Fast Exchange between Free and Co-ordinated Ligands in Bis(diethyl chalcogen)dihalogeno-palladium(II) and -platinum(II) Complexes†

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Variable-temperature n.m.r. spectra show that on addition of free ZEt_2 to $[MX_2(ZEt_2)_2]$ (Z = S, Se, or Te; M = Pd or Pt; X = Cl, Br, or I) exchange between free and co-ordinated ligand is fast in each case except for SEt_2–$[PtX_2(SEt_2)_2]$. The rate of exchange decreases in the orders $TeEt_2 \gg SeEt_2 > SEt_2$ and Pd > Pt. Coalescences due to chalcogen inversion are quite distinct from the exchange coalescences in the systems SEt_2–$[PdX_2(SEt_2)_2]$ and $SeEt_2$–$[PtX_2(SeEt_2)_2]$. This shows for the first time that sulphur inversion in the palladium complexes is not an association–dissociation process.

TEMPERATURE variations in the n.m.r. spectra of *trans*-$[MX_2(ZEt_2)_2]$ (Z = S, Se, or Te; M = Pd or Pt; X = Cl, Br, or I) have been described.[1] For the sulphide and selenide complexes of platinum, retention of $^3J(^{195}Pt-^1H)$ above the coalescence temperatures confirmed unambiguously that the fluxional processes were inversion at the pyramidal chalcogen atoms. For the other systems, however, ligand dissociation–recombination processes could not be ruled out, although the solvent- and concentration-independence of the coalescences observed were more in keeping with pyramidal inversion.

We describe here the effects on the n.m.r. spectra of adding free ligand to certain of these systems. Preliminary results have been published.[2]

RESULTS AND DISCUSSION

The behaviour of each of the systems *trans*-$[MX_2(ZEt_2)_2]$ with free ZEt_2 falls into one of three categories. These are described in turn.

(1) *trans*-$[PtCl_2(SEt_2)_2]$.—The presence of free diethyl sulphide had no effect on the spectra of this complex. Thus the A_2M_3 system of the free ligand was observed alongside and partly overlapping the signals of *trans*-$[PtCl_2(SEt_2)_2]$ at all concentrations achieved (up to *ca.* 0.5 mol dm^{-3} of each component) in either $CDCl_3$ or PhCl. The inversion coalescence of the complex was unaffected within experimental error (±4 °C). No signals due to the *cis* isomers were observed, and conductivity measurements ruled out the presence of appreciable amounts of species such as $[PtCl(SEt_2)_3]Cl$.

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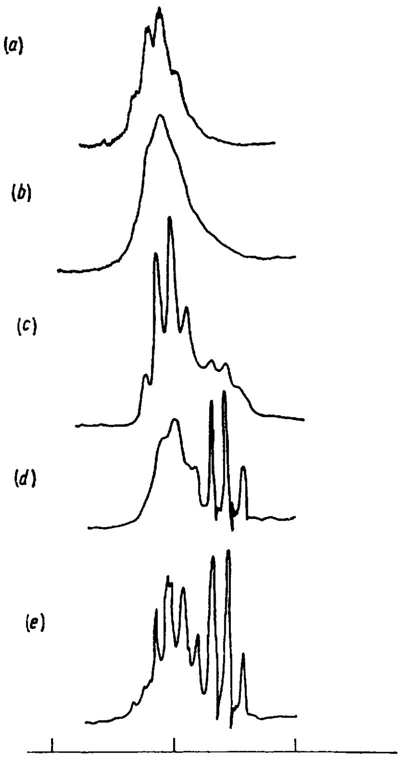
† No reprints available.

[1] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Dalton*, 1976, 1150.

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

These results indicate that exchange between free and co-ordinated ligand is not fast on the n.m.r. time scale.



Methylene proton signals for SEt_2 (0.180 mol dm^{-3}) and $[PdBr_2(SEt_2)_2]$ (0.128 mol dm^{-3}) in $CDCl_3$ at 373 (*a*), 333 (*b*), 315 (*c*), 245 (*d*), and 223 K (*e*)

This is perhaps surprising in view of the number of analogous phosphine complexes for which such exchange is observed.[3] Sulphides are readily displaced from Pt^{II} by tertiary phosphines. No rapid exchange was reported for the analogous system $[PtCl_2(SMe_2)_2]$–SMe_2.[4]

System	Concentration/mol dm^{-3} Ligand	Complex	T_c^1 [a] K	T_c^2 K
SEt_2–$[PtCl_2(SEt_2)_2]$ [b]	0.517	0.495	276 (279) [c]	>363
SEt_2–$[PdCl_2(SEt_2)_2]$ [d]	0.011	0.045	239 (249)	>363
	0.022	0.045	236	363
	0.089	0.045	239	343
	0.089	0.129	247	333
	0.180	0.129		330
SEt_2–$[PdBr_2(SEt_2)_2]$ [d]	0.090	0.128	239 (245)	353
	0.180	0.128		339
$SeEt_2$–$[PtCl_2(SeEt_2)_2]$ [e]	0.366	0.121	363 (363)	403
	0.549	0.121	>351	398
$SeEt_2$–$[PtBr_2(SeEt_2)_2]$ [e]	0.544	0.145	>351 (363)	413
	0.816	0.145	363	398
$SeEt_2$–$[PdBr_2(SeEt_2)_2]$ [b]	0.103	0.138	(316)	293
	0.206	0.138		286
	0.309	0.138		282
$TeEt_2$–$[PtI_2(TeEt_2)_2]$ [e]	0.359	0.181	(392)	<263
	0.060	0.163		<263
	<0.012	0.136		271
$TeEt_2$–$[PdBr_2(TeEt_2)_2]$ [b]	<0.019	0.160	(291)	<263

[a] Temperatures listed are the midpoints of the ranges over which no structure was resolved for the signal in question. [b] In PhCl. [c] Value in parentheses is for no added ligand. [d] In $CDCl_3$. [e] In $CHCl_2$–$CHCl_2$.

(2) *trans*-$[PdCl_2(SEt_2)_2]$, *trans*-$[PdBr_2(SEt_2)_2]$, *trans*-$[PtCl_2(SeEt_2)_2]$, *and trans*-$[PtBr_2(SeEt_2)_2]$.—In each case the low-temperature spectrum of the metal complex was unaffected by the presence of free ligand up to and beyond the coalescence temperatures reported.[1] Free-ligand signals were discernible alongside and overlapping those of the complex (Figure). At higher temperatures, however, a second coalescence was observed, this time involving both free and co-ordinated ligand. Above this temperature, signals of a simple A_2M_3 system were apparent. No ^{195}Pt–^1H coupling was found for the platinum complexes above this second coalescence. These high-temperature coalescences were dependent on the concentrations of both the free ligand and complex (Table). We assign them to fast exchange between free and co-ordinated ligands. Higher concentrations of either ligand or complex caused these coalescence temperatures to decrease. This is in accord with an associative mechanism, common for ligand exchanges[3] and replacements[5] in square-planar compounds. Since these high-temperature coalescences were on the whole rather ill defined, accurate investigations into the concentration dependence of the kinetics were not made. A kinetic investigation of the $[PdCl_2(SMe_2)_2]$–SMe_2 system showed first-order dependences on the concentrations of both components, however.[4] (In this case, lack of diastereotopic groups prevented observation of pyramidal inversion.)

The fact that ligand dissociation–recombination processes are quite distinct from the coalescences of the complexes alone confirms that the low-temperature coalescences are associated with pyramidal inversion. This was not in doubt for these platinum complexes,[1] but this is the first unequivocal proof of sulphur inversion in the palladium derivatives.

(3) *trans*-$[PdBr_2(SeEt_2)_2]$, *trans*-$[PdBr_2(TeEt_2)_2]$, *and trans*-$[PtI_2(TeEt_2)_2]$.—For these systems only one coalescence was observed from their n.m.r. spectra, and this

[3] R. J. Cross and N. H. Tennent, *J.C.S. Dalton*, 1974, 1444.
[4] R. Roulet and C. Barbey, *Helv. Chim. Acta*, 1973, **56**, 2179.
[5] A. Peloso, *Co-ordination Chem. Rev.*, 1973, **10**, 123.

involves both free and co-ordinated ligand (Table). No $^{195}Pt-^{1}H$ coupling was observed above this temperture for the platinum complex. It is thus not possible to rule out the possibility of an associative–dissociative process being responsible for the coalescence in the absence of free ligand (although the spectra may simply reflect a faster exchange than inversion for these complexes).

The effect of free $TeEt_2$ on the telluride complex is striking. The introduction of even the smallest quantities that could be accurately measured lowered the coalescence so much that it could not be observed. The addition of only a trace amount of $TeEt_2$ to $[PtI_2(TeEt_2)_2]$ allowed observation of a coalescence at greatly reduced temperatures, but this was not reproducible, due possibly to decomposition or evaporation of the ligand in the n.m.r. tube. This very marked effect indicates, however, that $TeEt_2$ is not a decomposition product of $[PtI_2(TeEt_2)_2]$, as the coalescence of the complex alone is quite constant, even when decomposition has begun!

These results allow a number of interesting comparisons to be made. First, the ease of exchange between free and co-ordinated ligand is $TeEt_2 \gg SeEt_2 > SEt_2$ for both the palladium(II) and platinum(II) systems. Since bond breaking and bond making should assume equal importance in a symmetrical exchange, the faster rates may reflect stabilisation of the five-co-ordinate intermediates. This could be due to lower basicity of the ligand atoms, or to better π back bonding. In either case the remarkably large effect of $TeEt_2$ is difficult to explain.

Secondly, ligand exchange at Pd^{II} is observed to be faster than at Pt^{II}. This is in accord with the general increased lability of complexes of the lighter atom in associative processes of this type. Thirdly, sulphur inversion in palladium(II) complexes is faster than in related derivatives of Pt^{II}. This has been observed before, although only now has it been shown that the fluxional processes are strictly comparable.

EXPERIMENTAL

N.m.r. spectra were recorded on a JEOL C60HL spectrometer. Complexes were prepared by standard methods, and their geometry has been determined as *trans* in solution.[6]

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[6/180 *Received, 27th January, 1976*]

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[6] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Dalton*, 1976, 382.