Effect of Variation in Ligand Ring Size upon the Inversion Barrier at Sulphur in Complexes of Palladium(II) and Platinum(II). A Dynamic Hydrogen-1 Nuclear Magnetic Resonance Study

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The series of complexes *trans*-$[MX_2\{S(CR_2)_n\}_2]$ (M = Pd^{II} or Pt^{II}; X = Cl, Br, or I; R = H and/or Me; *n* = 2—5) have been synthesised, and accurate analysis of their variable-temperature n.m.r. spectra by band-shape fitting methods has been used to determine the barrier to pyramidal inversion at the sulphur atom. Barrier energies in chloro-complexes are 2—3 kJ mol^{-1} higher than in the corresponding bromides, which are in turn 4—5 kJ mol^{-1} higher than in the iodo-complexes. The pyramidal inversion energies are very dependent upon ligand ring size; those for five- and six-membered rings are comparable with complexes of linear sulphides, but the complexes of four-membered rings show a considerable heightening of the pyramidal sulphur inversion barrier. For the complexes of the three-membered ring sulphides no inversion was detectable up to the temperature where decomposition commenced, this being the first reported example of such rigidity in dialkyl sulphide metal complexes.

PYRAMIDAL atomic inversions have been studied by a number of physical methods, but those with barrier energies to the inversion process of between *ca.* 20 and 80 kJ mol^{-1} are especially suitable for investigation by the dynamic n.m.r. technique.[1-3]

The majority of studies to date have involved pyramidal inversion at nitrogen.[1-3] Normally such inversion is too rapid to be studied by the n.m.r. technique, but it can be slowed down by structural artefacts, such as incorporation into a small[4,5] or medium-sized ring[6] (Table 6). Pyramidal inversion rates at sulphur atoms are, in contrast, usually much too slow for n.m.r. detection, as for example with sulphoxides[7] and sulphonium ions.[8] However, co-ordination of organic sulphides to transition metals has produced species wherein the inversion barrier at sulphur has been lowered into the 20—80 kJ mol^{-1} range.[9-11] In this context studies on the differences between sulphur, selenium, and tellurium,[12-15] and the effect of the nature and co-ordination number of the transition metal,[12,16,17] have been made.

We have extended these investigations to determine the effect of ring size upon the sulphur inversion barrier

TABLE 1

Ring sulphide complexes of palladium(II) and platinum(II)

Complex	Yield (%)	Colour	M.p. (θ_c/°C)	Analysis (%)			
				Calc.		Found	
				C	H	C	H
(1) *trans*-$[PtCl_2\{S(CMe_2)_2\}_2]$ [a]	32	Orange	123—124 (decomp.)	28.9	4.85	29.0	4.90
(2) *trans*-$[PdCl_2\{S(CH_2)_3\}_2]$	74	Orange	107—108 [b]	22.1	3.70	21.1	3.65
(3) *trans*-$[PdBr_2\{S(CH_2)_3\}_2]$	64	Orange-red	109—110	16.3	2.75	17.0	2.75
(4) *trans*-$[PdI_2\{S(CH_2)_3\}_2]$ [a]	70	Brown	112—113	14.2	2.40	14.1	2.60
(5) *trans*-$[PtCl_2\{S(CH_2)_3\}_2]$ [a]	88	Yellow	95—98 [b]	17.4	2.90	17.3	2.85
(6) *trans*-$[PdCl_2(SCH_2CMe_2CH_2)_2]$ [a]	76	Orange	163—165 [b]	31.5	5.30	31.1	5.35
(7) *trans*-$[PdBr_2(SCH_2CMe_2CH_2)_2]$ [a]	88	Orange-red	151—152	25.5	4.30	25.3	4.30
(8) *trans*-$[PdI_2(SCH_2CMe_2CH_2)_2]$ [a]	80	Red-purple	100 (decomp.)	21.3	3.55	20.9	3.60
(9) *trans*-$[PtCl_2(SCH_2CMe_2CH_2)_2]$ [a]	84	Yellow	150—160 [b]	25.5	4.30	25.2	4.25
(10) *trans*-$[PdCl_2\{S(CH_2)_4\}_2]$	78	Orange	163—165	27.2	4.55	26.6	4.50
(11) *trans*-$[PdBr_2\{S(CH_2)_4\}_2]$	77	Orange-red	114—117	21.7	3.65	21.3	3.55
(12) *trans*-$[PdI_2\{S(CH_2)_4\}_2]$	71	Purple	125—128	18.0	2.95	16.9	3.10
(13) *trans*-$[PtCl_2\{S(CH_2)_4\}_2]$	58	Yellow	143—145	21.7	3.65	21.2	3.55
(14) *trans*-$[PdCl_2\{S(CH_2)_5\}_2]$	75	Orange	139—143	31.5	5.30	30.9	5.25
(15) *trans*-$[PdBr_2\{S(CH_2)_5\}_2]$	80	Orange-red	130	25.5	4.30	25.3	4.40
(16) *trans*-$[PdI_2\{S(CH_2)_5\}_2]$	57	Brown	154—155	21.3	3.55	21.1	3.75
(17) *trans*-$[PtCl_2\{S(CH_2)_5\}_2]$	80	Yellow	140—142	25.5	4.30	25.4	4.25

[a] New compound. [b] Above their melting point these complexes undergo rearrangements which we are investigating further.

in the metal-co-ordinated small- and medium-sized ring sulphides $\overline{\mathrm{S(CH_2)}}_n$ (n = 2—5). We report the syntheses of and detailed n.m.r. studies upon the series of complexes *trans*-$[\mathrm{MX_2\{\overline{S(CR_2)}_n\}_2}]$ (M = $\mathrm{Pd^{II}}$ or $\mathrm{Pt^{II}}$; X = Cl, Br, or I; R = H and/or Me; n = 2—5), many of which are new compounds.

EXPERIMENTAL

The ligands trimethylene sulphide $\overline{\mathrm{S(CH_2)}}_3$, tetramethylene sulphide $\overline{\mathrm{S(CH_2)}}_4$ (tetrahydrothiophen), and pentamethylene sulphide $\overline{\mathrm{S(CH_2)}}_5$ were obtained commercially and purified by redistillation before use. 3,3-Dimethylthietan $\overline{\mathrm{SCH_2CMe_2CH_2}}$ and tetramethylethylene sulphide $\overline{\mathrm{S(CMe_2)}}_2$ were synthesized by literature methods.[18,19] *

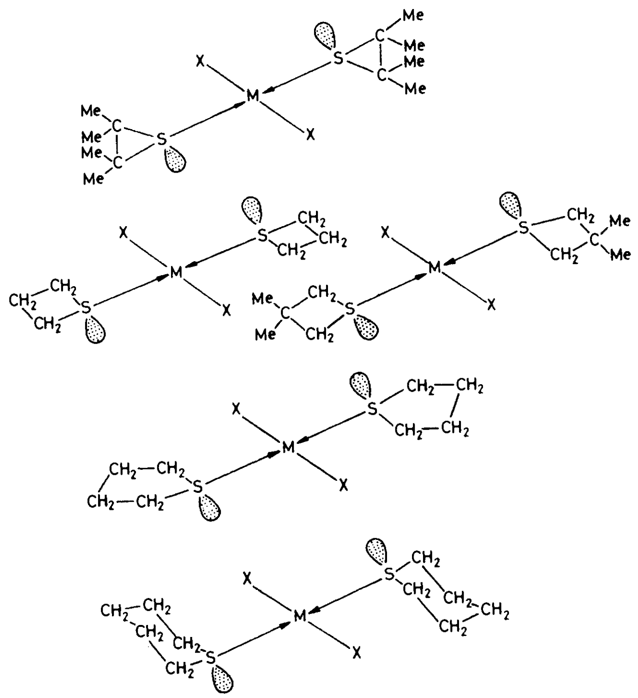

FIGURE 1 Metal-co-ordinated small- and medium-sized ring sulphides, *trans*-$[\mathrm{MX_2L_2}]$

The complexes prepared are numbered and characterized in Table 1. Some of these compounds have been reported previously,[20-23] but many are new. Figure 1 illustrates the types of complexes investigated. The complexes were made using the general procedures outlined below.

Preparation of Palladium(II) *Complexes*.—The palladium salt $\mathrm{K_2[PdX_4]}$ (X = Cl, Br, or I) (0.5 mmol) was dissolved in water (20 cm^3) and the sulphur ligand (1.1 mmol) added with stirring. The resulting mixture was stirred overnight; then the precipitated product was filtered off, washed copiously with water, followed by a small volume of cold ethanol, and dried. This residue was then dissolved in the minimum of hot acetone. Cooling this acetone solution slowly to −20 °C yielded crystals of the product (Table 1).

Preparation of Platinum(II) *Complexes*.—The platinum salt $\mathrm{K_2[PtCl_4]}$ (0.5 mmol) and the ligand (2 mmol) were stirred together in water (20 cm^3) overnight at room temperature. The yellow precipitate was filtered off and washed copiously with water, followed by a small quantity of cold ethanol. The residue was then dissolved in the minimum of dichloromethane, and the solution dried over anhydrous magnesium sulphate. The drying agent was filtered off, and the solvent removed at reduced pressure. The resulting solid was then recrystallized from a variety of solvents, dependent upon the ligand in the complex as follows: tetramethylethylene sulphide (ethanol), trimethylene sulphide (dichloromethane–hexane), 3,3-dimethylthietan, tetrahydrothiophen, and pentamethylene sulphide (tetrachloroethylene). In all cases crystals of the required *trans* complexes (Table 1) were obtained.

Spectra.—JEOL MH-100 or PS/PFT-100 spectrometers were used to record the 100-MHz ^{1}H n.m.r. spectra for solutions of the complexes in a variety of solvents (see Table 5 for details) over a wide temperature range. A standard JES-VT-3 unit was used as control for the probe temperature. The measurements of temperature were by a calibrated thermocouple immediately before and after recording of a spectrum, and recorded temperatures are considered accurate to at least ±1 °C. 220-MHz ^{1}H n.m.r. spectra were recorded on a Varian HR220 spectrometer at the P.C.M.U., Harwell.

Computations.—The computer program DNMR by Binsch [24,25] was used as the basis of the line-shape calculations, although modifications were made when dealing with some complicated spin systems.[13] The LAOCNR computer program was utilized for the analysis of the static spectra.

RESULTS

All of the complexes studied possess essentially the same ligand geometry, the tetrahedral sulphur atom [26] being attached to a prochiral alkane group in which either two methylene hydrogens or two methyl groups are diastereotopic and hence anisochronous in the absence of any exchange process. The precise nature of the alkane group, and hence the actual spin system involved, varies from ligand to ligand. The process of inversion about the tetrahedral sulphur atom causes interconversion of the otherwise anisochronous groups, giving rise to an averaged n.m.r. spectrum above the coalescence temperature.

For all of the platinum complexes, coupling between ^{195}Pt and ^{1}H was observed in spectra at temperatures well above the coalescence, which is indicative of an intramolecular process.[13] Although such observations are not possible for the palladium complexes, work by Cross *et al.*[27] has shown that here also the process is an intramolecular one.

Three-membered Rings.—The potential ligand ethylene sulphide $\overline{\mathrm{S(CH_2)}}_2$ undergoes polymerization on standing at room temperature in sunlight,[19] and even when using freshly distilled samples of ligand only polymeric products could be isolated from its reactions with $\mathrm{K_2[PdCl_4]}$ and $\mathrm{K_2[PtCl_4]}$. However, replacement of methylene hydrogen atoms with methyl groups considerably enhances the stability of the three-membered ring,[19] and facilitates the formation of a stable monomeric platinum complex *trans*-dichlorobis(tetramethylethylene sulphide)platinum. A corresponding

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* Systematic names for the five sulphides are thietan, thiolan, thian, 3,3-dimethylthietan, and tetramethylthiiran respectively.

monomeric product was formed for palladium(II), but this polymerized rapidly in solution.

At ambient temperatures the methyl region of the ^{1}H n.m.r. spectrum of *trans*-[PtCl$_2${S(CMe$_2$)$_2$}$_2$] could be analyzed as a single first-order MP spectrum, where the labels refer to the anisochronous methyl groups. Satellite lines were also observed due to couplings to ^{195}Pt(X). Table 4 lists the relevant data. As the temperature was raised the spectrum showed no evidence of an exchange process up to the point where decomposition of the complex commenced (*ca.* 100 °C). Indeed, the spectral lines were sharper at 80 °C than they were at 0 °C.

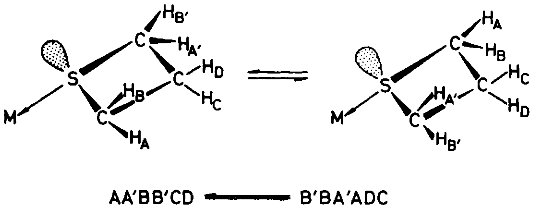
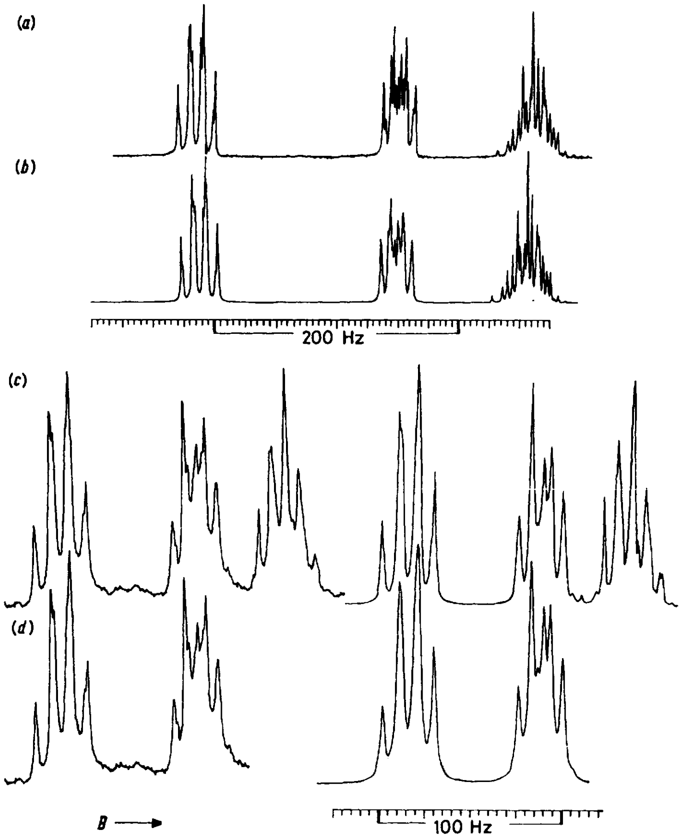


FIGURE 2 Spin system for inversion at the tetrahedral sulphur atom in the four-membered ring complexes *trans*-[MX$_2${S(CH$_2$)$_3$}$_2$]

Four-membered Rings.—The complexes *trans*-[MX$_2${S(CH$_2$)$_3$}$_2$] (M = Pd, X = Cl, Br, or I; M = Pt, X = Cl) were all stable in solution. This enabled an accurate dynamic n.m.r. study of their ^{1}H spectra to be undertaken, with the exception of *trans*-[PdI$_2${S(CH$_2$)$_3$}$_2$] which was insufficiently soluble to obtain useful spectra.



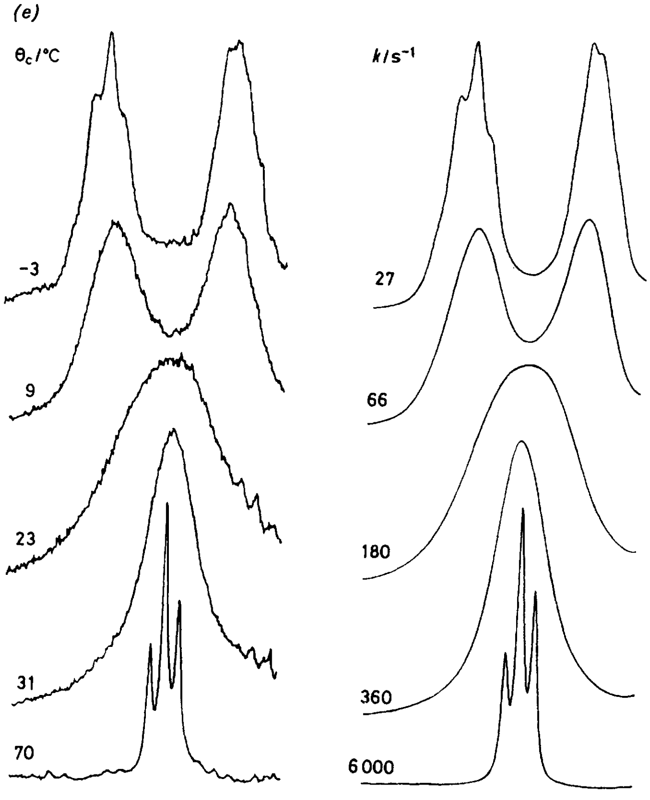


FIGURE 3 Methylene absorption region of the spectra of *trans*-[PdBr$_2${S(CH$_2$)$_3$}$_2$]: (*a*) 220-MHz spectrum at −40 °C; (*b*) computer simulation of (*a*); (*c*) 100-MHz spectrum at −40 °C and its computer simulation as a six-spin system; (*d*) 100-MHz spectrum at −40 °C and its computer simulation of the AB portion as a four-spin system; (*e*) variable-temperature spectra of the AB region

The spin system involved in the palladium(II) complexes is [AA'BB'CD]$_2$; however, no proton coupling between the ligands *trans* to one another was detectable, and we can simplify the system to AA'BB'CD (Figure 2). The effect of the pyramidal inversion process upon co-ordinated S(CH$_2$)$_3$ is illustrated in this Figure, where free rotation about the M–S bond is assumed.

In order to perform an accurate dynamic n.m.r. analysis, the static n.m.r. parameters of linewidth, coupling constants, and chemical shifts, along with any variation of these with temperature, must first be obtained by an analysis of spectra in the absence of an exchange process.

A spectral analysis of the free ligand S(CH$_2$)$_3$ has previously been performed [28] by a treatment of the spin system as AA'A''A'''BB'. The values of the couplings should alter little upon complexation, and an attempt was made with the LAOCNR computer program to fit our ^{1}H n.m.r. spectra of the complexes using these values. However, a good fit did not prove possible due to difficulties in assigning the experimental lines for iteration. In order to resolve this problem a 220-MHz ^{1}H n.m.r. spectrum was recorded at a temperature below the onset of exchange. Then by treating the spin system as AA'BB'CD it was possible to

TABLE 2

Chemical shifts and their temperature-variable coefficients for the methylene hydrogens in the ring sulphide complexes*

	ν_A/Hz		ν_B/Hz		ν_C/Hz		ν_D/Hz	
Compound	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
(2)	395.16	0.0588	335.91	−0.0261	309.19	0.0261	293.00	0.0000
(3)	414.97	0.0000	341.17	0.0000	289.35	0.0000	293.86	0.0000
$\overline{\text{S(C}}\text{H}_2)_3$	320		320					
(6)	372.40	0.0000	301.29	−0.1260				
(7)	393.80	0.0000	309.03	−0.0260				
(8)	422.60	0.0500	310.12	0.0500				
(9)	382.00	n	304.00	n				
(10)	365.57	0.1544	274.38	−0.1544	219.37	n	204.74	n
(11)	379.07	0.0883	287.74	−0.0441	226.72	n	209.00	n
(12)	404.30	0.1564	314.86	0.0000	212.86	n	203.55	n
$\overline{\text{S(C}}\text{H}_2)_4$	274		274					
(14)	327.20	0.0303	251.37	−0.0542	209.90	n	190.60	n
$\overline{\text{S(C}}\text{H}_2)_5$	254		254					

* Chemical shift (ν_i) from $SiMe_4$ (in Hz) at temperature θ_c/°C is given by the expression $\nu_i/\text{Hz} = a + b(\theta_c/°\text{C})$. n = Not computed.

perform an iteration using the LAOCNR program on the coupling constants and measured chemical shifts of the free ligand. In this way good computer simulations for the experimental 220-MHz spectra were obtained for *trans*-$[PdX_2\{\overline{\text{S(C}}\text{H}_2)_3\}_2]$ (X = Cl or Br). An example for X = Br is illustrated in Figure 3.

The spectral parameters extracted from the computer simulation are noted in Tables 2 and 3. It is of interest to see that in order to maintain $^3J_{AC} > {}^3J_{AD}$ and $^3J_{BD} > {}^3J_{BC}$, as is the case in the free ligand [28] and in *trans*-$[PdCl_2\{\overline{\text{S(C}}\text{H}_2)_3\}_2]$, the assignments of the protons C and D in *trans*-$[PdBr_2\{\overline{\text{S(C}}\text{H}_2)_3\}_2]$ must be reversed with respect to those of the corresponding chloride. This is not surprising in view of the small chemical shift (*ca.* 4.5 Hz) between C and D.

Assignment of proton A to the downfield signal is based upon the arguments relating to the values of *J*(Pt–X–C–H) in our earlier papers [12,13] and our further work upon *trans*-$[PdCl_2\{\overline{\text{S(C}}\text{H}_2)_5\}_2]$, to be published separately.[29] (It should be noted that such an assignment is not in fact critically important to the line-shape fitting.)

The transformation of the 220-MHz chemical shifts to 100-MHz shifts accurately reproduced the experimental 100-MHz spectrum as shown in Figure 3, thus supporting the correctness of the spectral analysis.

A complete dynamic n.m.r. band-shape fitting of the AA′BB′CD $\rightleftharpoons$ B′BA′ADC system of *trans*-$[PdX_2\{\overline{\text{S(C}}\text{H}_2)_3\}_2]$ (X = Cl or Br) would require excessive computation time, so approximations and modifications were made in order to perform the analysis.

The static spectra of these particular complexes showed the four-bond couplings $^4J_{AB'}$, $^4J_{B'A'}$ *etc.* to be $\leqslant 1.2$ Hz. These were therefore approximated to zero, and by fitting the AB region of the spectrum only an acceptable fit of the experimental spectrum was produced (Figure 3). It should be noted that a slightly larger spectral linewidth than previously was now required. However, the spin system is thus simplified to an ABCD $\rightleftharpoons$ BADC one, for which it was possible to perform a full dynamic n.m.r. analysis over a wide temperature range. It should be noted that this simplified spin-system treatment is considered a good approximation when fitting only the low-field AB region and is quite invalid for fittings of the high-field CD region since these methylene-proton nuclei couple equally to two pairs of adjacent methylenes. A complete set of experimental and computer-simulated spectra is illustrated in Figure 3.

In order to avoid the above approximations the alternative ligand 3,3-dimethylthietan $\overline{\text{SCH}_2\text{CMe}_2\text{CH}_2}$ with its more tractable spin system was utilized. Here the protons C and D (see Figure 2) of $\overline{\text{S(C}}\text{H}_2)_3$ are replaced by methyl groups. The metal complexes of $\overline{\text{SCH}_2\text{CMe}_2\text{CH}_2}$ have essentially the same structure as those of $\overline{\text{S(C}}\text{H}_2)_3$. With no coupling between the two individual *trans* ligands being

TABLE 3

Spin–spin coupling constants (Hz) for the methylene hydrogens in the ring sulphide complexes, and their transverse relaxation times [a]

Compound	J_{AB}	J_{AC}	J_{AD}	$J_{AA'}$	$J_{AB'}$	J_{BC}	J_{BD}	J_{CD}	J_{AX}	J_{BX}	T_2*/s
(2)	−11.04	9.63	7.33	1.20	−0.50	6.22	8.53	−12.32			0.106
(3)	−10.90	9.59	8.53	1.20	−0.95	5.38	8.75	−12.41			0.127
$\overline{\text{S(C}}\text{H}_2)_3$ [b]	−8.70	8.93	6.27	1.20	−0.14	6.27	8.93	−11.73			
(6)	−10.46			1.20	−0.99						0.212
(7)	−10.15			0.48	−1.54						0.212
(8)	−9.68			1.53	−1.82						0.159
(9)	−11.0			n	n				54.0	40.0	
(10)	−11.69	6.64	6.46			6.89	6.39	−12.86			
(11)	−12.02	6.12	6.08			6.01	5.95	−12.00			
(12)	−11.86	6.18	5.93			6.15	5.72	−12.00			
$[\overline{\text{S(C}}\text{H}_2)_4]$ [b]	−13.7	6.6	6.6			6.6	6.6	−13.5			
(14)	−13.0	2.09	8.87			6.78	2.09	−13.0			0.106

[a] n = Not computed; X = ^{195}Pt. T_2* determined from $\Delta\nu_{\frac{1}{2}} = (\pi T_2^*)^{-1}$, where $\Delta\nu_{\frac{1}{2}}$ = natural linewidth at half-height. [b] Values for free ligand.

TABLE 4

Spectral parameters (Hz) and free energies of activation for pyramidal sulphur inversions calculated from methyl resonances of the ring ligands

Complex	Solvent	$\nu_M - \nu_P$ / Hz	J_{MX} / Hz	J_{PX} / Hz	T_c / K	$\Delta G^\ddagger(T_c)$ / kJ mol^{-1}
trans-$[PtCl_2\{S(CMe_2)_2\}_2]$	$C_6D_5NO_2$	26.40	4.0	5.0	>373	>90
trans-$[PdCl_2(SCH_2CMe_2CH_2)_2]$	$CDCl_3$	17.25			278	59.5,[a] 60.3[b]
trans-$[PdBr_2(SCH_2CMe_2CH_2)_2]$	$CDCl_3$	*ca.* 4.0[c]				
trans-$[PdI_2(SCH_2CMe_2CH_2)_2]$	$CDCl_3$	13.0			242	52.0,[a] 52.5[b]
trans-$[PtCl_2(SCH_2CMe_2CH_2)_2]$	$C_6D_5NO_2$	19.02	0	0	330	70.8,[a] 70.9[d]

T_c = Coalescence temperature. J_{MP} = 0 Hz in each case.

[a] Calculated from the coalescence temperature of the methyl peaks. [b] Obtained from accurate DNMR fit of methylene protons. [c] Chemical-shift difference too small for accurate computation. [d] Obtained from accurate DNMR fit of methyl groups.

observed, the spin system becomes $AA'BB'M_3P_3$. The static spectra (Figure 4) show no coupling between the ligand methylene and methyl protons, thus the methylene spin system simplifies to $AA'BB' \rightleftharpoons B'BA'A$ for the dynamic analysis. Such a system may be rigorously treated by the DNMR computer program. The disadvantage of such a system is that the relatively simple line shapes give rise to greater uncertainty in the values for the rate constants at the extreme ends of the fitting range, where accurate values of the rate constants are most desirable.[30-33]

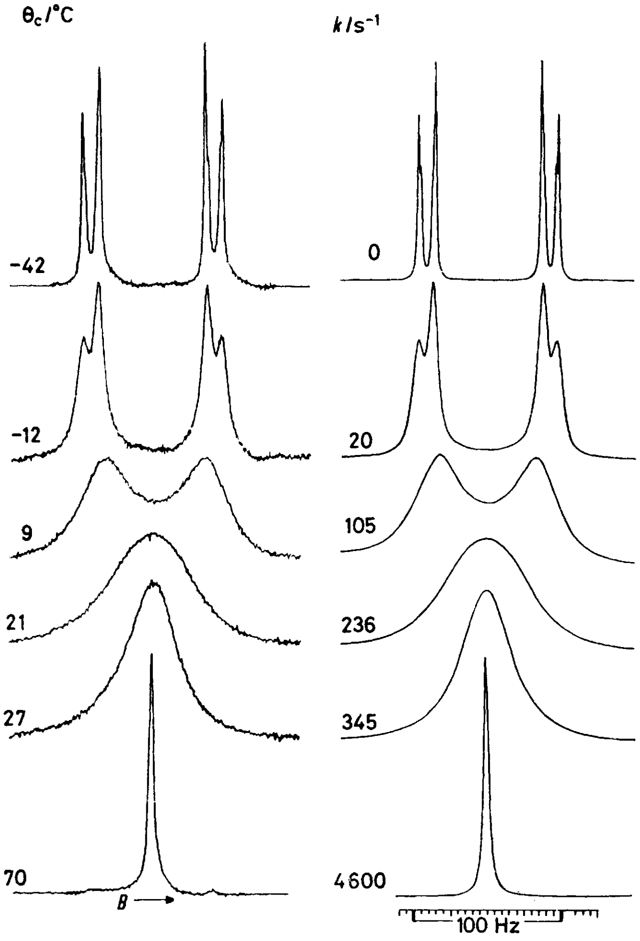


FIGURE 4 Variable-temperature spectra of the methylene absorption region of *trans*-$[PdBr_2(SCH_2CMe_2CH_2)_2]$ and their computer simulation

A further major advantage of the ligand $SCH_2CMe_2CH_2$ was in the platinum(II) complex *trans*-$[PtCl_2(SCH_2CMe_2CH_2)_2]$. The presence of ^{195}Pt satellite spectra in the methylene region precludes computations. However, the values of $J(^{195}Pt-S-C-C-Me)$ are < 1.0 Hz enabling the two methyl groups to be studied as an interconverting first-order MP system. In contrast, the spectra of *trans*-$[PtCl_2\{S(CH_2)_3\}_2]$ were intractable for band-shape fittings because of the presence of the ^{195}Pt satellite lines.

The spectral parameters extracted from the LAOCNR program fitting of the static spectra of *trans*-$[MX_2(SCH_2CMe_2CH_2)_2]$ (M = Pd, X = Cl, Br, or I; M = Pt, X = Cl) are reported in Tables 2—4.

We have observed that the complex *trans*-$[PtCl_2(SCH_2CMe_2CH_2)_2]$ undergoes *trans–cis* equilibration in solution over a period of time, as is indicated in the spectra of Figure 5. Such *trans*- to -*cis* isomerizations in the cyclic sulphide complexes of platinum(II) have been previously noted in the solid state,[34,35] but we have found no reference to such solution changes in the absence of free ligand.

Five-membered Rings.—The analyses of the spectra of the tetrahydrothiophen complexes *trans*-$[PdX_2\{S(CH_2)_4\}_2]$ were carried out in a very similar manner to those of the $S(CH_2)_3$ complexes. A diagram of the relevant spin system is shown in Figure 6. The static structure represents an AA'BB'CC'DD' system. However, even the 220-MHz spectra (Figure 7) failed to resolve the four-bond couplings $^4J_{AB'}$ *etc.*, indicating that they must be less than 1 Hz. This failure to resolve these couplings and the inability of the LAOCNR program to handle eight-spin systems necessitated the analysis of the 220-MHz spectra as an ABCD system with only the low-field AB portion being fitted. The unresolved four-bond couplings were incorporated in the choice of a somewhat larger natural linewidth as represented by the T_2* value. As previously, the analyses were performed by use of the LAOCNR program iterating on the values of the free-ligand coupling constants.[36]

Having successfully fitted the 220-MHz spectrum, the shift parameters were modified to fit the 100-MHz spectra, and a dynamic n.m.r. analysis performed (Figure 7) on these complexes treated as $ABCD \rightleftharpoons BADC$ systems.

The presence of the ^{195}Pt satellite spectra for *trans*-

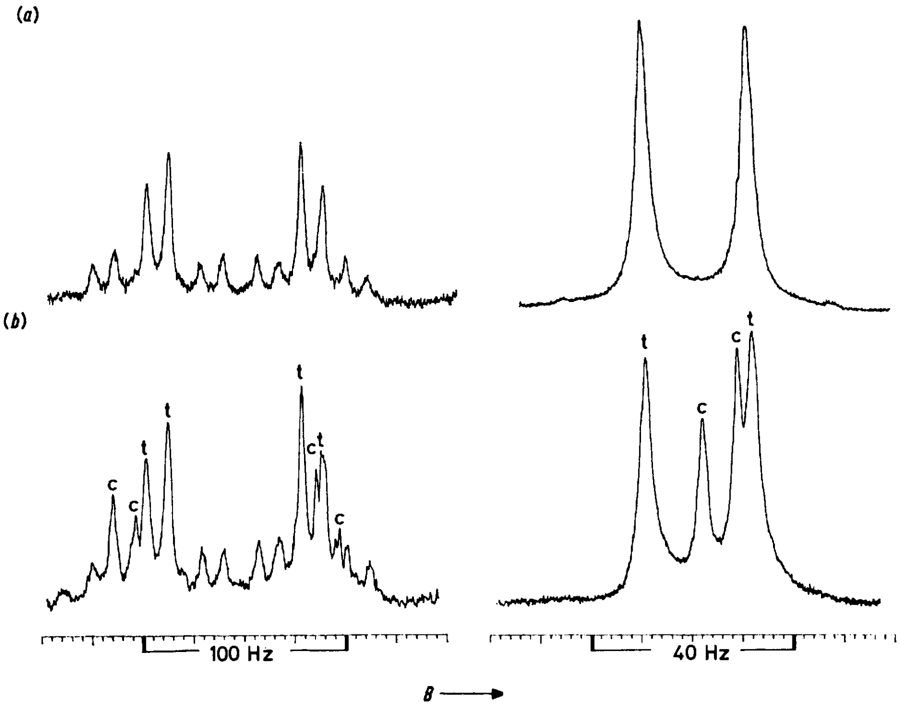


FIGURE 5 100-MHz spectra of the methyl and methylene absorption regions of *trans*-[PtCl$_2$(SCH$_2$CMe$_2$CH$_2$)$_2$]: (*a*) initial spectrum; (*b*) after standing for 1 week, showing the new peaks due to *cis* (c) isomer formation in addition to the original *trans* (t)

[PtCl$_2${S(CH$_2$)$_4$}$_2$] made an accurate analysis of the spectra inaccessible, and only a value for the coalescence temperature was recorded (Table 5).

Six-membered Rings.—The spectral analyses of the S(CH$_2$)$_5$ complexes were at first sight identical to those of S(CH$_2$)$_4$, but a more detailed investigation showed that there were two dynamic processes taking place. In addition to the pyramidal atomic inversion about sulphur, which is investigated in this study (Table 5), there was also an inversion process of the six-membered ligand ring. Detailed reporting of this latter process will be the subject of a separate communication.[29]

For all of the complexes mentioned above, spectra were recorded over as large a temperature range as possible in order that the variation of chemical shifts with temperature, in the absence of exchange, could be computed. Lineshape analyses were performed upon a minimum of eight spectra around the exchange region. Such fittings were again made over as wide a temperature range as feasible,

TABLE 5

Arrhenius and activation parameters for tetrahedral sulphur inversion in ring sulphide metal complexes

Complex	Solvent	T_c/K	$E^‡$/kJ mol^{-1}	$\log_{10} A$	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	$\Delta G^‡$/kJ mol^{-1}
(2) *trans*-[PdCl$_2${S(CH$_2$)$_3$}$_2$]	CDCl$_3$	301	65.0 ± 0.7	13.4 ± 0.1	62.5 ± 0.7	2.3 ± 2.2	61.8 ± 1.3
(3) *trans*-[PdBr$_2${S(CH$_2$)$_3$}$_2$]	CDCl$_3$	293	54.9 ± 0.5	12.0 ± 0.1	52.5 ± 0.5	−23.5 ± 1.8	59.5 ± 1.1
(5) *trans*-[PtCl$_2${S(CH$_2$)$_3$}$_2$]	C$_6$D$_5$NO$_2$	338					
(6) *trans*-[PdCl$_2$(SCH$_2$CMe$_2$CH$_2$)$_2$]	CDCl$_3$	303	50.7 ± 1.1	11.0 ± 0.2	48.2 ± 1.1	−42.7 ± 3.5	60.9 ± 2.1
(7) *trans*-[PdBr$_2$(SCH$_2$CMe$_2$CH$_2$)$_2$]	CDCl$_3$	293	48.0 ± 1.3	10.9 ± 0.2	45.6 ± 1.3	−44.6 ± 4.3	58.9 ± 2.6
(8) *trans*-[PdI$_2$(SCH$_2$CMe$_2$CH$_2$)$_2$]	CDCl$_3$	271	44.2 ± 0.8	11.0 ± 0.2	42.0 ± 0.8	−42.7 ± 2.9	54.7 ± 1.6
(9) *trans*-[PtCl$_2$(SCH$_2$CMe$_2$CH$_2$)$_2$]	C$_6$D$_5$NO$_2$	330	59.8 ± 1.1	11.1 ± 0.2	57.1 ± 1.1	−41.9 ± 3.4	69.6 ± 2.1
(10) *trans*-[PdCl$_2${S(CH$_2$)$_4$}$_2$]	CDCl$_3$	278	47.4 ± 1.1	11.3 ± 0.2	45.2 ± 1.1	−36.6 ± 4.0	56.1 ± 2.3
(11) *trans*-[PdBr$_2${S(CH$_2$)$_4$}$_2$]	CDCl$_3$	260	46.8 ± 1.3	11.7 ± 0.3	44.5 ± 1.3	−27.8 ± 5.0	52.8 ± 2.8
(12) *trans*-[PdI$_2${S(CH$_2$)$_4$}$_2$]	CDCl$_3$	235	45.0 ± 1.2	12.3 ± 0.3	43.1 ± 1.1	−15.4 ± 4.8	47.7 ± 2.6
(13) *trans*-[PtCl$_2${S(CH$_2$)$_4$}$_2$]	CDCl$_3$	315					
(14) *trans*-[PdCl$_2${S(CH$_2$)$_5$}$_2$]	CD$_2$Cl$_2$–CS$_2$	273	55.8 ± 1.2	12.8 ± 0.2	55.6 ± 1.2	−7.3 ± 4.5	55.7 ± 2.6
(17) *trans*-[PtCl$_2${S(CH$_2$)$_5$}$_2$]	CDCl$_3$	313					

$\Delta G^‡$ is calculated for $T = 298.15$ K.

ideally about 60 °C. Examples of such spectral fittings are illustrated in Figures 3, 4, and 7. All fittings were performed by visual matching of the experimental and computer-simulated spectra for a variety of rate constants. Those rate constants which gave the best fits to the experimental spectrum, along with their associated temperatures, were then utilized to obtain the Arrhenius and activation parameters given in Table 5. The range of error quoted in each case is based on a least-squares fitting of the experimental data using the THERMO [37] computer program.

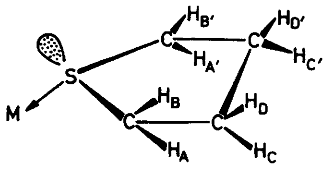


FIGURE 6 Spin system of the sulphur ring in *trans*-$[PdX_2\{S(CH_2)_4\}_2]$

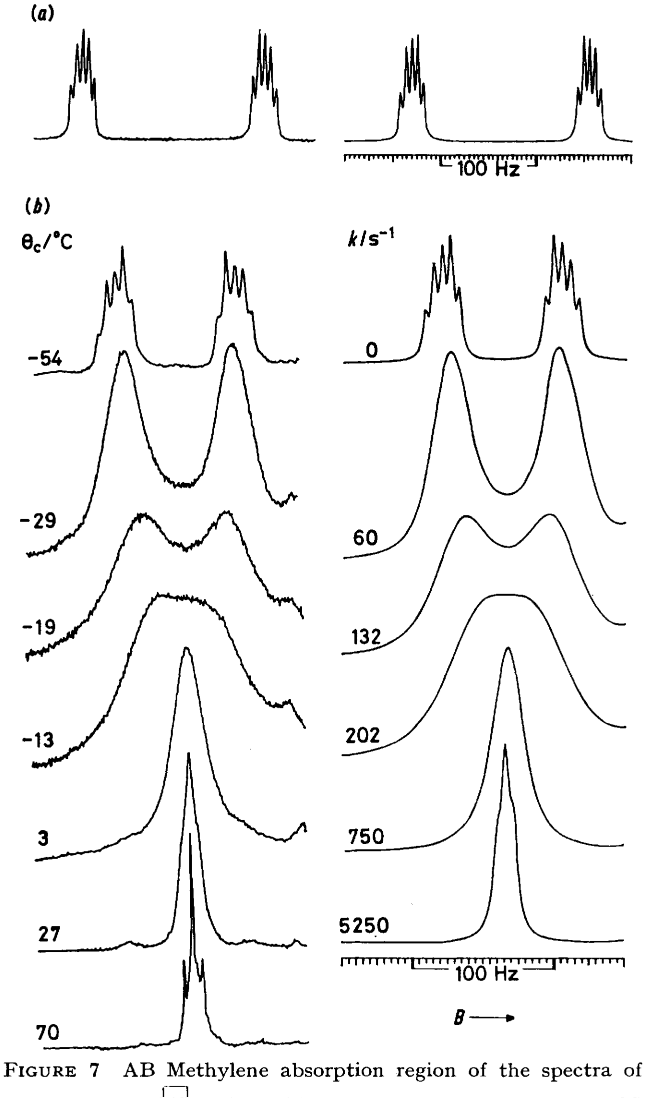


FIGURE 7 AB Methylene absorption region of the spectra of *trans*-$[PdBr_2\{S(CH_2)_4\}_2]$: (*a*) 220-MHz spectrum at −52 °C and its computer simulation; (*b*) variable-temperature 100-MHz spectra and their computer simulations

DISCUSSION

The data collected in Table 2 reveal a number of interesting trends in chemical-shift values, particularly of the methylene protons adjacent to sulphur. First, we see that the dependence on ring size is such that the small-ring methylenes resonate downfield from their counterparts in the larger rings, thus reflecting the greater shielding experienced by the SCH_2 protons in the larger-ring complexes. Similar trends have been noted for the analogous carbocyclic rings [38] and the free S-heterocyclic ligands (Table 2).

Secondly, the deshielding effects of the PdX_2 moiety on the SCH_2 protons cause downfield shifts of up to *ca.* 0.7 p.p.m. for the A,A′ protons which are appreciably closer to the PdX_2 group than the B,B′ protons which are deshielded by only *ca.* 0.4 p.p.m.

Thirdly, where the ring sulphide ligand is invariant in the three series *trans*-$[PdX_2\{S(CH_2)_3\}_2]$, *trans*-$[PdX_2(SCH_2CMe_2CH_2)_2]$, and *trans*-$[PdX_2\{S(CH_2)_4\}_2]$ the effect of increase of halogen size is to induce shifts of SCH_2 protons at lower fields. A parallel trend has been observed for the complexes *trans*-$[PtX_2(SMe_2)_2]$ [39] and *trans*-$[MX_2(PMe_3)_2]$ [40] and was thought to be due, not to changes in the nature of the M–L bond (as in the normal *trans* influence) but, more likely, to a combination of electric dipole and magnetic dipole anisotropy effects.

A comparison of the free energies of activation for pyramidal sulphur inversion listed in Tables 4 and 5 reveals a number of interesting features.

Variation of Metal.—As noted above, the presence of ^{195}Pt satellite spectra precludes really accurate studies on many of the platinum(II) complexes. This problem, however, does not arise in the complexes *trans*-$[MCl_2(SCH_2CMe_2CH_2)_2]$ (M = Pd or Pt) and activation energies are *ca.* 61 kJ mol^{-1} for the palladium complex and *ca.* 70 kJ mol^{-1} for the platinum complex. This higher energy for the transition state in platinum probably reflects [12] the greater strength of the Pt–S bond. Such a trend with increasing atomic mass of the co-ordinating transition metal has been noted previously.[12–14]

Variation of Halogen.—In studies of pyramidal sulphur inversion so far conducted upon *trans* metal sulphide complexes, no dependence upon the nature of the halogen atom has been detected.[13–15] In contrast, *cis* metal sulphide complexes show a pronounced dependence of the sulphur inversion barrier on the nature of the halide due to the well known *trans* influence.[11,16,41,42] In the present work, a careful examination of the data in Table 5 for both *trans*-$[PdX_2(SCH_2CMe_2CH_2)_2]$ and *trans*-$[PdX_2\{S(CH_2)_4\}_2]$ (X = Cl, Br, or I) reveals a small but clear decrease in $E^{\ddagger}$ and $\Delta G^{\ddagger}$ values for the inversion process as the size of the halogen increases. This is the trend to be expected with the analogous *cis* complexes where the *trans* influence will be operating. In the present complexes the explanation is less obvious and may be due to anisotropy effects of the M–X bonds

Table 6

Literature values for free energy of activation of tetrahedral inversion about nitrogen in small- and medium-sized rings, with coalescence temperatures (in °C) in parentheses

Compound	Method	Solvent	$\Delta G^{\ddagger}(T_c)$ kJ mol^{-1}	Ref
$\mathrm{MeN(CH_2)_3}$	*a*	$\mathrm{CHClF_2}$	42.7 (−69)	*c*
$\mathrm{MeNCH_2CMe_2CH_2}$	*b*	$\mathrm{CFCl_3}$	37.0 (−93)	5
$\mathrm{ClN(CH_2)_3}$	*b*	$\mathrm{CHClF_2}$	*ca.* 56 (−20)	*c*
$\mathrm{ClNCH_2CMe_2CH_2}$	*b*	$\mathrm{CFCl_3}$	48.1 (−54)	5
$\mathrm{EtN(CH_2)_2}$	*b*	None	81.2 (108)	*d*
$\mathrm{MeN(CH_2)_4}$	*a*	$\mathrm{CHClF_2}$	35.1 (−98)	*c*

[a] Complete line-shape analysis. [b] Coalescence-temperature calculation. [c] J. B. Lambert, W. L. Oliver, jun., and B. S. Packard, *J. Amer. Chem. Soc.*, 1971, **93**, 933. [d] A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, 1958, **80**, 5203.

rather than to the varying nature of the M–S bonds, as has been suggested to explain the variation in chemical shifts of the $\mathrm{SCH_2}$ protons.

Methylation of Ligand Ring.—A comparison of the complexes *trans*-$\mathrm{[PdX_2\{S(CH_2)_3\}_2]}$ and *trans*-$\mathrm{[PdX_2(SCH_2CMe_2CH_2)_2]}$ (X = Cl or Br) (Table 5) shows that replacement of the ring β-hydrogens by methyl groups causes a very small (*ca.* 1 kJ mol^{-1}) lowering of the free energy of activation of the sulphur inversion. Whereas this variation may not be significant as it comes within the experimental accuracies of the energy data, it should be noted that a similar, but somewhat larger, trend has been obtained for the analogous nitrogen rings (Table 6).

Variation in Ligand Ring Size.—The four-membered ring complexes *trans*-$\mathrm{[PdCl_2(SCH_2CMe_2CH_2)_2]}$, *trans*-$\mathrm{[PtCl_2(SCH_2CMe_2CH_2)_2]}$, and *trans*-$\mathrm{[PdCl_2\{S(CH_2)_3\}_2]}$ have free energies of activation for sulphur inversion of 61, 70, and 62 kJ mol^{-1} respectively. The values obtained previously for open-chain dialkyl sulphide complexes *trans*-$\mathrm{[MCl_2\{S(CH_2SiMe_3)_2\}_2]}$ were *ca.* 55 kJ mol^{-1} for palladium(II) complexes and *ca.* 61 kJ mol^{-1} for platinum(II) complexes; thus the presence of the four-membered ring has markedly raised $\Delta G^{\ddagger}$ for the sulphur inversion in both palladium and platinum complexes.

In the complexes of five- and six-membered rings, *trans*-$\mathrm{[PdCl_2\{S(CH_2)_n\}]}$ (n = 4 or 5), however, the values of $\Delta G^{\ddagger}$ at *ca.* 56 kJ mol^{-1} are essentially no different from those of the open-chain sulphide complexes.

For the three-membered ring complex *trans*-$\mathrm{[PtCl_2\{S(CMe_2)_2\}_2]}$ the inversion barrier was too high to be observed by n.m.r. measurements, and again the comparison with nitrogen ring systems (Table 6) is relevant. The change from four- to three-membered rings in nitrogen is *ca.* 40 kJ mol^{-1}, and on a comparable basis the inversion barrier to sulphur inversion in metal-coordinated three-membered rings would rise to over 100 kJ mol^{-1}, thus explaining its lack of detection in this work where the upper limit is *ca.* 80 kJ mol^{-1}.

In open-chain dialkyl sulphides the CSC angle is approximately tetrahedral, but in the inversion transition state this angle becomes ideally 120°. Approach to such a CSC transition geometry will be severely restricted for three-membered ring sulphides with ground-state CSC angles of *ca.* 66°,[43] and difficult for four-membered rings with CSC angles of *ca.* 80°,[44] thus accounting for the inversion energies discussed above. The five- and six-membered ring sulphur ligands will, however, be much more able to accommodate the changes required from the ground state to the transition state, and hence have activation energies very little different from those of the open-chain analogues.

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