(33)	154(3)	136(4)	−26(2)
O(2)	3 226(2)	2 177(3)	1 243(2)	H(41)	131(3)	−23(4)	−270(2)
O(3)	5 173(3)	2 646(3)	2 125(2)	H(42)	255(4)	−123(4)	−225(2)
O(4)	5 222(3)	924(3)	880(2)	H(43)	129(4)	−189(5)	−267(3)
O(5)	4 974(3)	3 578(4)	611(2)				

The position of the palladium atom was found by Patterson synthesis and all other non-hydrogen atoms were located in the subsequent Fourier map. All hydrogen atoms were located in the difference Fourier map after a few cycles of isotropic refinement. Finally, the structure was refined by full-matrix least squares using anisotropic thermal parameters for all non-H atoms and isotropic ones for hydrogens. Weights for the last cycle were applied according to the scheme given in Table 3. Final positional parameters are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

Cationic complexes of the type [M(N–N)(dmso)Cl][X], where N–N = bipy, phen, or en when M = Pd^{II} and bipy or phen when M is Pt^{II}, and where X is a non-co-ordinating anion, have been prepared by mixing $[M(N\text{–}N)Cl_2]$ with an equimolar amount of Ag[X] in dimethyl sulphoxide, filtering off the AgCl, and precipitating the complex with a nitromethane–diethyl ether mixture (see Experimental section). These complexes are stable in solution unless there is a competing ligand; they react readily with chloride ion to give the dichloro adducts $[M(N\text{–}N)Cl_2]$.

Dilution conductivity studies (Table 1) indicated that the complexes were 1:1 electrolytes in nitromethane solution having slope values (*B*) from a plot of $(\Lambda_0 - \Lambda_e)$ against $c^{\frac{1}{2}}$ typical for complexes of this ion type.[11]

I.r. Data.—The i.r. spectral studies of sulphoxide complexes have proved useful for the assignment of the co-ordination mode of sulphoxide ligands.[12,13] The S=O stretching mode in free dmso is observed at 1 055 cm^{-1}; co-ordination *via* the sulphur atom is indicated by an increase in the value of ν(S=O), co-ordination *via* the oxygen atom by a decrease. The choice of non-co-ordinating counter ion X was thus important since it may obscure the ν(S=O) region; both the perchlorate (*ca.* 1 080 cm^{-1}) and tetrafluoroborate (*ca.* 1 060 cm^{-1}) ions are adequate to ascertain the presence of O-bonded dmso, whereas the hexafluorophosphate ion, which absorbs at *ca.* 830 cm^{-1}, is transparent across the whole ν(S=O) region. Therefore, after the initial study of the complexes as tetrafluoroborate salts, the $[PF_6]^-$ ion was the preferred choice as counter ion for i.r.

Table 6. Bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex (**1**)

Pd–Cl	2.284(1)	N(1)–C(1)	1.347(4)	C(3)–C(4)	1.334(6)	B–F(2)	1.298(6)
Pd–O	2.024(2)	N(1)–C(5)	1.348(3)	C(4)–C(5)	1.376(5)	B–F(3)	1.282(7)
Pd–N(1)	1.996(2)	N(2)–C(6)	1.354(3)	C(6)–C(7)	1.368(5)	B–F(4)	1.386(5)
Pd–N(2)	2.006(2)	N(2)–C(10)	1.331(3)	C(7)–C(8)	1.381(4)	B–F(11)	1.393(6)
S–O	1.538(3)	C(1)–C(2)	1.378(4)	C(8)–C(9)	1.358(5)	B–F(21)	1.227(8)
S–C(11)	1.773(4)	C(1)–C(6)	1.473(4)	C(9)–C(10)	1.375(5)	B–F(31)	1.337(7)
S–C(12)	1.776(3)	C(2)–C(3)	1.382(5)	B – F(1)	1.303(8)	B–F(41)	1.323(7)
Average C–H	0.89(6)						
Cl–Pd–O	92.49(8)	Pd–N(1)–C(5)	126.3(2)	C(3)–C(4)–C(5)	120.0(3)	F(1)–B–F(4)	110.2(5)
Cl–Pd–N(1)	96.43(8)	C(1)–N(1)–C(5)	118.8(2)	N(1)–C(5)–C(4)	121.2(3)	F(2)–B–F(3)	122.2(4)
Cl–Pd–N(2)	177.27(8)	Pd–N(2)–C(6)	115.1(2)	N(2)–C(6)–C(1)	113.9(2)	F(2)–B–F(4)	109.2(4)
O–Pd–N(1)	170.2(1)	Pd–N(2)–C(10)	125.9(2)	N(2)–C(6)–C(7)	121.0(2)	F(3)–B–F(4)	109.9(4)
O–Pd–N(2)	90.2(1)	C(6)–N(2)–C(10)	119.0(3)	C(1)–C(6)–C(7)	125.2(2)	F(11)–B–F(21)	102.3(6)
N(1)–Pd–N(2)	80.8(1)	N(1)–C(1)–C(2)	121.4(3)	C(6)–C(7)–C(8)	119.4(3)	F(11)–B–F(31)	107.9(4)
O–S–C(11)	104.6(2)	N(1)–C(1)–C(6)	115.2(2)	C(7)–C(8)–C(9)	119.5(3)	F(11)–B–F(41)	111.6(5)
O–S–C(12)	100.8(2)	C(2)–C(1)–C(6)	123.4(3)	C(8)–C(9)–C(10)	118.9(3)	F(21)–B–F(31)	96.7(6)
C(11)–S–C(12)	99.0(2)	C(1)–C(2)–C(3)	118.6(3)	N(2)–C(10)–C(9)	122.2(3)	F(21)–B–F(41)	99.0(6)
Pd–O–S	124.7(2)	C(2)–C(3)–C(4)	120.0(3)	F(1)–B–F(2)	120.1(4)	F(31)–B–F(41)	132.9(4)
Pd–N(1)–C(1)	114.9(2)			F(1)–B–F(3)	82.9(4)		

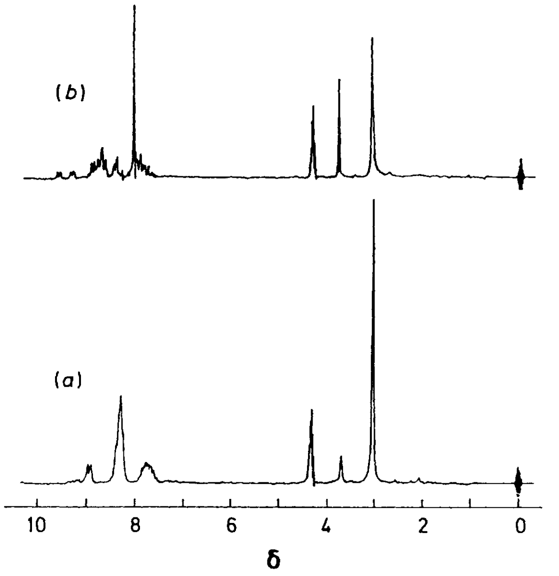

Figure 1. Proton n.m.r. spectra of 0.06 mol dm^{-3} solutions of (*a*) [Pd(bipy)(dmso)Cl][BF$_4$] and (*b*) [Pd(phen)(dmso)Cl][BF$_4$] in CD$_3$NO$_2$ (90 MHz; standard SiMe$_4$)

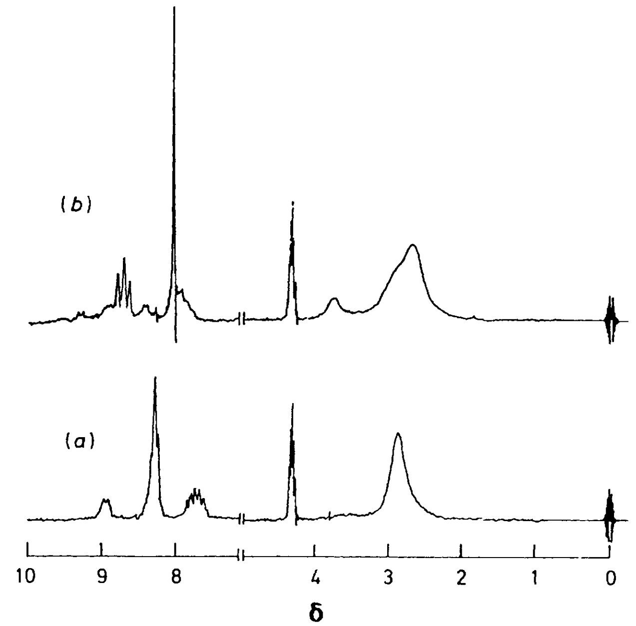

Figure 2. Proton n.m.r. spectra of 0.06 mol dm^{-3} solutions of (*a*) [Pd(bipy)(dmso)Cl][BF$_4$] and (*b*) [Pd(phen)(dmso)Cl][BF$_4$] in CD$_3$NO$_2$ after addition of dmso (*ca.* 2 × 10^{-3} mol dm^{-3})

purposes; significant i.r. data for the complexes we have prepared are reported in Table 2.

Platinum(II) complexes all exhibit strong absorption in the range expected for sulphur-bonded dmso; the same co-ordination mode has also been found in [Pt(en)(dmso)Cl]Cl.[14] In the palladium(II) cations, on the contrary, the bonding site of dmso depends upon the type of chelated diamine; for N–N = en, absorption at 1 130 cm^{-1} indicates S-bonding as in the case of platinum, whereas when N–N is bipy or phen, the S=O stretching mode is observed near 920 cm^{-1} indicating oxygen-bonding {*cf.* bands at 920 and 905 cm^{-1} for O-bonded dmso in [Pd(dmso)$_4$]$^{2+}$,[13] and 950 and 955 cm^{-1} for [Pd(dppe)-(dmso)Cl]$^+$ [dppe = 1,2-bis(diphenylphosphino)ethane]}.[15]

N.M.R. Data.—Proton n.m.r. data for the complexes in CD$_3$NO$_2$ solution are reported in Table 2. Unco-ordinated dmso gives a singlet δ(CH$_3$) at 2.53 p.p.m. relative to SiMe$_4$ whereas sulphur-bonded dmso gives a downfield shift of *ca.* 1.0 p.p.m. and oxygen-bonded dmso a downfield shift of at most 0.5 p.p.m.[1] The n.m.r. spectra of solutions of the platinum complexes show a single methyl proton resonance at *ca.* 1 p.p.m. relative to free dmso with ^{195}Pt satellites; a single resonance at δ 3.37 p.p.m. (relative to SiMe$_4$) is also observed in the spectrum of [Pd(en)(dmso)Cl]$^+$. Therefore it is clear that the cationic complexes in which dmso is sulphur-bonded in the solid state retain their structure in nitromethane solution. The spectra of palladium complexes with N–N = bipy and phen, on the other hand, show two peaks attributable to co-ordinated dmso (Figure 1); the integration ratio of the sum of these two peaks with the area under the diamine multiplet is 6:8 as required by

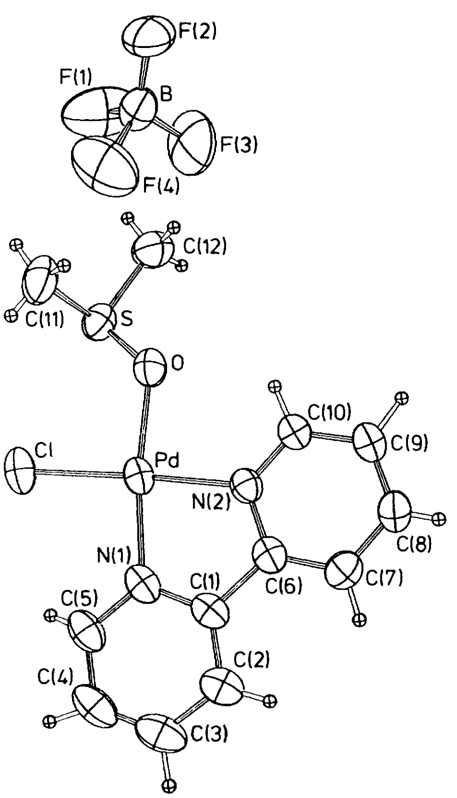

Figure 3. An ORTEP view of [Pd(bipy)(dmso)Cl][BF_4] (**1**) with the atomic numbering scheme

the stoicheiometry. This is consistent with a mixture of O-bonded ($\delta \approx 3$) and S-bonded ($\delta \approx 3.7$) isomers of [Pd(N–N)(dmso)Cl]$^+$. At 35 °C the ratio between the concentration of S- and O-bonded forms is 0.14 and 0.3 for the bipy and phen adduct respectively. Addition of small amounts of $(CH_3)_2SO$ causes broadening of both dmso resonances (Figure 2). It is therefore concluded that the palladium complexes, which exist as the O-bonded forms in the crystalline solid, rapidly form a mixture of O- and S-bonded isomers on dissolving in nitromethane, the O-bonded form predominating. Although the solution has time to equilibrate before the n.m.r. spectrum can be measured, interconversion is slow on the n.m.r. time-scale at room temperature, as is the case for [Pd(dmso)$_4$]$^{2+}$,[16] but, in contrast to this system, addition of free dmso (in the lowest concentration used, only *ca.* 0.3 mol per mol of complex) causes rapid exchange of all sulphoxides.

Structure of Compounds (**1**) *and* (**2**).—ORTEP[17] views for compounds (**1**) and (**2**) are shown in Figures 3 and 4 respectively, bond distances and angles in Tables 6 and 7.

Crystal (**1**) consists of [Pd(bipy)(dmso)Cl]$^+$ cations and disordered [BF_4]$^-$ anions. The square-planar co-ordination of the Pd atom is slightly deformed, the maximum displacement from the weighted least-squares plane through N(1), N(2), O, Cl atoms being 0.048 Å. The Pd atom is at a distance of 0.025 3(2) Å from this plane and thus lies almost perfectly on it. The 2,2′-bipyridyl ligand is essentially planar, the torsion angle N(1)–C(1)–C(6)–N(2) being −1.1(4)° and the angle between the two pyridyl rings 1.72(8)°. The average plane through the bipy ligand makes an angle of 4.01° with the plane of the four square-planar ligand atoms. The packing is controlled mainly by short F, Cl, O • • • H inter- and intra-molecular contacts.

Table 7. Bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex (**2**)

Pd–Cl(1)	2.299 1(8)	N(1)–C(2)	1.468(4)
Pd–S	2.256 7(7)	N(2)–C(1)	1.481(4)
Pd–N(1)	2.040(3)	C(1)–C(2)	1.467(5)
Pd–N(2)	2.048(3)	Cl(2)–O(2)	1.428(2)
S–O(1)	1.471(2)	Cl(2)–O(3)	1.423(3)
S–C(3)	1.775(3)	Cl(2)–O(4)	1.426(3)
S–C(4)	1.762(3)	Cl(2)–O(5)	1.401(3)
Average N–H	0.89[9]	Average C–H	0.99[10]
Cl(1)–Pd–S	89.20(3)	C(3)–S–C(4)	101.7(1)
Cl(1)–Pd–N(1)	90.54(8)	Pd–N(1)–C(2)	109.7(2)
Cl(1)–Pd–N(2)	173.62(8)	Pd–N(2)–C(1)	108.9(2)
S–Pd–N(1)	178.03(6)	N(2)–C(1)–C(2)	110.9(3)
S–Pd–N(2)	97.15(8)	N(1)–C(2)–C(1)	108.4(2)
N(1)–Pd–N(2)	83.1(1)	O(2)–Cl(2)–O(3)	107.6(2)
Pd–S–O(1)	113.91(8)	O(2)–Cl(2)–O(4)	110.0(2)
Pd–S–C(3)	114.0(1)	O(2)–Cl(2)–O(5)	110.8(2)
Pd–S–C(4)	109.5(1)	O(3)–Cl(2)–O(4)	108.3(2)
O(1)–S–C(3)	108.1(2)	O(3)–Cl(2)–O(5)	108.4(2)
O(1)–S–C(4)	108.9(1)	O(4)–Cl(2)–O(5)	111.6(2)

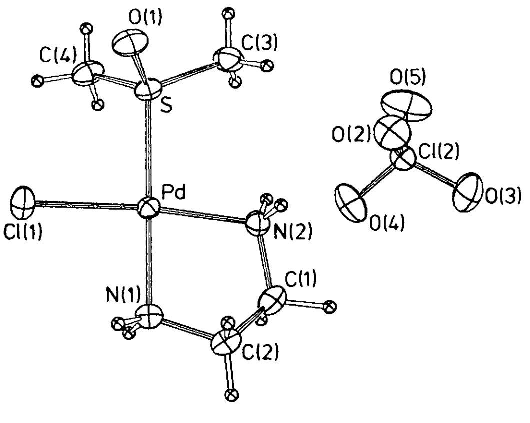

Figure 4. An ORTEP view of [Pd(en)(dmso)Cl][ClO_4] (**2**) with the atomic numbering scheme

The crystal of (**2**) is built up of [Pd(en)(dmso)Cl]$^+$ cations and [ClO_4]$^-$ anions. The co-ordination around palladium is square planar; N(1), N(2), S, and Cl(1) are displaced from the least-squares plane passing through them by not more than 0.023 Å and the Pd atom is at a distance of 0.023 6(4) Å from the plane. The ethylenediamine ligand shows a twisted conformation, of approximate C_2 symmetry. The relative torsion angles are: Pd–N(1)–C(2)–C(1) −39.5(3); Pd–N(2)–C(1)–C(2) −33.9(3); and N(1)–C(2)–C(1)–N(2) 48.7(4)°. The molecules are held together by van der Waals interactions and hydrogen bonds, involving the amine protons.

As was inferred from the i.r. spectra, the mode of co-ordination of dmso differs in the two complexes. In (**1**) the ligand is co-ordinated *via* the oxygen atom, while in (**2**) it displays the usual S-co-ordination. The Pd–S bond in the ethylenediamine complex is remarkably stronger than the Pd–O bond in (**1**) as can easily be shown by comparing covalent radii of the ligands (1.04 for S, and 0.74 Å for O) with the actual bond distances [Pd–S 2.256 7(7) and Pd–O 2.024(2) Å]; the covalent radius of Pd is some 1.22 Å in the Pd–S bond and considerably longer (1.28 Å) in the Pd–O bond according to the previous considerations.

The geometries of O- and S-co-ordinated dmso differ

Table 8. Selected bond distances (Å) and angles (°) for Pd^{II}–O-dmso or Pd^{II}–S-dmso complexes

Complex	Pd–O	Pd–O–S	Pd–S	Pd–S–O	S=O	O–S–C	C–S–C	Ref.
$[Pd(bipy)Cl(dmso\text{-}O)]^+$	2.024(2)	124.7(2)			1.538(3)	104.6(2) 100.8(2)	99.9(2)	p.w.
$[Pd(dmso\text{-}O)_2(dmso\text{-}S)_2]^{2+}$	2.061(9)	124.7(6)			1.531(10)	101.5(10) 103.0(7)	100.3(11)	4
	2.065(10)	119.1(6)			1.573(11)	101.1(9) 103.1(9)	98.9(11)	
			2.240(4)	118.8(5)	1.460(13)	109.6(9) 109.8(9)	101.7(10)	
			2.249(4)	112.8(5)	1.461(13)	109.4(9) 108.7(7)	104.2(10)	
$[Pd(en)Cl(dmso\text{-}S)]^+$			2.257(1)	113.9(1)	1.471(2)	108.9(1) 108.1(2)	101.7(1)	p.w.
$[PdLCl_2]^a$			2.199(6)	115.8(6)	1.495(14)	109.6(9) 109.2(10)	104.9(10)	*b*
$[Pd(dmso\text{-}S)_2Cl_2]$			2.299(5)	114.7(2)	1.461(5)	107.8(3) 107.9(3)	102.1(3)	20

p.w. = Present work.

[a] L = $MeS(O)CH_2CH(NH_2)CO_2H$. [b] A. Allain, M. Kubiak, B. Jezowska-Trzebiatowska, H. Kozlowski, and T. Glowiak, *Inorg. Chim. Acta*, 1980, **46**, 127.

considerably (Table 8). In dmso-*S* the S=O distance, O–S–C and C–S–C angles average to 1.47(1) Å, 102(1) and 99.4(8)° respectively, which practically correspond to the geometry of free dmso.[18] The group displays an approximate C_3 symmetry as far as the bond angles alone are concerned and the S=O distance is that of a pure double bond showing that co-ordination through the S lone pair does not affect significantly the geometry of the ligand itself. In dmso-*O* the S=O distance [on average 1.55(2) Å] is significantly longer and intermediate between single (1.66 Å) and double (1.47 Å) bond lengths, according to an increased contribution of the polar form $(CH_3)_2S^+–O^-$ in O-co-ordination. The shift of electron density towards the O atom should decrease the angular space occupied by the sulphur lone pair (valence shell electron pair repulsion VSEPR theory[19]) allowing a flattening of dmso. Accordingly the two O–S–C angles [on average 108.9(7)° in O-bonded dmso] increase by some 7° with respect to S-bonded dmso while the C–S–C angle [on average 103(1)°] increases only by 3.6°.

Comparison of Pd–N distances [2.040 *trans* to S-dmso, 2.048 Å *trans* to Cl^- in (**2**); 1.996 *trans* to dmso-*O*, 2.006 Å *trans* to Cl^- in (**1**)] shows that the *trans* influence exerted by both S- and O-bonded dmso on nitrogen is weak and of the order of magnitude of that exerted by Cl^-. The mutual effects of the two *trans* dmso-*S* groups can be seen in the structure of $[Pd(dmso)_2Cl_2]$[20] where the Pd–S distance is 2.299 Å, which is 0.042 Å longer than in (**2**), where the *trans* atom is a nitrogen. Relative effects of S- and O-bonded dmso are observed in the structure of $[Pd(dmso\text{-}O)_2(dmso\text{-}S)_2]^{2+}$;[4] taking Pd–S and Pd–O distances found in (**1**) and (**2**) as references, the *trans* S–Pd–O arrangement causes a small shortening of the Pd–S distances (*ca.* −0.012 Å) and a lengthening of the Pd–O ones by +0.039 Å in agreement with the hard–soft acid–base principles.[21]

Conclusions

The question arises as to why the binding mode of dmso in cationic complexes of the type $[M(N\text{–}N)(dmso)Cl]^+$ depends upon the nature of M (Pt or Pd) and of the chelated diamine. The analysis of the molecular geometries of the bipy (O-bonded) and en (S-bonded) palladium complexes does not suggest any specific bonding consideration able to explain the different co-ordination mode of dmso. Steric factors would seem to control the ligand binding by means of the overcrowding of the basal plane produced by bipy with respect to the out-of-plane distorted en ligand in connection with the relevant angular space occupied by the almost conical dmso in its S-co-ordination [external Cl(1)–Pd–N(2) angle 186.4(1)°]. Nevertheless, the very fact that dmso binds through sulphur in the platinum cations with N–N = bipy and phen, and through oxygen in the palladium analogues, rules out the possibility of repulsion, between the N–N ligand and dmso, being large enough to cause the change of the co-ordination mode. *trans*-(*O*,*S*)-Chloro(dimethyl sulphoxide)(pyridine-2-carboxylato)platinum(II), in which sulphoxide is bound through sulphur,[22] shows no short non-bonding interactions between dmso and the pyridyl group; indeed the Pt–S bond is the shortest ever observed in this type of complexes. The difference in the radii of Pd^{II} and Pt^{II} (some 0.04 Å in square-planar complexes[23]) is not large enough to account for the change in behaviour from Pd to Pt either.

A possible explanation of our findings is that S-bonding in dmso is stabilized, with respect to O-bonding, by metal-to-sulphur π back donation. A transition from S- to O-bonded dmso may therefore be expected if (*i*) the π-acceptor capacity of the N–N ligand is increased, and (*ii*) the electron-withdrawing ability of the metal ion increases.

There are reports in the literature which indicate that the electron-withdrawing ability of palladium is higher than that of platinum; moreover it is known that bipy and phen, when co-ordinated to a transition-metal ion, are capable of forming relatively strong π back bonding, this tendency being greater for the former ligand.[24]

Similar arguments have been made by some authors[25] to account for the observation of linkage isomers in thiocyanate complexes of palladium and platinum, although in that case both the $[Pt(bipy)(NCS)_2]$ and $[Pd(bipy)(NCS)_2]$ complexes exist as the N-bonded isomers; $[Pd(phen)(SCN)_2]$ exists, however, only as the S-bonded compound.[26]

Finally, we have shown that the palladium complexes in which dmso is O-bonded in the solid state, when dissolved in nitromethane, equilibrate to a mixture of O- and S-bonded isomers whose concentration ratio depends upon the nature of the chelated diamine. The interconversion between the two isomers is slow on the n.m.r. time-scale in the absence of dmso exchange; this fact rather weakens the idea that the low nucleophilicity of sulphoxides, which is consistent with that of oxygen donors, is due to the nucleophile entering by way of its oxygen and then undergoing an intramolecular rearrangement to the S-bonded form.

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