Dynamic Nuclear Magnetic Resonance Studies of Conformational Changes occurring in 1,4-Oxathian and 1,4-Oxaselenan Complexes of Platinum(II) and Palladium(II) Halides [1]

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The ^{1}H n.m.r. spectra of the complexes [MX_2L_2] [M = Pd or Pt, X = Cl or Br, L = 1,4-oxathian or 1,4-oxaselenan] are temperature dependent and exhibit coalescence phenomena. The spectra are particularly well suited for total band-shape fitting studies, and it has been shown that the observed coalescence phenomena are caused by site inversion about the ligand atom rather than by ring reversal of the cyclic ligand. Thermodynamic parameters are reported for site inversion occurring at co-ordinated sulphur and selenium atoms.

As with most other six-membered heterocycles, 1,4-oxachalcenans can probably exist in a variety of conformations and the energy barriers to their interconversion are such that these processes can be observed by temperature-dependent n.m.r. spectroscopy. Moreover, as there are only four close-coupled protons in the ring system, the most complicated spectrum for an isolated system will be an ABCD multiplet, for which, provided that sufficient lines are resolved, spectral analysis using programs such as LAOCOON3 [2] is quite feasible. Once accurate spectral parameters have been obtained, band-shape fitting programs such as DNMR3,[3] which allow complex spin spectra to be simulated under exchange conditions, can be used to obtain thermodynamic parameters for conformational interconversion processes. Such studies have already been reported for unco-ordinated 1,4-oxathian and -selenan, for which ABCD spectra observed at low temperatures collapse to AA'BB' multiplets as the temperature is increased.[4,5]

We have observed similar collapses of well resolved ABCD spectra to AA'BB' multiplets with increasing temperature in the ^{1}H n.m.r. spectra of the complexes [MX_2L_2] [M = Pd or Pt, X = Cl or Br, L = 1,4-oxathian (oth) or 1,4-oxaselenan (ose)] and now report the results of band-shape fitting studies of these systems.

RESULTS AND DISCUSSION

The complexes [MX_2L_2] were readily prepared by allowing the 1,4-oxachalcenans to react with the appropriate metal(II) halide, and are sufficiently soluble in organic solvents such as CH_2Cl_2, $CHCl_3$, and $PhNO_2$ to enable high-quality ^{1}H n.m.r. spectra to be obtained over a wide temperature range. The collapse of the ABCD spectra to AA'BB' multiplets generally occurred below 300 K for the 1,4-oxathian complexes and above 300 K for their 1,4-oxaselenan analogues. As with the spectra of the free ligands,[4,5] absorptions at lower field were assigned to the protons of the methylene group attached to the oxygen atom, and those at higher field were assigned to protons of the methylene group attached to the co-ordinated heavier chalcogen atom. There was no evidence to suggest that co-ordination occurred *via* the oxygen atom in any of the complexes. In the temperature range examined for band-shape fitting studies (210—410 K), only one coalescence phenomenon was detected. As coalescence in the spectra of the free ligands occurred between 175 and 190 K, attempts were made to examine the spectra of the complexes for a second coalescence phenomenon at these temperatures. The spectra of dichloromethane solutions at 185 K were sufficiently different from those at 200 K to indicate that further major spectral changes were possibly occurring, but as no suitable solvent was available for the complexes at temperatures below *ca.* 180 K these changes could not be confirmed.

In the spectra of the platinum(II) complexes, ^{195}Pt–^{1}H coupling persisted throughout the temperature range examined. Addition of small amounts of free ligand to solutions of the complexes did not noticeably affect their

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[1] Presented in part at the Autumn Meeting of the Chemical Society, University of Reading, September 1975.

[2] A. A. Bothner-by and S. Castellano, Program 111, Quantum Chemistry Program Exchange, Indiana University.

[3] G. Binsch and D. A. Kleier, Program 140, Quantum Chemistry Program Exchange, Indiana University.

[4] J. C. Barnes, G. Hunter, and M. W. Lown, *J.C.S. Perkin II*, 1975, 1354.

[5] F. R. Jensen and R. A. Neese, *J. Amer. Chem. Soc.*, 1975, **97**, 4922.

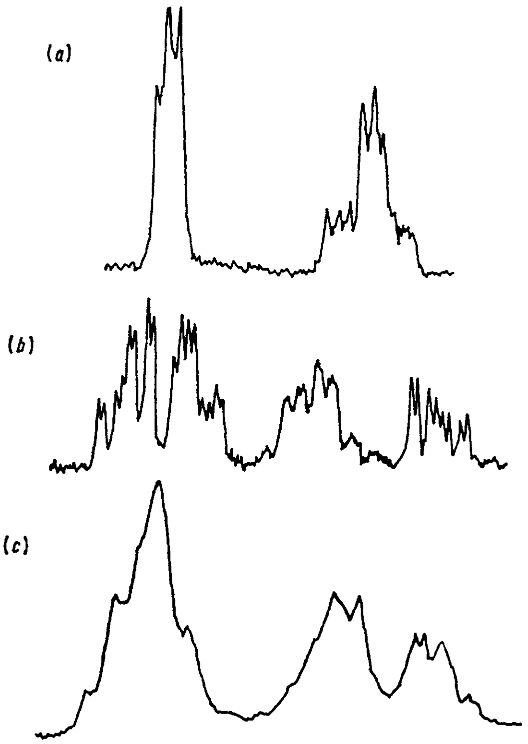

FIGURE 1 90-MHz ^1H n.m.r. spectra of $[PtCl_2(oth)_2]$ at (*a*) 410 (in $PhNO_2$), (*b*) 230 (CD_2Cl_2), and 185 K (CD_2Cl_2)

spectra, and the coalescence phenomenon was therefore considered to be of intramolecular rather than intermolecular origin and moreover does not involve fission of the metal–ligand atom bond.

For all the complexes, ^1H n.m.r. spectra were obtained at both 90 and 220 MHz although, as no control could be exercised over the operation of the 220-MHz spectrometer, band-shape fitting studies were confined to spectra at 90 MHz. Analyses of the ABCD spectra were made with the LAOCOON3 program. Only for $[PdBr_2(oth)_2]$ were insufficient lines resolved at either frequency to preclude reliable spectral analysis, and no band-shape fitting studies were undertaken for this complex. For all the other complexes, spectral parameters obtained from the spectral analyses at 90 MHz satisfactorily generated the 220-MHz spectra, indicating that they are almost certainly correct. In the spectra of the complexes of Pt^{II} additional splitting of the ABCD spectra was caused by heteronuclear coupling with the isotope ^{195}Pt (33.8%), although sufficient high-intensity lines were resolved to allow satisfactory analysis without having to assign any low-intensity lines which could conceivably have arisen from this heteronuclear coupling. No attempt was made to obtain accurate values for $J(^{195}Pt-^1H)$, although the subsidiary fine structure attributable to heteronuclear coupling on the Pt–X–CH_2 absorptions indicated values for $^3J(^{195}Pt-^1H)$ of *ca.* 25 Hz, and the lack of any resolved fine structure on the O–CH_2 absorptions indicated a value for $^4J(^{195}Pt-^1H)$ of less than 2 Hz.

The ABCD spectral parameters are recorded in Table 1. J_{AB} and J_{CD} represent the geminal coupling constants for the OCH_2 and X–CH_2 groups respectively and are substantial and negative as expected for protons attached to sp^3-hybridised carbon atoms; J_{AC}, J_{AD}, J_{BC}, and J_{BD} represent the four vicinal coupling constants, and it can be seen that a consistent pattern of one major and three minor vicinal coupling constants applies for all the complexes, although $[PtBr_2(oth)_2]$ is anomalous in that it has J_{BC} as its largest vicinal coupling constant whereas J_{AD} is largest for all the others.

The coalescence phenomenon observed in the spectra

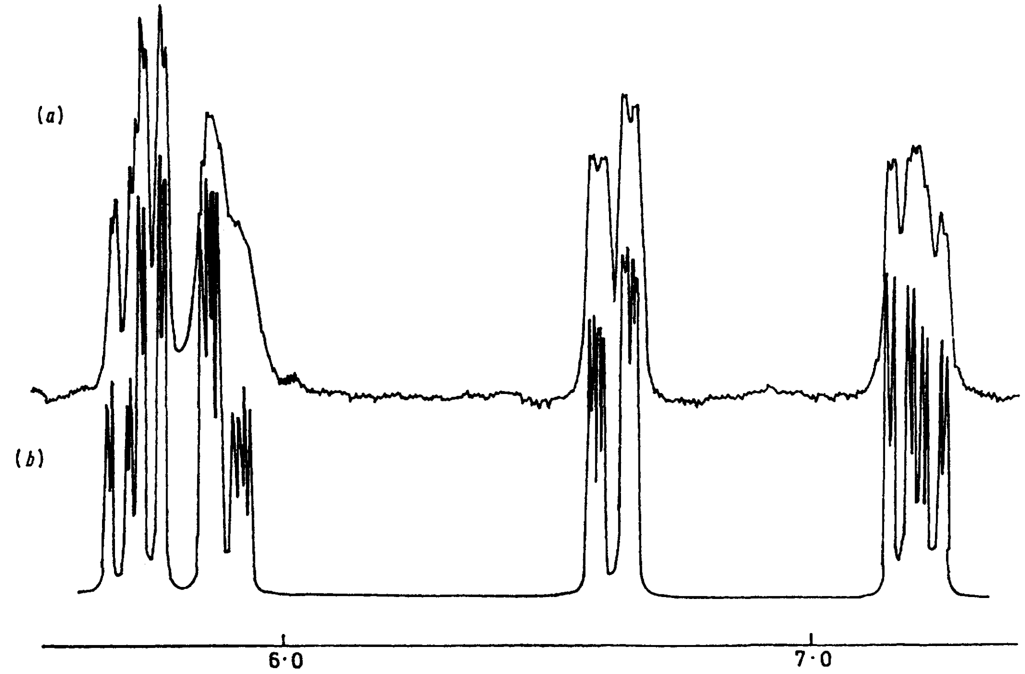

FIGURE 2 220-MHz ^1H N.m.r. spectra of $[PdCl_2(oth)_2]$ in $CDCl_3$ at 233 K: (*a*) experimental; (*b*) calculated

TABLE 1

Spectral parameters for ' frozen-out ' ABCD multiplets exhibited by palladium(II) and platinum(II) halide complexes of 1,4-oxathian and 1,4-oxaselenan

						J/Hz					
Complex	Solvent	τ_A	τ_B	τ_C	τ_D	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}
$[PdCl_2(oth)_2]$	$CDCl_3$	5.723	5.882	6.623	7.193	−13.4	1.5	8.5	4.3	2.1	−13.6
$[PdBr_2(oth)_2]$											
$[PdCl_2(ose)_2]$	$PhNO_2$	5.746	5.961	6.775	7.269	−13.2	2.0	10.3	3.9	3.2	−12.2
$[PdBr_2(ose)_2]$	$PhNO_2$	5.735	5.928	6.499	6.998	−12.7	2.0	8.9	5.1	2.7	−11.9
$[PtCl_2(oth)_2]$	$CDCl_3$	5.666	5.980	6.536	7.152	−12.7	1.8	8.1	6.3	2.7	−13.7
$[PtBr_2(oth)_2]$	$CDCl_3$	5.733	6.074	6.393	7.046	−12.5	2.6	5.7	8.4	1.4	−13.2
$[PtCl_2(ose)_2]$	$CDCl_3$	5.629	5.960	6.676	7.249	−12.9	2.0	9.9	3.8	3.5	−12.4
	$PhNO_2$	5.630	6.031	6.667	7.236	−12.9	2.3	9.6	4.6	3.2	−12.7
$[PtBr_2(ose)_2]$	$CDCl_3$	5.683	5.981	6.486	7.102	−13.1	2.0	9.1	5.4	3.0	−12.4
	$PhNO_2$	5.680	6.034	6.481	7.075	−13.6	2.1	8.9	5.5	2.9	−12.3

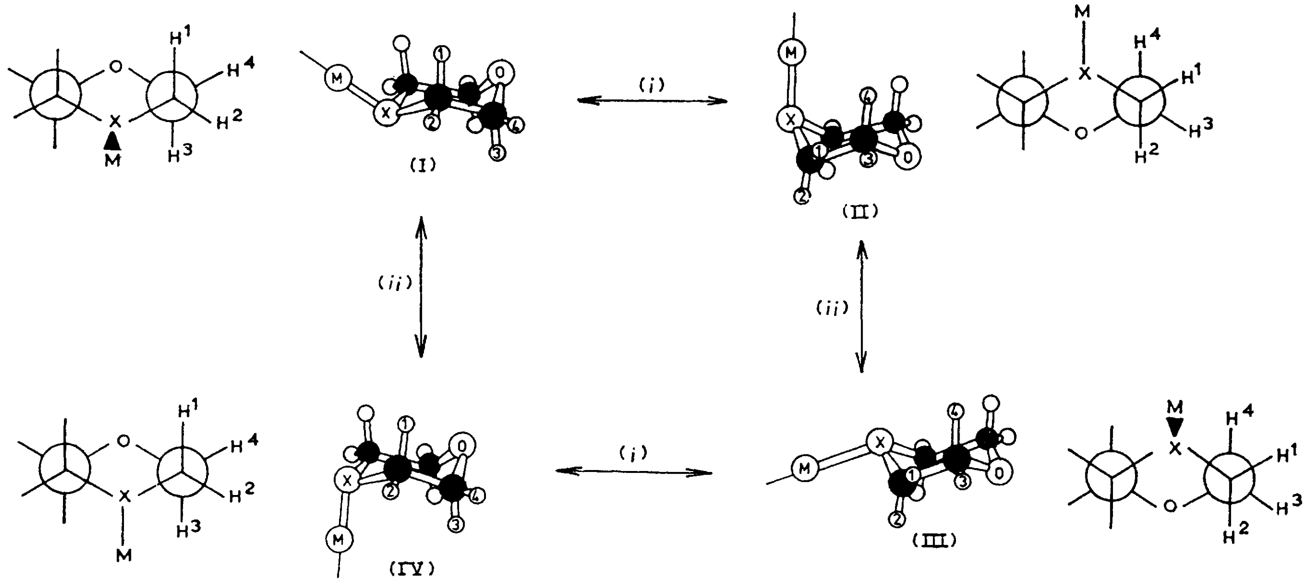

FIGURE 3 Sequential ring reversal (*i*) and site inversion (*ii*) occurring in complexes of 1,4-oxachalcenans

of the free 1,4-oxachalcenans can plausibly be attributed to simple ring reversal of the flexible molecule. For the complexes the situation is more complicated as there are two intramolecular processes with different energy requirements which can conceivably occur in these molecules: (*i*) ring reversal of the flexible 1,4-oxachalcenan ligand; and (*ii*) inversion of the second uncoordinated lone pair of electrons about the ligand atom. Moreover, the two symmetric-chair conformations of the complexed ligand are no longer equivalent as the metal is in an axial position in one and in an equatorial position in the other. Neither ring reversal nor site inversion can by themselves generate the observed high-temperature AA′BB′ spectrum as this requires a process by which a hydrogen atom in, say, an equatorial position on a given carbon atom can move to an axial position in an exactly equivalent conformation. This can only be attained by means of the scheme shown in Figure 3 in which the molecule sequentially undergoes both ring reversal and site inversion. The ABCD spectra observed below the coalescence temperature can thus be plausibly represented by one of three situations: (*a*) slow synchronous ring reversal and site inversion with either only metal–axial or only metal–equatorial configurations present; and with both metal–axial and metal–equatorial configurations present, (*b*) slow site inversion combined with rapid ring reversal or (*c*) rapid site inversion combined with slow ring reversal.

$$\left.\begin{array}{c} \text{Conformer (I)} \xleftrightarrow{\text{Slow}} \text{Conformer (III)} \\ \text{or} \\ \text{Conformer (IV)} \xleftrightarrow{\text{Slow}} \text{Conformer (II)} \end{array}\right\} (a)$$

$$\begin{tikzcd}
\text{Conformer (I)} \arrow[r, leftrightarrow, "\text{Rapid}"] \arrow[d, leftrightarrow, "\text{Slow}"] & \text{Conformer (II)} \\
\text{Conformer (IV)} \arrow[r, leftrightarrow, "\text{Rapid}"'] & \text{Conformer (III)}
\end{tikzcd} \quad (b)$$

$$\begin{tikzcd}
\text{Conformer (I)} \arrow[dd, leftrightarrow, "\text{Rapid}"'] & & \text{Conformer (II)} \arrow[dd, leftrightarrow, "\text{Rapid}"] \\
{} \arrow[rr, leftrightarrow, "\text{Slow}"] & & {} \\
\text{Conformer (IV)} & & \text{Conformer (III)}
\end{tikzcd} \quad (c)$$

Situation (*a*) seems improbable in view of the suggestion of further major spectral changes occurring at very low temperatures, indicating that the two exchange processes have different energy requirements. For situations (*b*) and (*c*) collapse of the ABCD spectra would occur when both exchange processes are rapid, and it can be easily shown that in such circumstances the proton labelled H^1 becomes chemically equivalent to H^2 and H^3 becomes chemically equivalent to H^4, as in equations (1)—(4) where ν_n(averaged) is the chemical shift for H^n

$$\nu_1 \text{ (averaged)} = P_I\nu_1^{I} + P_{II}\nu_1^{II} + P_{III}\nu_1^{III} + P_{IV}\nu_1^{IV} \quad (1)$$

$$\nu_2 \text{ (averaged)} = P_I\nu_2^{I} + P_{II}\nu_2^{II} + P_{III}\nu_2^{III} + P_{IV}\nu_2^{IV} \quad (2)$$

$$\nu_1 \text{ (averaged)} = \nu_2 \text{ (averaged)} = P_I(\nu_1^{I} + \nu_1^{III}) + P_{II}(\nu_1^{II} + \nu_1^{IV}) \quad (3)$$

$$\nu_3 \text{ (averaged)} = \nu_4 \text{ (averaged)} = P_I(\nu_3^{I} + \nu_3^{III}) + P_{II}(\nu_3^{II} + \nu_3^{IV}) \quad (4)$$

when both ring reversal and site inversion are rapid, P_I, *etc.*, are the conformer populations ($P_I = P_{III}$, $P_{II} = P_{IV}$), and ν_n^I is the chemical shift of H_n in conformer (I) ($\nu_1^I = \nu_2^{III}$, $\nu_1^{II} = \nu_2^{IV}$, $\nu_1^{III} = \nu_2^{I}$, *etc.*).

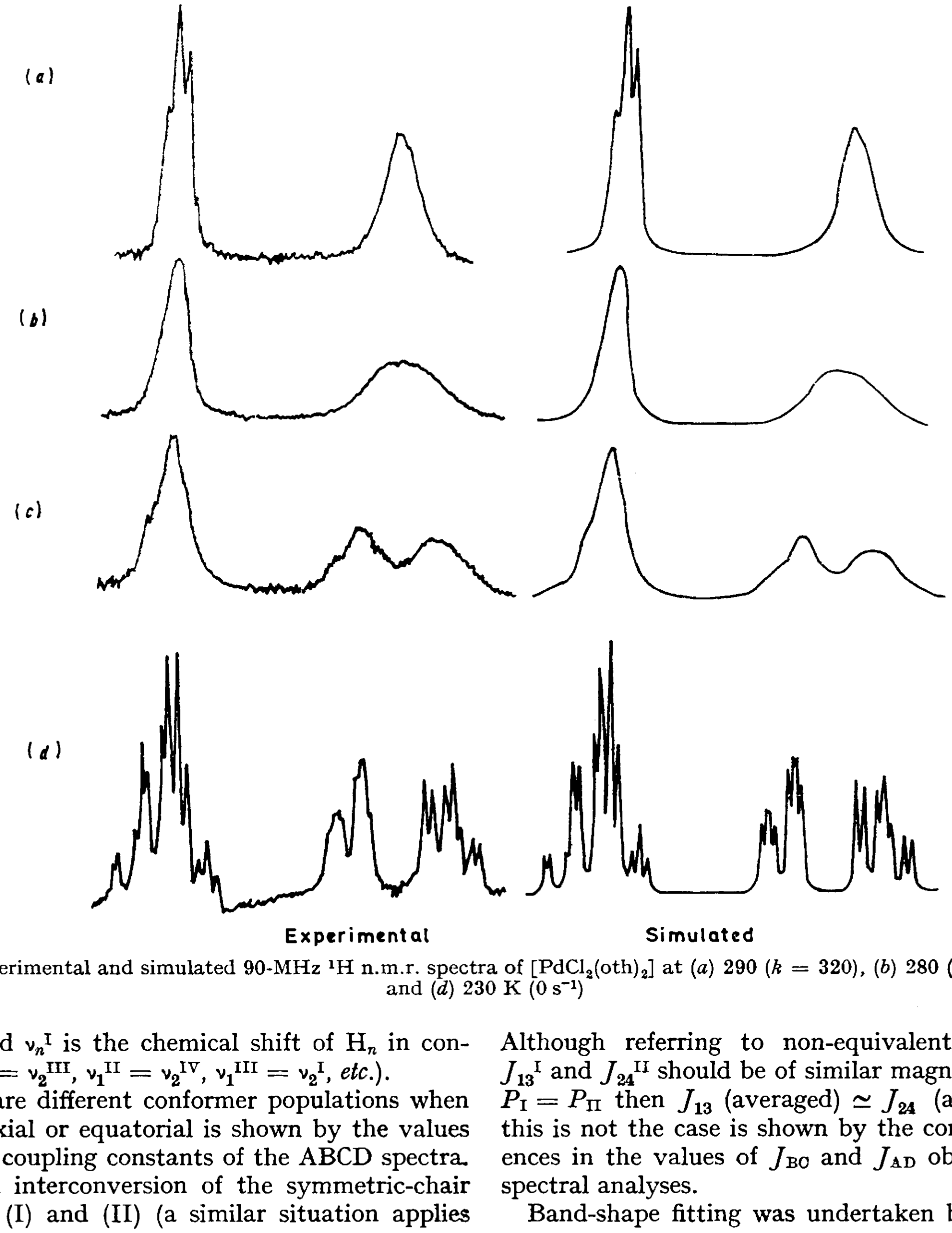

FIGURE 4 Experimental and simulated 90-MHz ^{1}H n.m.r. spectra of [PdCl$_2$(oth)$_2$] at (*a*) 290 (k = 320), (*b*) 280 (105), (*c*) 270 (36), and (*d*) 230 K (0 s^{-1})

That there are different conformer populations when the metal is axial or equatorial is shown by the values for the vicinal coupling constants of the ABCD spectra. Consider rapid interconversion of the symmetric-chair conformations (I) and (II) (a similar situation applies for the other three individual interconversions shown in Figure 3) [equations (5)—(8)]. The relation between

$$J_{13} \text{ (averaged)} = P_I J_{13}^{I} + P_{II} J_{13}^{II} \quad (5)$$

$$J_{14} \text{ (averaged)} = P_I J_{14}^{I} + P_{II} J_{14}^{II} \quad (6)$$

$$J_{23} \text{ (averaged)} = P_I J_{23}^{I} + P_{II} J_{23}^{II} \quad (7)$$

$$J_{34} \text{ (averaged)} = P_I J_{24}^{I} + P_{II} J_{24}^{II} \quad (8)$$

vicinal-proton couplings and the H–C–C–H dihedral angles is given by a Karplus equation of the type (9) where ϕ is the dihedral angle and A and n are constants.

$$J = A \cos^2 \phi + n \cos \phi \quad (9)$$

Obviously for the symmetric-chair conformations, J_{13}^{I} and J_{24}^{II}, where $\phi \simeq 180°$, should be much larger than the other vicinal coupling constants, where $\phi \simeq 60°$. Although referring to non-equivalent conformations, J_{13}^{I} and J_{24}^{II} should be of similar magnitude. Hence if $P_I = P_{II}$ then J_{13} (averaged) $\simeq J_{24}$ (averaged). That this is not the case is shown by the considerable differences in the values of J_{BC} and J_{AD} obtained from the spectral analyses.

Band-shape fitting was undertaken by means of the

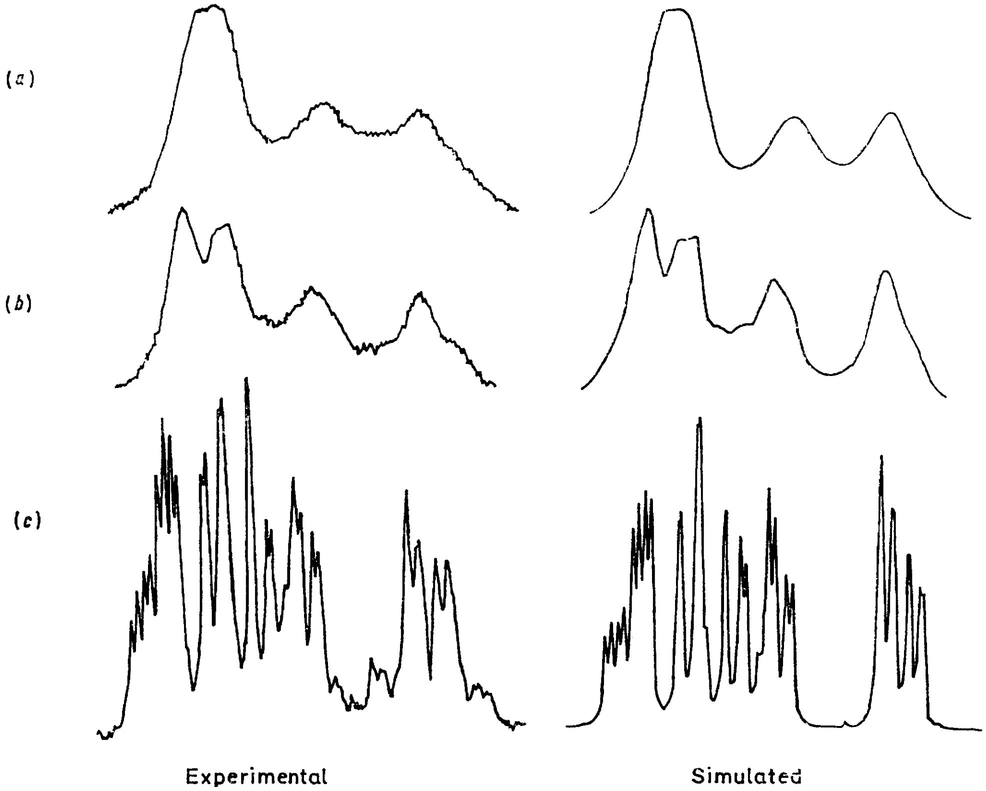

FIGURE 5 Experimental and simulated 90-MHz ^{1}H n.m.r. spectra of $[PtBr_2(oth)_2]$ at (*a*) 300 (k = 65), (*b*) 290 (31), and (*c*) 240 K (0 s^{-1})

TABLE 2

Thermodynamic parameters (kJ mol^{-1}) for site inversion occurring in palladium(II) and platinum(II) halide complexes of 1,4-oxathian and 1,4-oxaselenan

Complex	Solvent	E ‡	ΔH_{300} ‡	ΔG_{300} ‡
$[PdCl_2(oth)_2]$	$CDCl_3$	57.6 ± 2.1	55.1 ± 2.1	57.7 ± 0.1
$[PdBr_2(oth)_2]$				
$[PdCl_2(ose)_2]$	$PhNO_2$	87.0 ± 4.8	84.5 ± 4.8	72.8 ± 0.6
$[PdBr_2(ose)_2]$	$PhNO_2$	60.5 ± 2.6	58.1 ± 2.6	70.7 ± 0.4
$[PtCl_2(oth)_2]$	$CDCl_3$	51.4 ± 3.8	48.9 ± 3.8	65.7 ± 0.4
$[PtBr_2(oth)_2]$	$CDCl_3$	60.3 ± 2.4	57.9 ± 2.4	63.5 ± 0.1
$[PtCl_2(ose)_2]$	$PhNO_2$	107.4 ± 7.6	104.9 ± 7.6	92.6 ± 2.1
$[PtBr_2(ose)_2]$	$PhNO_2$	69.6 ± 6.3	67.1 ± 6.3	80.9 ± 1.8

DNMR3 program. Assuming that either of situations (*b*) or (*c*) applies and the observed ABCD spectra are already time-averaged in one exchange process, the experimental spectra can be satisfactorily simulated throughout the region of intermediate and rapid exchange for the other process by treating this as for an ABCD $\rightleftharpoons$ BADC exchanging system. Comparisons of experimental and simulated spectra at various temperatures and corresponding rate constants are illustrated for $[PdCl_2(oth)_2]$ in Figure 4 and for $[PtBr_2(oth)_2]$ in Figure 5. As simulation of the ABCDX $\rightleftharpoons$ BADCX exchanging system necessary to allow for $^3J(^{195}Pt-^1H)$ would have required excessive computing time and as no heteronuclear-decoupling facilities were available, the spectra of the platinum(II) complexes were fitted only over the region of the O–CH_2 absorptions. For all the complexes, reasonable straight-line Arrhenius plots were obtained over a temperature range of *ca.* 55 K and thermodynamic parameters obtained from these plots are in Table 2. Errors quoted in Table 2 were assessed by considering the maximum and minimum gradients of the Arrhenius plots obtained when allowing for errors in temperature measurement of ±1.0 K and errors in the rate constant sufficiently great that the simulated spectrum just no longer resembled the experimental spectrum.

Values of $\Delta G_{cc}^{\ddagger}$ and $\Delta H_{cc}^{\ddagger}$ for ring reversal of the free ligands are far lower than the parameters obtained from the Arrhenius plots for the complexes. We therefore consider that it is almost certain that these latter values refer to site inversion and not ring reversal. Although values of $\Delta G^{\ddagger}$ for pyramidal inversion about ligand sulphur atoms have previously been reported,[6-8]

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[6] P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, 1967, **89**, 4611.

[7] P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, 1967, **89**, 4617.

[8] E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Comm.*, 1966, 58.

the present values are the first for either sulphur or selenium that have been obtained by band-shape fitting methods. Even with these methods the errors in $E^{\ddagger}$ and $\Delta H_{300}{}^{\ddagger}$, which we think are reasonable but may be too pessimistic, are depressingly large. Much more meaningful are comparisons of the $\Delta G_{300}{}^{\ddagger}$ values, when it can be seen that the barriers to pyramidal inversion are lower for the complexes of Pd^{II} than for Pt^{II}, are *ca.* 25—40% higher for the 1,4-oxaselenan complexes than their 1,4-oxathian analogues, and that, with the exception of $[PtCl_2(ose)_2]$ and $[PtBr_2(ose)_2]$, changing the balancing halide has no appreciable effect.

EXPERIMENTAL

The complexes of the 1,4-oxachalcenans were prepared by published procedures.[9]

N.m.r. spectra at 220 MHz were obtained by the Physico-Chemical Measurement Unit, Harwell, Berkshire. Spectra at 90 MHz were obtained using a Bruker HX 90 spectrometer equipped with a variable-temperature probe. Temperatures were measured with a thermocouple mounted in the probe which was found to be accurate to ±1° by calibration with methanol and ethylene glycol using the formulae of Van Geet.[10] Kinetic analysis was as previously described.[4]

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[10] A. C. Van Geet, *Analyt. Chem.*, 1968, **40**, 2227.