Geometry of Palladium(II) and Platinum(II) Complexes of Diethylchalcogens in Solution †

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Dipole-moment determinations coupled with n.m.r., i.r., and Raman spectroscopic investigations indicate that in solutions of $[ML_2X_2]$ ($L = SEt_2$, $SeEt_2$, or $TeEt_2$; M = Pd or Pt; X = Cl, Br, or I) the *trans* geometry predominates, often exclusively. The telluro-complexes $[PdCl_2(TeEt_2)_2]$, $[PtCl_2(TeEt_2)_2]$, and $[PtBr_2(TeEt_2)_2]$ are isolated as the *cis* isomers in the solid state, but rapidly isomerize to their *trans* forms in solution. The trend towards *trans* geometry in solution increases along the series Pt < Pd, Cl < Br < I, and S < Se < Te in these complexes.

CONSIDERABLE effort has been spent on synthesizing and identifying *cis* and *trans* isomers of neutral halogeno-complexes $[ML_2X_2]$ (M = Pd or Pt; X = halogeno). In particular, the recognition of which isomers are present in solutions is of general concern. N.m.r. spectrometry has greatly alleviated the problem for phosphine complexes of the type $[M(PR_3)_2X_2]$ since the discovery of ' virtual coupling ' of mutually *trans* phosphorus atoms and its relation to P–P coupling constants.[1] No suitably abundant magnetic isotopes exist amongst the chalcogen (Group 6B) elements, however, so structural assignments on complexes of SR_2, SeR_2, and TeR_2 are somewhat more difficult. Most assignments that have been made are based on solid-phase i.r. spectrometry or solution dipole-moment determinations, although ^{195}Pt chemical-shift determinations offer an alternative method for complexes of platinum, particularly if both isomers can be obtained.[2] In general, however, data are incomplete, and discrepancies between physical and spectroscopic properties are not uncommon.[3]

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† No reprints available.

[1] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770; R. J. Goodfellow and B. F. Taylor, *J.C.S. Dalton*, 1974, 1676.

[2] W. McFarlane, *J.C.S. Dalton*, 1974, 324.

[3] J. R. Allkins and P. J. Hendra, *J. Chem. Soc.* (*A*), 1967, 1325.

TABLE 1

Complex	I.r. spectra (cm^{-1}),[a] ν(M–X)	Raman spectra (cm^{-1}),[b] ν(M–X)	μ/D	M.p. (θ_c/°C)
[PtCl$_2$(SEt$_2$)$_2$]	343 (342) [c]	330	2.4 [d]	93—100 (107—108) [e]
[PtBr$_2$(SEt$_2$)$_2$]	239 (253) [c]	204	2.3 [d]	125—127 (128—129) [f]
[PtI$_2$(SEt$_2$)$_2$]	190	148	2.4 [d]	130—134 (139—140) [f]
[PtCl$_2$(SeEt$_2$)$_2$]	339 (337) [c]	328	2.4 [d]	55—59 (55—60) [f]
[PtBr$_2$(SeEt$_2$)$_2$]	245 (241) [c]	207		77—79 (75) [f]
[PtI$_2$(SeEt$_2$)$_2$]	206 or 177	151		91—94
[PdCl$_2$(SEt$_2$)$_2$]	361 (358),[g] (357) [h]	305	2.2 [d]	79—81 (81) [i]
[PdBr$_2$(SEt$_2$)$_2$]	271 (270) [h]	189		98—103 (98—103) [i]
[PdI$_2$(SEt$_2$)$_2$]	(185) [h]			
[PdCl$_2$(SeEt$_2$)$_2$]	356	300	2.2	43—44 (43—44) [i]
[PdBr$_2$(SeEt$_2$)$_2$]	269	190	1.9	65—67 (167) [i]
[PdI$_2$(SeEt$_2$)$_2$]	218 (220) [h]	137	2.1	57—61 (60) [i]
cis-[PtCl$_2$(SEt$_2$)$_2$]	329, 316 (330, 318) [c]		9.5 [d]	100—107 (107—108) [e]

[a] Nujol mulls. [b] In PhCl solution. [c] Ref. 10. [d] Ref. 12. [e] G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, 1960, **6**, 211. [f] Ref. 6*b*. [g] G. E. Coates and C. Parkins, *J. Chem. Soc.*, 1963, 421. [h] J. E. Fergusson and K. S. Loh, *Austral. J. Chem.*, 1973, **26**, 2615. [i] Ref. 6*a*.

During the course of our investigations into chalcogen-atom inversion [4] and ligand exchange [5] in complexes [MX$_2$(ZEt$_2$)$_2$] (Z = S, Se, or Te; M = Pd or Pt; X = Cl, Br, or I) we required to identify the geometry of these complexes in solution, and determined the dipole moments of some of the more troublesome species. We report our findings here.

TABLE 2

Complex	Colour	M.p. (θ_c/°C)	I.r. spectra (cm^{-1}), ν(M–X)	Raman spectra (cm^{-1}), ν(M–X)	μ/D
[PtCl$_2$(TeEt$_2$)$_2$]	Brown-yellow	126—129 (126—127) [a]	310, 304, 282 (302, 282) [b]		2.3 (6.0) [c]
[PtBr$_2$(TeEt$_2$)$_2$]	Brown-yellow	127—128 (125—127) [b]	218, 210 (217, 208) [b]	203	1.9
[PtI$_2$(TeEt$_2$)$_2$]	Maroon	87—89	200 or 135	153	1.8
[PdCl$_2$(TeEt$_2$)$_2$]	Maroon	97—99	298, 275	300	1.8
[PdBr$_2$(TeEt$_2$)$_2$]	Maroon	110—112	259	190	1.8
[PdI$_2$(TeEt$_2$)$_2$]	Black	87—89		160	1.9

[a] Ref. 6*a*. [b] Ref. 10. [c] Ref. 14.

EXPERIMENTAL

Complexes were prepared by standard methods [6] and recrystallized from ethanol. Satisfactory C and H analyses were obtained for all compounds. Far-i.r. spectra were recorded on an Intek FTC spectrometer as Nujol mulls on Rigidex discs. Raman spectra in chlorobenzene solution were obtained on a Spex Ramalog (Kr and Ar ion laser) instrument. ^{1}H N.m.r. spectra were recorded at 60 MHz on a Jeol C60 HL spectrometer.

Dipole-moment Determinations.—These were at room temperature in benzene solution (concentration range 0.015—0.029 mol dm^{-3}) by the dielectric-constant–refractive-index method,[7] using a Universal TF2700 bridge and variable condenser to measure capacitance and an Abbe refractometer to measure refractive indices. Densities were determined by weighing aliquot portions (10 cm^3) of solution. The results are presented in Tables 1 and 2, together with literature values for related complexes. The standard deviation was calculated to be $\pm$0.5 D,* the error arising mainly from the capacitance measurements. Multiple redeterminations for some complexes, however, showed a spread of values of 0.4 D, and the value obtained for *cis*-[PtPh$_2$(PPh$_3$)$_2$] (7.3 D) compares well with the literature value of 7.2 D.[8] The values of the dipole moments for all the ZEt$_2$ complexes are *ca.* 2.0 D, indicating *trans* structures. The non-zero values reflect the large atom polarizations commonly found in complexes of this type {*trans*-[Pt(C$_6$H$_4$Me-*o*)$_2$(TeEt$_2$)$_2$], μ = 2.5 D},[9] rather than the presence to a *cis* isomer in solution.

RESULTS AND DISCUSSION

Thio- and Seleno-complexes.—Both *cis* and *trans* isomers have been isolated as solids for platinum complexes with Cl or Br as halogens (X),[6b] and ν(Pt–X) bands have been listed.[10] The iodo-complexes of Pt^{II}, however, and all those of palladium, seem generally restricted to the *trans* isomer. Thus the palladium(II) series with both ZEt$_2$ [6a] and ZMe$_2$ [3] are incomplete, and geometry assignments are accordingly less certain. A crystal-structure analysis on [PdCl$_2$(SeEt$_2$)$_2$] established a *trans* geometry with a centre of symmetry.[11]

Dipole-moment measurements have been reported for both *cis* and *trans* isomers of [PtCl$_2$(SEt$_2$)$_2$], [PtBr$_2$(SEt$_2$)$_2$], and [PtCl$_2$(SeEt$_2$)$_2$] in benzene,[12] although it was noted that the dielectric constants of the solutions of the *cis* isomer changed with time, most markedly for the seleno-complexes. Also, both *cis* and *trans* isomers of a number of platinum(II) complexes of SMe$_2$, SEt$_2$,

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* 1 D ≈ 3.33 × 10^{-30} Cm.

[4] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Chem. Comm.*, 1974, 207.

[5] R. J. Cross, T. H. Green, R. Keat, and J. F. Patterson, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 145.

[6] (*a*) Gmelin, vol. 65 (Palladium); (*b*) *ibid.*, vol. 68 (Platinum).

[7] G. J. Moody and J. D. R. Thomas, 'Dipole Moments in Inorganic Chemistry,' University Press, Aberdeen, 1971.

[8] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.

[9] S. Sergi, F. Faraone, and L. Silvestro, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 869.

[10] D. M. Adams, J. Chatt, J. Gerratt, and A. P. Westland, *J. Chem. Soc.*, 1964, 734.

[11] P. E. Skakke and S. E. Rasmussen, *Acta Chem. Scand.*, 1970, **24**, 2634.

[12] K. A. Jensen, *Z. anorg. Chem.*, 1935, **225**, 97.

$SeMe_2$, and $SeEt_2$ have been detected by ^1H n.m.r. in solution and identified by ^{195}Pt chemical shifts.[2]

With the exception of $[PtCl_2(SEt_2)_2]$, our n.m.r. studies[4,5] revealed only one isomer in solution for the series $[MX_2(ZEt_2)_2]$ in a wide range of solvents. Solutions of *cis*-$[PtCl_2(SEt_2)_2]$ were slowly converted into the *trans* isomer (rapidly at temperatures above **333** K). Moreover, the ^1H n.m.r. coalescence temperatures due to inversion at the pyramidal chalcogen atoms are constant irrespective of the halogen atoms for each of the series $[Pt(SEt_2)_2X_2]$, $[Pt(SeEt_2)_2X_2]$, and $[Pd(SEt_2)_2X_2]$.[4] This indicates strongly that these complexes are all *trans*, since for *cis* isomers the coalescence temperatures are strongly dependent on the halogen atom *trans* to the chalcogen.[13] I.r. and m.p. data for these complexes in the solid state also compare well with literature values for *trans* complexes (Table 1).

For the seleno-complexes $[Pd(SeEt_2)_2X_2]$ the coalescence temperatures do depend on the halogen atoms [**323** (X = Cl), **316** (Br), and **305** K (I)].[4] We find that the dipole moments of these complexes in benzene (Table 1) are all *ca.* 2 D, the usual value arising from atom polarization in such complexes. We conclude, therefore, that these three complexes also adopt a *trans* configuration in solution. The observation of one ν(M–X) band in the Raman spectra of all these complexes, which is not coincident with the corresponding i.r. band, is also in accord with a *trans* geometry in solution (Table 1).

Telluro-complexes.—A sparsity of literature information has led to a misleading situation. Jensen[14] assigned a *cis* configuration to $[PtCl_2(TeEt_2)_2]$ when he determined its dipole moment as 6.0 D, and the detection of two ν(Pt–X) bands in the i.r. spectra of this and its bromide analogue confirmed this geometry in the solid state.[10] The complexes $[PtCl_2(TeMe_2)_2]$ and $[PtCl_2(TePr_2)_2]$[10] also conformed to this geometry, but i.r. and Raman studies on $[PtBr_2(TeMe_2)_2]$, $[PtI_2(TeMe_2)_2]$, and $[PdI_2(TeMe_2)_2]$ suggested *trans* configurations.[3]

Our dipole-moment measurements (Table 2) indicate a *trans* geometry for all six diethyltelluro-complexes in benzene. ^1H N.m.r. examinations again showed the presence of only one isomer in solution for each complex, although a short-lived second isomer of $[PtBr_2(TeEt_2)_2]$ was apparent immediately after dissolving this complex.

The i.r. and Raman spectra of $[PtI_2(TeEt_2)_2]$, $[PdBr_2(TeEt_2)_2]$, and $[PdI_2(TeEt_2)_2]$ are in accord with a *trans* geometry. The presence of two ν(M–X) bands in the i.r. spectra of $[PtCl_2(TeEt_2)_2]$, $[PtBr_2(TeEt_2)_2]$, and $[PdCl_2(TeEt_2)_2]$, however, suggests *cis* complexes in the solid phase (Table 2), although the individual values in the Raman spectra in chlorobenzene are again indicative of *trans* configurations. It thus appears that *cis–trans* isomerization occurs for these three complexes in solution.

Jensen's value of $\mu = 6$ D for $[PtCl_2(TeEt_2)_2]$ is difficult to explain. N.m.r. spectra recorded immediately after dissolution revealed only the *trans* isomer, so it is unlikely that any of the *cis* isomer could persist in solution long enough to affect a dipole determination. Since the amount of complex Jensen obtained in solution was very small, compared to our determination, the possibility of a large error on his part might be considered. It certainly seems that the value of 6.0 D should be treated with caution, as should any derivations therefrom. (Pluščec and Westland[15] calculated Pt–$TeEt_2$ group moments from Jensen's value).

Conclusions.—Although *cis* and *trans* isomers might be obtained for some of these complexes in the solid phase, in solution the *trans* isomers predominate (often exclusively) and isomerizations to produce them seem facile. The tendency towards forming *trans* isomers, in solution at least, follows the orders Pd > Pt, Te > Se > S, and I > Br > Cl.

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