

Nuclear Magnetic Resonance Detection of Ready Inversion at Selenium and Tellurium Bonded to Platinum-group Metals

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Summary N.m.r. coalescence phenomena, unambiguously related to inversion of configuration at selenium and tellurium, have been observed for the first time in complexes of the type $(Et_2X)_2Pt(Hal)_2$ ($X = Se$ or Te); palladium analogues display similar characteristics.

It is well established¹ that the coalescence phenomena detected in the variable temperature (v.t.) 1H n.m.r. spectra of the platinum(II) complexes $(R^1R^2S)_2PtCl_2$ [$R^1R^2 = Me_2, Et_2, (PhCH_2)_2$, or $(PhCH_2)Me$] are associated with inversion of configuration at pyramidal sulphur. Inversion at single sulphur atoms has also been invoked to explain the v.t. n.m.r. characteristics observed for sulphur chelates of

the methylene protons are diastereotopic, forming part of an ABM_3 spectrum with ^{195}Pt satellites. On raising the temperature the signals coalesce ($T_c = +90^\circ C$; $\Delta G^\ddagger = ca.$

TABLE

Compound	Coalescence temperatures ^a		
	Hal = Cl	Hal = Br	Hal = I
$(Et_2S)_2PtHal_2$..	6	4	2
$(Et_2S)_2PdHal_2$..	-24	-28	—
$(Et_2Se)_2PtHal_2$..	90 (76) ^b	90 (76) ^b	90 (76) ^b
$(Et_2Se)_2PdHal_2$..	50 (68) ^b	43	28
$(Et_2Te)_2PtHal_2$..	107	110	105
$(Et_2Te)_2PdHal_2$..	30	51	18
$(EtSeC_2H_4SeEt)PtHal_2$	— ^c	150	140
$(EtSeC_2H_4SeEt)PdHal_2$	95	85	70

^a In $^\circ C$; spectra of monodentate compounds in chlorobenzene and bidentate compounds in nitrobenzene solutions. ^b ΔG^\ddagger /(KJ mol⁻¹) in parentheses; estimated by coalescence temperature method. ^c Decomposition occurred before coalescence was reached.

palladium(II) and platinum(II),² $(RSC_2H_4SR)M(Hal)_2$. Whilst a similar process would be expected in analogous selenium complexes, it has recently been proposed³ that the coalescence of the methylene proton signals in the selenium-containing complex, $(Pr^1SeC_2H_4SePr^1)PdCl_2$, is the result of total chelate ring inversion ($T_c = 107^\circ C$; $\Delta G^\ddagger = ca. 80$ kJ mol⁻¹). In view of these findings, and interest⁴ in the barriers to inversion of the elements of groups V and VI, we report here the results of variable-temperature n.m.r. studies of the complexes, $(Et_2X)_2MHal_2$ ($X = Se$ or Te ; $M = Pd$ or Pt ; $Hal = Cl, Br, \text{ or } I$).

An example is provided by the methylene-proton spectra of $(Et_2Se)_2PtI_2$, which are shown in the Figure. At $-40^\circ C$

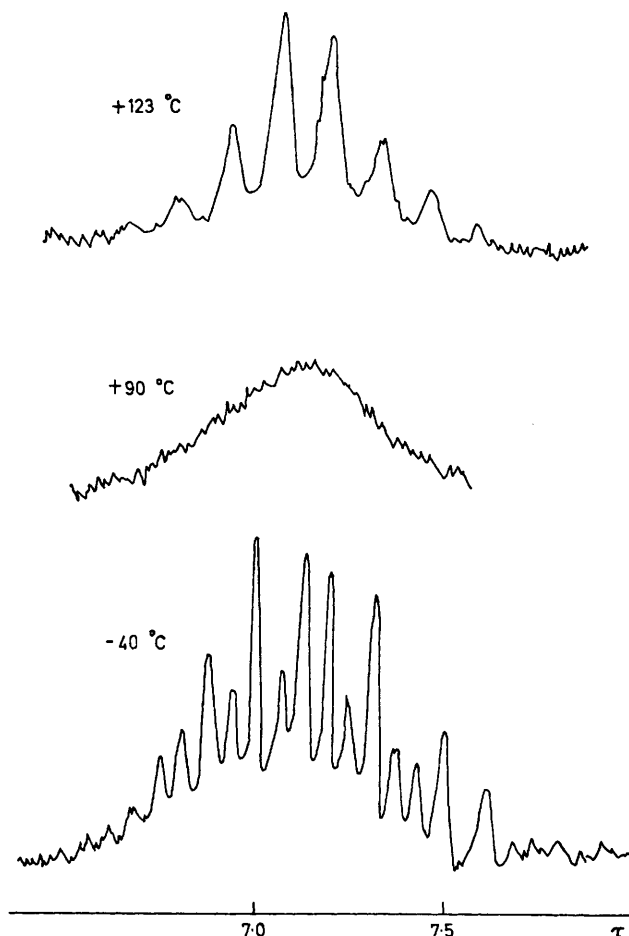


FIGURE. Temperature dependence of the CH_2 signals in the n.m.r. spectrum of $(Et_2Se)_2PtI_2$.

76 kJ mol⁻¹) and at 120 °C and higher the methylene protons appear equivalent with $J(\text{Pt-Se-C-H})=47$ Hz. Retention of Pt-H coupling indicates no dissociation of the Et₂Se ligands from Pt. In the absence of any bond-dissociation process the methylene protons can only appear equivalent as a result of the rapidity of inversion of configuration at selenium on the n.m.r. time-scale.

The v.t. n.m.r. spectra of the other Et₂Se and the Et₂Te complexes, as well as the Et₂S complexes of platinum¹ and palladium (which have not previously been reported), show the same phenomena. Coalescence temperatures are shown in the Table. We cannot rigorously exclude the possibility of a dissociative process causing the coalescence in the palladium derivatives, but there is no evidence at present to suggest that this reflects any process other than inversion at S, Se, or Te.

For all three ligand atoms, the barrier to inversion in the platinum complexes is higher than that in those of palladium. Also, inversion at sulphur seems easier than at selenium or tellurium. A similar increase in the barrier to inversion has been found on descending group v from phosphines to

arsines.⁵ The coalescence temperature is dependent on the other ligands present (see Table), particularly for the palladium derivatives. This may reflect the *trans*-influence of the other ligands (as has been reported for the chelating disulphides^{2a}) but we have not yet confirmed the geometry of these complexes in solution.

Bidentate *cis*-complexes of the diselenide EtSeC₂H₄SeEt (Table) show coalescence phenomena at somewhat higher temperatures than the Et₂Se compounds. The coalescence temperature falls as the *trans*-influence of the halogens increases, and the same relationship between palladium and platinum derivatives is found. Whilst a ring inversion process of the type reported for (Pr¹SeC₂H₄SePr¹)PdCl₂³ may be operative, it is clear that inversion at selenium must merit very serious consideration as a contributing factor to the coalescence phenomena observed for compounds of this type.

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