Vibrational and ^{1}H Nuclear Magnetic Resonance Spectra of Complexes of Gold(I), Palladium(II), and Platinum(II) Containing Dimethyl Sulphide as a Terminal Ligand

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Vibrational (below 800 cm^{-1}) and ^{1}H n.m.r. spectra of complexes AuXSMe$_2$ (X = Cl or Br), $Pr^n_4NMX_3SMe_2$ (M = Pd or Pt), $Pd_2X_4(SMe_2)_2$, $PtX(SMe_2)_3BF_4$, *trans*-$MX_2(SMe_2)_2$ (including MX = PtI) and *cis*-$PtCl_2(SMe_2)_2$ are reported and assignments proposed. The last can be obtained in a number of solid forms which have markedly different vibrational spectra.

We are currently engaged in a study of some platinum complexes in which dimethyl sulphide is a bridging, dibasic ligand and for comparison we required as firm an understanding as possible of the vibrational and ^{1}H n.m.r. spectra of complexes containing terminal, monobasic dimethyl sulphide groups. Coates [1] has reported the i.r. absorptions only in the range 450—200 cm^{-1} for AuXSMe$_2$ (X = Cl or Br). I.r. and Raman spectra of solid *trans*-$MX_2(SMe_2)_2$ (X = Cl, Br, or I) and their interpretation have been reported [2] but aspects of these assignments have been questioned as a result of studies on complexes of other sulphide ligands.[3] Less detailed (mainly i.r. only) accounts of the spectra of some of these complexes have been reported by other workers[1,4] and also results for *cis*-$PtX_2(SMe_2)_2$ (X = Cl or Br),[2,4] $[PdCl_3SMe_2]^-$, $[PtCl_3SMe_2]^-$ [5] and $Pd_2Cl_4(SMe_2)_2$ [6] (the platinum analogue contains bridging sulphur groups [7]). Only for $PtCl_2(SMe_2)_2$ do details of ^{1}H n.m.r. seem to have been reported.[8] Here we report more complete details for AuXSMe$_2$, $[MX_3SMe_2]^-$, $Pd_2X_4(SMe_2)_2$, and $[PtX(SMe_2)_3]^+$ as well as a re-examination of $MX_2(SMe_2)_2$.

Vibrational Spectra

Complexes AuXSMe$_2$.—Complexes of the type AuXL provide a useful guide for the interpretation of the spectra of more complicated molecules containing L. As the inorganic complex chemist is usually only interested in features related to the immediate metal–ligand skeleton, we restrict our considerations to frequencies below 800 cm^{-1}. These are listed in Table 1 with assignments based on C_s symmetry for the free molecule. The assignment of SC$_2$ stretching and bending vibrations follows from the free ligand [9] and the structurally similar ion, $[HgMeSMe_2]^+$, where Raman polarisation data is particularly useful.[10] There is no reason to dispute the assignments of Coates and Parkin [1] for Au–S and Au–X stretching and the assignment of the Au–Cl stretch is further verified by the observation of a shoulder at 319 cm^{-1} due to the ^{37}Cl isotope. The L–Au–X bend in the analogous trimethylphosphine complexes occurs below 100 cm^{-1} and in the solid state is probably strongly mixed with lattice vibrations.[11] As dimethyl sulphide is of comparable mass to trimethylphosphine, the S–Au–X bend may be assigned to one of the bands observed below 100 cm^{-1} but as the complexes are not sufficiently soluble in a suitable solvent, we cannot distinguish it from the lattice vibrations. Thus, the strong bands observed around 200 cm^{-1} are not so far accounted for and must arise from the ligands loss of rotational freedom *i.e.* AuSC deformations. This provides direct support for Clark *et al.*[3] who disagreed with the previous assignment [2] of bands in this region of the spectra of *trans*-$PdX_2(SMe_2)_2$ to SPdS deformations.

Table 1

I.r. and Raman Spectra (below 800 cm^{-1}) of AuXSMe$_2$ (X = Cl or Br)

	AuClSMe$_2$		AuBrSMe$_2$	
	I.r. mull	Raman solid	I.r. mull	Raman solid
SC$_2$ str (asym)	730vw	725ms	730vw	724m
SC$_2$ str (sym)	675vw	675ms	677vw	676m
Au–S str	345s	343w	331w	329m
Au–X str	326s 319sh	324s	229s	229s
SC$_2$ def	279m	277m	277m	279m
CSAu def		226m		197s
	198s	200m	189s	181sh
SAuX bend and lattice modes	109m		102m	
	93m		92m	
	83m		81m	
			62s	
			40w	
Other bands	304vvw	180vw		
Limit of study	20	150	20	120

Complex Anions $MX_3SMe_2^-$.—Vibrational spectra and assignments for M = Pt or Pd, X = Cl or Br are summarised in Table 2. Although $(Pr^n_4N)_2Pt_2I_6$ reacts with the stoicheiometric amount of dimethyl sulphide to form a deep red solution which no doubt contains $PtI_3SMe_2^-$, attempts to isolate the pure solid salt resulted in the loss of dimethyl sulphide and partial reversion to the

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[1] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, 421.

[2] J. R. Allkins and P. J. Hendra, *J. Chem. Soc.* (*A*), 1967, 1325.

[3] R. J. H. Clark, G. Natile, U. Belluco, L. Cattalini, and C. Filippin, *J. Chem. Soc.* (*A*), 1970, 659.

[4] D. M. Adams and P. J. Chandler, *J. Chem. Soc.* (*A*), 1969, 588.

[5] R. J. Goodfellow, P. L. Goggin, and D. A. Duddell, *J. Chem. Soc.* (*A*), 1968, 504.

[6] R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 1897.

[7] P. L. Goggin, R. J. Goodfellow, D. L. Sales, J. Stokes, and P. Woodward, *Chem. Comm.*, 1968, 31.

[8] W. McFarlane and R. F. M. White, *Chem. Comm.*, 1969, 439.

[9] J. R. Allkins and P. J. Hendra, *Spectrochim. Acta*, 1967, **22**, 2075.

[10] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, and J. G. Eary, *J.C.S. Dalton*, 1972, 647.

[11] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc.* (*A*), 1970, 545.

starting material. We have, therefore, only made ^{1}H n.m.r. measurements on $PtI_3SMe_2^-$ (and its palladium analogue as a tetraphenylphosphonium salt). Raman spectra could not be obtained from $PdBr_3SMe_2^-$ because of its colour. As well as comparison between the four anions, we base our interpretation on the relationships between $MX_3PMe_3^-$, $AuXPMe_3$, and $AuXSMe_2$. Thus it is anticipated that ν_{MX} *trans* to SMe_2 will be higher than when *trans* to PMe_3 but that the MX_2 frequencies will not be substantially different. In fact, the order of the symmetric and asymmetric $PtCl_2$ frequencies is the reverse of normal in $PtCl_3SMe_2^-$, but this order is clearly established by the polarisation results. The M–S stretching vibration is most easily identified in the i.r. spectrum of $PdBr_3SMe_2^-$ at 312 cm^{-1}. For the platinum analogue there are bands, at 334 and 306 cm^{-1} both of which are close to features of the cation * but the relative intensity and polarised nature of the higher band indicates it has another origin and we assign it as the Pt–S stretching vibration. The MCl stretching modes occur in the same region as M–S but assigning the PtCl bands by comparison with $MCl_3PMe_3^-$ leaves the M–S vibrations at 344 and 322 cm^{-1} for platinum and palladium respectively. It is not clear why the latter frequency was not observed in the Raman spectrum but it would be more unreasonable not to observe $PdCl_2$ (sym) or PdCl (*trans* to S) stretching. As with $MX_3PMe_3^-$,[11] the only deformation that can be identified with reasonable certainty is the in-plane vibration related to the 'scissors' vibration of *trans*-$MX_2(SMe_2)_2$ as this should be the strongest Raman active deformation.

TABLE 2

I.r. and Raman Spectra (below 800 cm^{-1}) of $Pr^n{}_4NMX_3SMe_2$ (M = Pd or Pt; X = Cl or Br)

	$Pr_4NPdCl_3SMe_2$			$Pr_4NPdBr_3SMe_2$		$Pr_4NPtCl_3SMe_2$				$Pr_4NPtBr_3SMe_2$			
	I.r. mull	I.r.[a] soln	Raman solid	I.r. mull	I.r.[c] soln	I.r. mull	I.r.[b] soln	Raman solid	Raman[b] soln	I.r. mull	I.r.[b] soln	Raman solid	Raman[b] soln
SC_2 str (asym)	735vw	†	732vw	723vvw	†	722vw	†	726w	730vw,dp	722vw	†	727w	†
SC_2 str (sym)	687vw	†	683vw	687w	†	682vw	†	682w	†	688vw	†	685w	†
M–S str	322s	321s		321m	313m	348w	344vw	349sh	344sh,p	336vvw		339w	334vvw,p
M–X_2 str (asym)	342s	344vs		265s 258sh	259vs	323vs	325s			239m	240m		
M–X_2 str (sym)	295sh	293m	297s	180w		333sh		330vs	328vs,p	208sh		207s	207s,p
MX str	310s	307s	309s	218ms	225m	309s	308m	311s	308m,p	218m	218m	217sh	
SC_2 def	278w	283m	279w	288m	286m	301sh				295vw			
CSM def	227w		231m			221w	*ca.* 222vw	220m	214m,p	194m		197s	198sh
	203w		200m,bd	204m,sh						176vw			
In plane def ('scissors')	162m		159s	134sh		167w		162s	168m,dp	134wm		132w	
Other defs and lattice	143sh			125w		134w				103vw		105ms	
	135m			113vw		50w,bd						95m	
	53m			104vw						53m,bd			
				73w									
				50w									
Cation and other bands	760ms			752ms		752m				753m			
	515wm			614vvw		515m				515w			
	474vw			515m						316vw			
				378vvw								313w	306vvw,p
				344w									
Limit of study	40	200	140	40	200	40	200	140	150	40	200	70	140

[a] In *cis*-1:2 dichloroethylene. [b] In nitromethane. [c] In dibromomethane.
† Not investigated or obscured by solvent.

Halogen Bridged Complexes $Pd_2X_4(SMe_2)_2$.—The deep colour prevented Raman studies of these complexes. The spectra of bridged complexes, $M_2X_4L_2$, show a strong, clear relationship to the related anion MX_3L^- (*cf.* ref. 11, p. 550). The assignments in Table 3 make use of this and comparison with other halogen-bridged palladium complexes.

trans-*Compounds* $MX_2(SMe_2)_2$.—We have repeated the measurements of Allkins and Hendra.[2] In general we agree with their results but as we have observed some additional bands, have made solution measurements and need to reassign some bands as PtSC deformations, we have reported the spectra in full in Table 4. Descriptions are based on C_i symmetry and the general lack of coincidence between i.r. and Raman spectra suggest a centrosymmetric structure. However, whilst all Raman active vibrations are totally symmetric for this point group, in solution only those that would be totally symmetric for a structure with C_{2h} symmetry, *e.g.* with the methyl groups placed symmetrically above and below the plane of the molecule, are observed to be polarised. In view of the orientation of the dimethyl sulphide group in $Pd_2Br_4(SMe_2)_2$ [12] such arrangements seem unlikely in the solid state. Our study of $PdI_2(SMe_2)_2$ was confined to i.r. measurements below 250 cm^{-1}

TABLE 3

I.r. Spectra (below 800 cm^{-1}) of $Pd_2X_4(SMe_2)_2$
(X = Cl or Br)

	$Pd_2Cl_4(SMe_2)_2$	$Pd_2Br_4(SMe_2)_2$
SC_2 str (asym)	732vw	735vw
SC_2 str (sym)	679vw	678vw
PdS str	340ms	336s
Pd–X str (terminal)	360s	274s
Pd–X str (bridging, *trans* to X)	282s	195ms
Pd–X str (bridging, *trans* to S)	308ms	223s
SC_2 def		295ms
CSPd def	209m,bd	185sh
Skeletal def and lattice modes	151sh	124sh
	148ms	119m
	132wm	109vw,sh
	93ms	73wm
	85m	68wm
Limit of study	40	40

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* Solid $Pr^n{}_4NI$ shows i.r. bands 752ms, 721w, 614vw, 516wm, 370vw, and 340vw, whilst an aqueous solution of $Pr^n{}_4NCl$ has Raman features at 781m,p, 762vw,sh, 518vw,dp, 375m,p, 334m,dp, and 311s,p.

[12] D. L. Sales, J. Stokes, and P. Woodward, *J. Chem. Soc.* (*A*), 1968, 1852.

as the higher sample temperature (*ca.* 30°) of the Perkin-Elmer 225 spectrometer caused this unstable complex to decompose. The compound was not analysed, its nature being inferred from the ^1H n.m.r. results and our observations are not entirely in agreement with those previously reported.

We have previously shown [11] that the MI_2 asymmetric stretches in *trans*-MI_2L_2 cannot be reliably assigned to strong i.r. bands as they are frequently weak even to the extent of being unobservable. Allkins and Hendra appear to have assigned these vibrations by selecting strong bands and this results in a sequence 188, 179, and 147 cm^{-1} for $PtI_2(SMe_2)_2$, $PtI_2(SeMe_2)_2$, and $PtI_2(TeMe_2)_2$ respectively, which is totally out of keeping with the almost invariant frequencies observed for the comparable MCl_2 and MBr_2 vibrations, *e.g.* the equivalent $PtBr_2$ frequencies are 240, 250 and 245 cm^{-1}. We would not expect that the MI_2 frequency would be substantially different in these sulphide complexes from that observed for phosphine and arsine complexes and hence should fall in the range 200—220 cm^{-1}. As the MSC deformations also occur here, there is bound to be some confusion and overlap.

TABLE 4

I.r. and Raman Spectra (below 800 cm^{-1}) of *trans* $MX_2(SMe_2)_2$ (M = Pd or Pt; X = Cl, Br, or I)

		$PdCl_2(SMe_2)_2$				$PdBr_2(SMe_2)_2$			$PdI_2(SMe_2)_2$	$PtCl_2(SMe_2)_2$		$PtBr_2(SMe_2)_2$				$PtI_2(SMe_2)_2$		
		I.r. mull	I.r.[a] soln	Raman solid	Raman[c] soln	I.r. mull	I.r.[b] soln	Raman solid	I.r. mull	I.r. mull	Raman solid	I.r. mull	I.r.[c] soln	Raman solid	Raman[c] soln	I.r. mull	Raman solid	Raman[c] soln
SC_2 asym str	A_g			727wm	730w,bd,dp						725w			724w	728wm,dp		722wm	726wm,dp
	A_u	727vw	†			723vw	†		†	726vw		722vw	†			722vw		
SC_2 sym str	A_g			683m	686m,p						684w			682wm	684ms,p		679m	683ms,p
	A_u	680vw	†			677vw	†		†	679vw		682vw	†			675vw		
MS_2 str	A_g			323m	313s,p			317s			343m			341m	339m,p		336m	335m,p
	A_u	308m	307m			315ms	313ms		†	311m		315m	303m			311m		
MX_2 str	A_g			304vs	305s,p			200vs			329s			213vs	208vs,p		150vvs	150vvs,p
	A_u	359s	363s			262ms	264ms		218wm	344s		245s	250ms			218w		
SC_2 def	A_g			289wm				282s			293w			293wm	*ca.* 300w,bd		284wm	288w,p
	A_u	292m	285m			302sh	277sh		†	301m		301vvw	285w			295w		
CSM def	A_g			193wm,bd	198wm,bd,p						203w			202m,sh			210ms,bd	*ca.* 209sh,p
	A_u	218wm	218m			226sh			238wm	231w		236wm	222ms			236m		
	A_u					210wm	211m,bd		202wm	219wm		213m				192m		
In plane def	A_g			167s	149m,dp			137sh			170s 158sh			140vs			131s	
Other defs and lattice	A_u	172m				134m			126s	173m		134s	131ms			131s		
	A_u	163sh								138wm						103sh		
	A_u	127s				114wm			102wm	131wm		110wm	115w			97w		
	A_u	93m				76wm			63wm	118wm		80m		84sh		67wm		
		89sh								95wm	97sh	70sh		75sh			69m	
										71w	75s			56m			39ms	
											63s			46m			23vs	
											41vs			34vs				
Other bands								240sh 181sh								322vw,sh	299sh	
Limit of study		40	200	100	135	40	200	120	40	40	25	40	40	28	180	40	15	135

[a] In *cis*-1:2 dichloroethylene. [b] In dibromomethane. In benzene.
† Not investigated or obscured by solvent.

For these compounds there is only one centrosymmetric in-plane deformation which is, hence, easily located in the Raman spectra and shows halogen dependence particularly between chloride and bromide. We feel that without polarised single crystal studies specific descriptions of the four i.r. active skeletal deformations are unjustified and, in any case, labels such as δ X–M–X used by other workers are misleading since the bond angles being altered during in-plane vibrations are X–M–L.

Complex Cations $PtX(SMe_2)_3^+$.—These may be prepared from equimolar quantities of $PtX_2(SMe_2)_2$ and $AgNO_3SMe_2$. The vibrational spectra of the chloro- and bromo-derivatives as their fluoroborate salts are given in Table 5. The band at 326 cm^{-1} in the Raman spectrum of the bromo complex in nitromethane moves to lower frequency under the perpendicular polarisation conditions and hence includes a less polarised second band at lower frequency, as is found in the i.r. spectrum of the solid. These are probably the two PtL_2 stretching vibrations which are nearly coincident in other MXL_3^+ cations [11] whilst the strong Raman band at 348 cm^{-1} is the PtS (*trans* to Br) vibration. The strong polarised Raman band at 215 cm^{-1}, with corresponding feature in the i.r., had no counterpart in the spectra of the chloro-complex and must be PtBr stretching. The assignment of the chloro-complex follows from this but the strong band at 337 cm^{-1} in both i.r. and Raman spectra, which is mainly due to PtCl stretching, must conceal the PtS_2 symmetric stretching vibration.

cis-$PtX_2(SMe_2)_2$.—We have found *cis*-$PtCl_2(SMe_2)_2$ to exist in several forms which give rise to different vibrational spectra (Table 6 and Figure). Dissolving the *trans*-isomer in hot water usually results in form A whilst redissolving the yellow solid formed by the reaction of aqueous K_2PtCl_4 and SMe_2 on refluxing the reaction mixture yields form B on cooling the filtered solution, but we have obtained both forms on recrystallisation from water on different occasions. Form A, as initially produced gives an i.r. spectrum corresponding to that reported by Adams and Chandler [4] but the trace of *trans*-isomer present (as in the case of form B) was removed by washing with benzene for the spectrum given

TABLE 5

I.r. and Raman Spectra (below 800 cm^{-1}) of $PtX(SMe_2)_3BF_4$ (X = Cl or Br)

	$PtCl(SMe_2)_3BF_4$			$PtBr(SMe_2)_3BF_4$		
	I.r. mull	Raman solid	Raman soln.[a]	I.r. mull	Raman solid	Raman soln.[a]
SC_2 asym str	722vw	723m	726wm,dp	722vw	726m	726m,dp
SC_2 sym str	678m	679ms	680ms,p	679m	678ms	678ms,p
PtS str	352w	353m	351m,p	351vw	348m	348ms,p
PtS_2 str (sym)				329w,bd	323m	326wm,p
PtS_2 str (asym)	329m,sh	329m,sh	328dp?	323w,bd		323?
PtX str	337s	336s	335s,p	218ms,bd	214s	215s,p
SC_2 def	303wm	306wm			305vw	302w,p
	289w	287vw	288vw,p	290vw,bd	285vw	284w,dp
CSPt def		247vw			226sh	230sh,p
	237w,bd	231vw		202ms		
	215wm,bd	205vs	203m,bd,p	198ms	195vs	196s,dp
	208sh					
Skeletal def and lattice modes	173w	173ms	165sh,dp	147w,bd	145m	145sh,dp
				137m,sh		
	147wm	146m		131ms		
	132wm	130wm,bd		122w,sh	121m,sh	
	104w,bd			60s,bd		
	72wm,bd					
BF_4^-	766vw	764w	764wm,p	764vw	763w	764m,p
	521s			521s		
Other bands			703w,p			700w,p
Limit of study	40	100	150	40	100	105

[a] In nitromethane.

TABLE 6

I.r. (below 1100 cm^{-1}) and Raman Spectra of *cis*-$PtCl_2(SMe_2)_2$

	Form A		Form B		Form C	
	I.r. mull	Raman solid	I.r. mull	Raman solid	I.r. mull	Raman solid
CH_3 rocking	1053ms		1036s		1040ms	
	1029ms				1029s	
			992s		992s	
	979s				987s	
	961w		957w		947vw	
			951sh			
	928vw		919w		925vw	
	908vw		914sh		914w	
SC_2 asym str	720vw?	727m	729vw	726w		727m
				723m		
SC_2 sym str	684vw,bd	686ms,bd	690vw,sh	682m		682m
			681w	676wm		
PtS_2 str (sym)	349ms	352ms	353w	353m	349w	353wm
PtS_2 str (asym)	338ms	338ms	339m	337wm	337sh	336w
$PtCl_2$ str (sym)	325s	325vs	319s	316s	324vs	322s
$PtCl_2$ str (asym)	312vs,bd	314ms,bd	305s,bd	305ms,bd	312vs,bd	310m,bd
SC_2 def			294sh		308sh	
					290sh	294w
CSPt bend		233m,sh	235m	235sh		246w
	216m,bd	217s,bd	226m	226ms	235m	232wm
				206bd,sh	211wm	218m
Skeletal def and lattice modes	165m	163s	166m	165ms	180m	170s
			150vw			
		139w	141wm		138wm	144w
	130w,bd		130vw,sh	130wm,bd	127wm	132w
		123w	117sh			
			114w	111wm		
			96wm		100m	
		91sh		89m	87sh	89w
	40—80w			76m	76m	
			65m	63m		65wm
				50m		59wm
				32m		46sh
						36sh
Limit of study	40	80	40	25	40	30

in Table 6. When form B is recrystallised from hot chloroform, the lustrous crystals initially produced become opaque on standing in air (form C). Previous workers state that the initial product contains one mole of solvent which is readily lost.[13] If, after decanting the solvent, the product is washed with benzene, further changes in the spectrum are observed (Figure). The ^1H n.m.r. spectra of dichloromethane solutions of all

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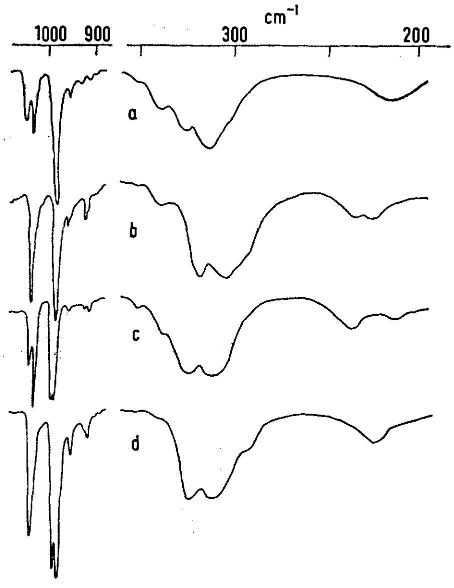
[13] C. W. Blomstrand and C. Enebuske, *J. prakt. Chem.*, 1888, **38**, 358.

forms are consistent with the presence of *cis*-isomer which slowly changes with time into the *trans*-isomer.

In view of the differences between form A and the other forms in the PtCl and PtS stretching region, it is possible that this is not just another crystal form but a different isomeric structure. We can exclude any sulphur bridged species from the absence of any vibrational features in the 450—360 cm^{-1} region [7]. The ^{1}H n.m.r. spectrum of the *cis*-isomer in D_2O does show *ca.* 10% of the $PtCl(SMe_2)_3^+$ cation and $[PtCl(SMe_2)_3]$-$[PtCl_3SMe_2]$ would be isomeric with $PtCl_2(SMe_2)_2$ but there is no evidence for $[PtCl_3SMe_2]^-$ in the D_2O solution. An aqueous solution of $PtCl(SMe_2)_3NO_3$, prepared *in situ* does produce a precipitate of form A (together with some *trans*-isomer) when added to aqueous $Pr^n_4NPtCl_3SMe_2$. As the spectra of form A do not completely correspond to the sum of those of $Pr^n_4NPtCl_3SMe_2$ (Table 2) and $PtCl(SMe_2)_3BF_4$ (Table 5), we cannot reach any definite conclusion and include form A amongst the forms of *cis*-$PtCl_2(SMe_2)_2$. Amongst the other forms, the most notable differences in the spectra are in the methyl rocking and CSPt bending regions (Figure). This supports the conjecture that these different forms involve different orientations of the dimethyl sulphide groups. The existence of different orientations of ligands which lack axial symmetry has been suggested as the cause of two crystal forms of *cis-mer*-$[MoOCl_2(PMe_2Ph)_3]$ [14] and three species of *trans*-$[RhCl(CO)(PBu^t_2Et)_2]$ in solution.[15] The three-fold symmetry of the YMe_3 (Y = N, P, or As) group probably explains why we have not observed multiple crystal habits with complexes of these ligands.



I.r. spectra of *cis*-$PtCl_2(SMe_2)_2$; a, form A; b, form B; c, form C; d, form C after washing with benzene

The skeletal frequencies reported by Allkins and Hendra [2] for *cis*-$PtCl_2(SMe_2)_2$ do not agree with any form prepared by us but they do not give enough information to justify any comment on its nature. These authors also report results for *cis*-$PtBr_2(SMe_2)_2$. The yellow solid obtained by recrystallisation of *trans*-$PtBr_2(SMe_2)_2$ from hot water contains some *trans*-isomer which can be removed by washing with benzene. The residue has i.r. absorptions at 440 and 376 cm^{-1} which imply the presence of bridging dimethyl sulphide groups and accordingly its nature will be discussed in a subsequent paper. However, the ^{1}H n.m.r. of a deuteriochloroform solution is essentially that of *cis*-$PtBr_2(SMe_2)_2$ which isomerises to the *trans*-isomer.

^{1}*H N.m.r. Spectra*

The results are listed in Tables 7 and 8. In general, methylene chloride solutions showed a sharp methyl resonance in the τ 7—8 region with satellites in the case of platinum complexes. Dimethyl sulphide itself in dichloromethane has the methyl resonance at τ 7·88. The spectra of $PtCl_2(SMe_2)_2$ and $PtBr_2(SMe_2)_2$ showed both *cis*- and *trans*-isomers, the ratios being about 1 : 2 and 1 : 6 respectively at equilibrium at 30°. The cations, $PtX(SMe_2)_3^+$, show resonances due to the SMe_2 (*trans* to SMe_2) and SMe_2 (*trans* to X) groups which integrate as 2 : 1.

TABLE 7

^{1}H N.m.r. shifts (in τ) for dimethyl sulphide complexes of palladium(II) and gold(I)

	X = Cl	X = Br	X = I
$Ph_4PPdX_3SMe_2$	7·78	7·63	7·47
$Pr^n_4NPdX_3SMe_2$	7·74	7·60	
$Pd_2X_4(SMe_2)_2$	7·72	7·54	
trans-$PdX_2(SMe_2)_2$	7·62	7·48	7·26
$AuXSMe_2$	7·33	7·31	

TABLE 8

^{1}H N.m.r. data for some dimethyl sulphide complexes of platinum(II)

	X = Cl		X = Br		X = I	
	τ_{Me}	$^3J_{PtH}$	τ_{Me}	$^3J_{PtH}$	τ_{Me}	$^3J_{PtH}$
$Ph_4PPtX_3SMe_2$	7·70	47·3	7·63	47·9	7·52	50·3
$Pr^n_4NPtX_3SMe_2$	7·66	47·3	7·58	48·2	7·47	51·5
trans-$PtX_2(SMe_2)_2$	7·56	41·6	7·47	41·5	7·31	44·4
cis-$PtX_2(SMe_2)_2$	7·46	49·3	7·43	50·1		
$PtX(SMe_2)_3BF_4$	7·37	51·0 [a]	7·39	51·4 [a]		
	7·38	43·8	7·32	44·5		

[a] *trans* to X.

The dark red complex, $PdI_2(SMe_2)_2$ which tends to decompose to a black insoluble material (presumably PdI_2) was freshly prepared and recrystallised from cold dichloromethane but on redissolving in this solvent some black residue remained. The observed resonance was broad at 30° but gave a single sharp line at −20°. As the complex appears to be dissociating, one might have expected the bridged dimer, $Pd_2I_4(SMe_2)_2$ to be involved but we have not found a resonance that could be attributed to this species in the ^{1}H n.m.r. spectra of SMe_2–PdI_2 systems. In the past, we have examined the anions MX_3L^- as tetraphenylphosphonium salts pre-

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[14] J. Chatt, L. Manojlović-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 655.

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pared *in situ* by dissolving stoicheiometric quantities of Ph_4PX and $M_2X_4L_2$ in dichloromethane.[16] With the dimethylsulphide complexes, this only gave the expected result for $PdCl_3SMe_2^-$. The reaction of Ph_4PX with the sulphur bridged $Pt_2Cl_4(SMe_2)_2$ and its bromo-analogue produces several species including some with sulphur bridges which we are studying in more detail. However, a fivefold excess of Ph_4PX suppresses side reactions and appears to give the desired product. Surprisingly, the tetrapropylammonium salts can be prepared using only a small excess of $Pr^n{}_4NX$ and the data for these is also included in the Tables. The spectrum of $Pr^n{}_4NPtI_3SMe_2$ showed in addition, the resonances of *trans*-$PtI_2(SMe_2)_2$, the lines being rather broad at 30° but much sharper at −20°. A 1 : 1 mixture of Ph_4PBr and $Pd_2Br_4(SMe_2)_2$ showed a broad doublet which resolves at −40° into two almost equal peaks corresponding to $PdBr_3SMe_2^-$ and *trans*-$PdBr_2(SMe_2)_2$. The formation of the *trans*-compound was suppressed by a fivefold excess of Ph_4PBr. The spectra of $Pr^n{}_4NPdCl_3SMe_2$ and $Pr^n{}_4NPdBr_3SMe_2$ also showed a small amount of the *trans*-complex. In the absence of $Pd_2I_4(SMe_2)_2$, $PdI_3SMe_2^-$ was formed from $PdI_2(SMe_2)_2$, excess of PdI_2 and a fivefold excess of Ph_4PI and examined at −60° to slow the exchange of sulphide groups between the anion and the *trans*-complex. The tendency to form the *trans*-compound is greater than for the bromide as under these conditions only about one third of the ligand is present as the anion.

DISCUSSION

In trimethylphosphine complexes, the mean of the primarily M–P stretching frequencies were in the order *cis*-$MCl_2(PMe_3)_2 > MCl_3PMe_3^- >$ *trans*-$MCl_2(PMe_3)_2$ and for the platinum complexes ${}^3J_{PtH}$ followed the same order with ratios 1 : 0·86 : 0·60 for *cis* : anion : *trans*. For the dimethyl sulphide complexes the order of M–S stretching frequencies broadly follows this pattern but these are 30—50 cm^{-1} lower even though the effective mass of the ligand must be lower than for trimethylphosphine. Whilst ${}^3J_{PtH}$ follows the same order, the ratios are much closer, 1 : 0·96 : 0·84 and the two couplings in $PtCl(SMe_2)_3^+$ are much closer (43·8 and 51·0 Hz) than in the trimethylphosphine (24·0 and 43·0 Hz) or trimethylarsine (18·0 and 26·5 Hz) equivalents.[17] This is in keeping with a much lower *trans*-influence of SMe_2 compared to PMe_3, previously deduced from vibrational studies.[5] It also implies that sulphur has a greater *trans*-influence than chloride. The mean M–S frequencies are above the M–Cl frequencies for the anion and *cis*-complexes in spite of the fact that dimethyl sulphide can hardly have an effective mass less than that of chloride: however, the order is reversed for the *trans*-complex.

The shift of the methyl resonance on change of halide shows the same dependence on *cis*-halides as observed for PMe_3 and $AsMe_3$ complexes[16] and can presumably be ascribed to the same causes.

EXPERIMENTAL

We have described the general methods for the i.r.,[11] Raman,[18] and ${}^1H$ n.m.r.[16] measurements previously. For the ${}^1H$ n.m.r. spectra, 0·1M solutions in dichloromethane were used except for the gold complexes and the dimeric palladium complexes which were not soluble to this extent and saturated solutions were used. For $PtX_3SMe_2^-$, the solutions were 0·1M in Ph_4PX but 0·01M in $Pt_2X_4(SMe_2)_2$.

Preparation of the Complexes.—Many of the complexes have been described previously and were verified by elemental analysis and m.p.[5,13,19,20] The halogen bridged palladium compounds were prepared by the method of Chatt and Venanzi.[21] $Pd_2Cl_4(SMe_2)_2$, m.p. 183—185°d. (Found: C, 10·20; H, 2·50. $C_4H_{12}Cl_4Pd_2S_2$ requires C, 10·05; H, 2·55%). $Pd_2Br_4(SMe_2)_2$, m.p. 169° (Found: C, 7·40; H, 1·80. $C_4H_{12}Br_4Pd_2S_2$ requires C, 7·30; H, 1·85%). $AuBrSMe_2$ was prepared by a method similar to that for the corresponding chloride[19] starting from $NaAuBr_4$: preparation *via* halogen exchange from the chloride was not satisfactory, m.p. 130—140°d. (Found: C, 7·20; H, 1·70. C_2H_6AuBrS requires C, 7·00; H, 1·80%). $Pr^n{}_4NPdBr_3SMe_2$ was prepared in 90% yield by the analogous method to that used for the chloride[5] and is dark red, m.p. 99—100° (decomp.) (Found: C, 28·20; H, 5·60; N, 2·30. $C_{14}H_{34}Br_3NPdS$ requires C, 28·30; H, 5·75; N, 2·35%). $Pr^n{}_4NPtX_3SMe_2$ (X = Cl or Br) was prepared by stirring SMe_2 with $(Pr^n{}_4N)_2Pt_2X_6$ (mole ratio, 2·2 : 1) in dimethylformamide for 3 h. The crude product was precipitated by addition of ether and extracted with cold acetone. After drying the solution with $MgSO_4$, the product crystallised out on slow addition of ether. $Pr^n{}_4NPtCl_3SMe_2$, orange-yellow needles, m.p. 117° yield 40% (Found: C, 30·60; H, 6·10; N, 2·65; Cl, 19·30; S, 6·15. $C_{14}H_{34}Cl_3NPtS$ requires C, 30·55; H, 6·25; N, 2·55; Cl, 19·35; S, 5·80%). $Pr^n{}_4NPtBr_3SMe_2$, orange-red needles, m.p. 132—133°, yield 85% (Found: C, 24·85; H, 4·95; N, 2·10; Br, 35·50; S, 4·65. $C_{14}H_{34}Br_3NPtS$ requires C, 24·60; H, 5·00; N, 2·05; Br, 35·10; S, 4·70%). The complexes, $PtX(SMe_2)_3BF_4$ were prepared by stirring equimolar quantities of $PtX_2(SMe_2)_2$ and $AgNO_3SMe_2$ in acetone for 3 h. The silver halide precipitated was filtered off and the solvent removed *in vacuo*. The crude $PtX(SMe_2)_3NO_3$ was dissolved in a minimum of cold water and addition of 40% aqueous fluoroboric acid precipitated $PtX(SMe_2)_3BF_4$ which was recrystallised from water, keeping heating to a minimum. $PtCl(SMe_2)_3BF_4$, off-white needles, m.p. 106—107° (Found: C, 14·65; H, 3·70; S, 19·10; Cl, 7·15; F, 14·90. $C_6H_{18}BClF_4S_3Pt$ requires C, 14·30; H, 3·60; S, 19·10; Cl, 7·05; F, 15·10%). $PtBr(SMe_2)_3BF_4$, off-white needles, m.p. 108—110° (Found: C, 13·25; H, 3·30; S, 17·40; Br, 14·70; F, 13·50. $C_6H_{18}BBrF_4S_3Pt$ requires C, 13·15; H, 3·30; S, 17·50; Br, 14·60; F, 13·90%).

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