Inversion of Configurations at Pyramidal Sulphur, Selenium, and Tellurium in Diethyl Chalcogen Complexes of Platinum(II) and Palladium(II)†

By **Ronald J. Cross,* Thomas H. Green,** and **Rodney Keat,** Chemistry Department, The University, Glasgow G12 8QQ

The variable-temperature n.m.r. spectra of the complexes *trans*-[$MX_2(ZEt_2)_2$] (Z = S, Se, or Te; M = Pd or Pt; X = Cl, Br, or I) indicate that inversion of configuration at the pyramidal chalcogen atoms is a facile process. Retention of $^3J(^{195}Pt-^1H)$ coupling above the coalescence temperatures for the sulphur and selenium complexes, and for *cis*-[$Pt(C_6H_4Me\text{-}4)_2(TeEt_2)_2$], confirms that the dynamic processes are intramolecular for these complexes at least. The chelate complexes [$MX_2(EtSeC_2H_4SeEt)$] show related spectroscopic phenomena, which can be interpreted in terms of single inversions at the selenium atoms. The barriers to inversion are in the order Te > Se > S, and are sensitive to the *trans* influence of the opposite ligands. These barriers are lower than in related pyramidal systems such as sulphoxides or selenoxides, and this may be due to stabilisation of the transition states by the π-acceptor capacity of the metal atoms. The barriers to inversion are less in the palladium complexes than in the analogous platinum derivatives.

INVERSION of configuration at the pyramidal sulphur atoms of complexes of thioethers is a well established phenomenon. Variable-temperature n.m.r. spectrometry has been used to monitor the process for complexes of Pt^{II}, Au^{I}, and Au^{III} with unidentate ligands,[1,2] and for complexes of Pd^{II} and Pt^{II} with chelating ligands.[3-6] We have examined the complexes [$MX_2(ZEt_2)_2$] and [$MX_2(EtSeC_2H_4SeEt)$] (Z = S, Se, or Te; M = Pd or Pt; X = Cl, Br, or I) in order to compare the inversion behaviours of selenium and tellurium with that of sulphur. A preliminary report has been published.[7] The temperature dependence of a few sulphide and selenide complexes of Pd^{II} has been briefly described.[8]

RESULTS AND DISCUSSION

The complexes of the unidentate ligands were examined both in chlorobenzene and in either deuteriochloroform or 1,1,2,2-tetrachloroethane solutions. No solvent dependence was found. The stereochemistry of the complexes in solution was established[9] as *trans* in every case, except [$PtCl_2(SEt_2)_2$] for which both *cis* and *trans* isomers were obtained. Even here the *cis* isomer was slowly converted into the *trans* form at elevated temperatures.

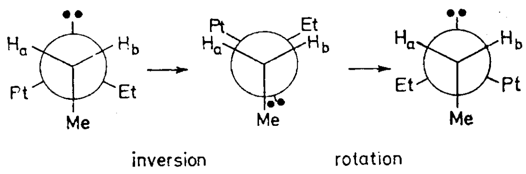
The ^1H n.m.r. spectra analyse at low temperatures as ABM_3 systems for the palladium complexes and as $ABM_3 + ABM_3Y$ systems for those of platinum ($Y = {}^{195}Pt$, 33% abundant, $I = \frac{1}{2}$). Coupling to selenium was not detected. As the temperatures were increased, the methylene regions of the spectra coalesced, and at high temperatures A_2M_3 (or $A_2M_3 + A_2M_3Y$) systems emerged (for figure see ref. 7). Coalescence temperatures for [$MX_2(ZEt_2)_2$] are shown in Table 1. The temperature variations are reversible, although the $TeEt_2$ complexes of Pt begin to decompose above their coalescence temperatures.

The only dynamic process which can bring about the apparent equivalence of the AB protons in these complexes is atom inversion and rotation (Figure). Rotation about the C–Z bonds is likely to be fast on the n.m.r. time scale at all temperatures (the barrier to C–S rotation in SEt_2 has been estimated as *ca.* **7.3** kJ mol^{-1}),[10]

TABLE 1

Complex	Coalescence temperature [a] K	$\Delta G^{\ddagger}$ kJ mol^{-1}	$^3J(^{195}Pt-^1H)$ [b] Hz
cis-[$PtCl_2(SEt_2)_2$]	329	68.2	44
trans-[$PtCl_2(SEt_2)_2$]	279		38
trans-[$PtBr_2(SEt_2)_2$]	277	56.9	39
trans-[$PtI_2(SEt_3)_2$]	275	56.9	42
trans-[$PtCl_2(SeEt_2)_2$]	363	76.2	30
trans-[$PtBr_2(SeEt_2)_2$]	363	76.2	30
trans-[$PtI_2(SeEt_2)_2$]	363	76.2	32
trans-[$PtCl_2(TeEt_2)_2$]	380		
trans-[$PtBr_2(TeEt_2)_2$]	383		
trans-[$PtI_2(TeEt_2)_2$]	378		
trans-[$PdCl_2(SEt_2)_2$]	249		
trans-[$PdBr_2(SEt_2)_2$]	245		
trans-[$PdCl_2(SeEt_2)_2$]	323	67.8	
trans-[$PdBr_2(SeEt_2)_2$]	316	66.9	
trans-[$PdI_2(SeEt_2)_2$]	301	65.7	
trans-[$PdCl_2(TeEt_2)_2$]	303		
trans-[$PdBr_2(TeEt_2)_2$]	324		
trans-[$PdI_2(TeEt_2)_2$]	291		
cis-[$Pt(C_6H_4Me\text{-}4)_2$-($TeEt_2)_2$]	<216		29

[a] Recorded for the methylene protons at **60** MHz in PhCl.
[b] Recorded above the coalescence temperature. Error ±1 Hz.



FIGURE

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† No reprints available.

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so the coalescences reflect the barriers to inversion of configuration. Free energies of activation, $\Delta G^{\ddagger}$, were calculated from K for most complexes using the approximate coalescence-temperature method.* Values are given in Table 1. The accuracy of this approximation is uncertain, as the spin systems are more complex than those for which the formula was designed. The systems are all closely related, however, so comparisons at least seem valid.

The observation that ^{195}Pt–^{1}H coupling is retained above the coalescence point for the Pt–S and Pt–Se systems indicates that ligand dissociation–recombination is not responsible for the spectroscopic temperature variations, and that pyramidal inversion at S or Se is thus operative. High-temperature coupling constants are included in Table 1. The failure to observe such couplings for $[PtX_2(TeEt_2)_2]$ or any of the palladium complexes (Pd has no such convenient magnetic isotope) means that similarly firm conclusions cannot be drawn regarding the fluxional processes of these molecules. The coalescence temperatures appear to be both solvent independent and concentration independent (although a rigorous check on each complex was not made) within experimental error (±5 °C), and this behaviour is compatible with lone-pair inversion at the chalcogen atoms. On the other hand *trans*-$[PdX_2(SeEt_2)_2]$ and *trans*-$[PdX_2(TeEt_2)_2]$ display a range of coalescence temperatures depending on the halogen atoms. Since, for a given metal and chalcogen, the *trans* influence of the ligands opposite the inversion centre has a critical effect on the coalescence temperature,[5] the variations shown by these complexes are difficult to explain in terms of only chalcogen inversion.

The absence of ^{195}Pt–^{1}H coupling in the telluride complexes posed the problem of whether the rate process observed was a genuine tellurium inversion, since, like Se, no cases of Te inversion had previously been reported. As decomposition occurs above the coalescence temperatures, the possibility existed that free $TeEt_2$ was produced, and that this might promote fast ligand exchange. This was discounted, however, as the temperature variations of the n.m.r. spectra were reversible despite formation of metallic mirrors (shown by *X*-ray powder photography to contain tellurium metal) on the n.m.r. tubes. Also, attempts to scavenge any free $TeEt_2$ by addition of $[(PhMe_2P)IPt(\mu\text{-}I)_2PtI(PMe_2Ph)]$ to the solutions of *trans*-$[PtI_2(TeEt_2)_2]$ had no effect. The constancy of the coalescence temperature and the similarity of the values for the different halides of *trans*-$[PtX_2(TeEt_2)_2]$ are both consistent with pyramidal inversion at Te being responsible for the spectroscopic change.

Two new diethyltelluride complexes were prepared in an attempt to observe $^{3}J(^{195}Pt\text{–}^{1}H)$ above the coalescence point. The first, $[(Et_2Te)IPt(\mu\text{-}I)_2PtI(TeEt_2)]$, revealed $ABM_3 + ABM_3Y$ systems at room temperature, but decomposed as the temperature was raised before any coalescence was observed. The other complex, $[Pt(C_6H_4Me\text{-}4)_2(TeEt_2)_2]$, produced spectra consistent with $A_2M_3 + A_2M_3Y$ systems at ambient temperatures. Thus either the tellurium atoms are planar in this complex (unlikely, in view of their pyramidal nature in the halogen complexes thus far encountered), or inversion at Te is rapid and does not involve Pt–Te bond dissociation. Cooling the CD_2Cl_2 solutions to 213 K produced no broadening, setting an upper limit to the coalescence temperature of this complex. Aryl groups are known to markedly increase the rate of inversion at sulphur,[5] presumably because of their high *trans* influence. The apparent similarity of their effect on tellurium inversion suggests that this complex has a *cis* configuration.

The relative barrier to inversion in these complexes is Te > Se > S. The higher barriers for the heavier elements resembles the situation for pyramidal Group 5 compounds,[12] although such an extensive series of structurally similar compounds has not been examined here. A *trans*-effect order of $SEt_2 < SeEt_2 < TeEt_2$ has been assigned[13] for Pt^{II}. If this is correct, the bond weakening, or antisymbiotic,[14] effects in *trans*-$[MX_2(SeEt_2)_2]$ and *trans*-$[MX_2(TeEt_2)_2]$ will, to an extent, counteract the increased barriers to inversion at these chalcogens, and their magnitude in the absence of such effects could be even greater. In order to examine this further, a series of *cis*-chelate complexes, $[MX_2(EtSeC_2H_4SeEt)]$, was prepared. The low-temperature spectra of these complexes were too complicated for complete analysis (overlapping patterns from *meso* and *dl* isomers are expected,[3,5] and the two methyl signals observed are compatible with this), but as the temperatures were increased coalescences were observed (Table 2) and $A_4 + A_2M_3$ systems were apparent at high temperatures. This behaviour is compatible with inversion about single selenium atoms.[5]

TABLE 2

Complex	Coalescence temperature [a]/ K	δ(C_2H_4 bridge) [b]
$[PtCl_2(EtSeC_2H_4SeEt)]$	>453	3.30
$[PtBr_2(EtSeC_2H_4SeEt)]$	423	3.29
$[PtI_2(EtSeC_2H_4SeEt)]$	413	3.26
$[PdCl_2(EtSeC_2H_4SeEt)]$	368	3.53
$[PdBr_2(EtSeC_2H_4SeEt)]$	358	3.57
$[PdI_2(EtSeC_2H_4SeEt)]$	343	3.41

[a] Recorded for the methylene protons of the ethyl groups at 60 MHz in $PhNO_2$. [b] In p.p.m., above the coalescence temperature.

The coalescence temperatures of the chelate complexes are all *ca.* 50 °C higher than those for complexes of the unidentate ligands, and presumably reflect the lower *trans* influences of the halogen atoms. The

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* $K = (\pi/2)\ (6J^2 + \Delta\nu_{AB}{}^2)^{\frac{1}{2}}$.[11]

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relative order of X = Cl > Br > I is also in accord with increasing *trans* influence. Thus, although $^3J(^{195}Pt-^1H)$ coupling was not observed above the coalescence point (the high temperatures involved limited the range available, and prevented us from obtaining high resolution), selenium inversion seems to operate in these complexes also. A report on the coalescence phenomena for the related complex $[PdCl_2(Pr^iSeC_2H_4SePr^i)]$ [15] assigned the fluxional process to conformational changes of the chelate ring. The similar temperatures involved ($T_c = 380$ K), however, suggest that the same process is involved as in our molecules. This report [15] would thus be the first of a fluxional selenium compound assignable to Se inversion.

The inversion barrier at pyramidal selenoxides is high enough to allow resolution of optical isomers,[16] and is clearly much higher than in our transition-metal complexes. A similar disparity exists between sulphide complexes and sulphoxides, and to account for this a mechanism has been proposed [1] which involves intramolecular nucleophilic attack of a sulphur lone pair at the metal atoms. This is not in fact a realistic alternative mechanism to the conventional *p*-orbital tunnelling route,[17] since, applying the Franck–Condon principle, electronic readjustments will be fast compared to the molecular bending modes involved in the inversion. Possibly the lower barriers to inversion in the metal complexes depend on the π-acceptor abilities of the metals to stabilise the planar transition states by delocalising the p_z orbitals of the chalcogen atoms.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on a JEOL C60HL spectrometer. The halogen complexes were prepared by standard methods, and their geometry in solution was shown to be *trans*.[9]

Di-μ-iodo-bis[(*diethyl telluride*)*iodoplatinum*(II)].—To an aqueous solution of $K_2[PtCl_4]$ (1.48 g, 3.58 mmol) was added LiI (5.8 g) under a nitrogen atmosphere. After stirring for 10 min, $TeEt_2$ (0.66 g, 3.56 mmol) was added. The mixture was stirred in the absence of light for 9 d. The brown solid *product* (2.15 g) was filtered off and washed with water. It was recrystallised by dissolution in cold *sym*-tetrachloroethane (500 cm³), reducing the volume to *ca.* 40 cm³, and adding n-heptane, m.p. 160—163 °C (Found: C, 7.50; H, 1.75. $C_8H_{20}I_4Pt_2Te_2$ requires C, 7.55; H, 1.60%).

Bis(*diethyl telluride*)*di*-p-*tolylplatinum*(II).—To a solution of $[PtI_2(TeEt_2)_2]$ (0.81 g, 0.99 mmol) in diethyl ether (200 cm³) was added *p*-tolyl-lithium (8.4 cm³ of an 0.281 mol dm^{-3} solution in diethyl ether, 2.4 mmol) under nitrogen. The initial maroon solution became yellow. Water was added after stirring for 95 h, and the yellow-orange organic layer was separated and dried. The diethyl ether was removed at low pressure, to yield a yellow precipitate of the *product*, m.p. 114—116 °C. An n.m.r. spectrum in CD_2Cl_2 indicated the presence of only one isomer. Recrystallisation from methanol–water produced another isomer (presumably the *trans* form), m.p. 64—65 °C, which resolidified and then melted at 95—100 °C (Found: C, 35.8; H, 5.10. $C_{18}H_{24}PtTe_2$ requires C, 35.3; H, 4.55%).

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