Preparation and Identification by Proton Nuclear Magnetic Resonance and Proton–Platinum-195 INDOR and Vibrational Spectroscopy of some Platinum(II) Complexes containing Dimethyl Sulphide as a Bridging Ligand

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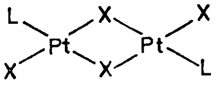
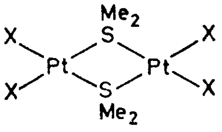
The anions $[Pt_2X_6(SMe_2)]^{2-}$ (X = Cl and Br), in which SMe_2 is the sole bridging group, and the anions $[Pt_2X_5(SMe_2)]^-$ containing both a SMe_2 bridge and a halide bridge have been characterised as their $[Pr^n_4N]$ salts. Their ^1H n.m.r. and vibrational spectra are reported and assigned. ^1H N.m.r. and ^1H $\{^{195}Pt\}$ INDOR spectroscopy are used to identify $[Pt_2Cl_5(SMe_2)_2]^-$ as a product of the reaction of $[PPh_4]Cl$ with $Pt_2Cl_4(SMe_2)_2$. The vibrational spectra of $Pt_2X_4(SMe_2)_2$ (X = Cl or Br) are assigned on the basis of a sulphur-bridged structure but it is proposed that the analogous iodide is halide bridged. The sulphur-bridged anion $[Pt_2Cl_5SMePh]^-$ has been prepared but $Pt_2X_4(SPh_2)_2$ are halide bridged. Two *cis*-$[PtCl_2SMe_2]$ groups linked by a single bridging SMe_2 is postulated as the structure of $Pt_2Cl_4(SMe_2)_3$. Bands in the infrared spectrum of the benzene insoluble form of $PtBr_2(SMe_2)_2$ are shown to be due to the impurity *cis*-$PtBr_2Me_2SO{\cdot}SMe_2$ rather than bridging SMe_2. The significance of bridging dimethyl sulphide is discussed in the light of the chemical and spectroscopic results.

OUR infrared studies on the dimeric platinum and palladium complexes $M_2Cl_4L_2$ for a range of carbon, phosphorus, and arsenic ligands[1] showed that all had the *trans*-chloro-bridged structure (I). The infrared spectrum[1] of $Pd_2Cl_4(SMe_2)_2$ also agrees with this structure, but those of $Pt_2Cl_4(SR_2)_2$ (R = Me or Et) cannot be accounted for on the same basis. Further, the colour and solubility of the latter do not bear the usual relationship of the properties of structure (I) to *cis*- and *trans*-MCl_2L_2. Sulphides are potentially dibasic ligands and single crystal *X*-ray studies[2,3] confirmed that in $Pt_2Br_4(SEt_2)_2$ the sulphur atoms occupy bridging positions [structure (II)] in contrast to $Pd_2Br_4(SMe_2)_2$ which has structure (I). In our preliminary communication,[3] we noted that bands assignable as Pt–S stretching vibrations occurred at significantly higher wavenumbers when the sulphide is bridging than when it is terminal,[4] which is consistent with the markedly shorter bridging Pt–S bond compared to the terminal Pd–S bond.[2] We were interested in obtaining other types of complexes containing bridging sulphide groups and now report a range of systems involving bridging dimethyl sulphide, together with the spectroscopic evidence on which the formulations are based. We have also made some parallel studies using methyl phenyl sulphide and diphenyl sulphide.



(I)



(II)

Anionic Complexes containing bridging Dimethyl Sulphides.—Binuclear complexes such as $Pt_2X_4(PMe_3)_2$ readily react with two equivalents of $[Ph_4P]X$ to give $[Ph_4P][PtX_3PMe_3]$ and we have used this reaction to form these complexes *in situ* for ^1H n.m.r. measurements.[5] When applied to $Pt_2Cl_4(SMe_2)_2$, not all the solid dissolves and the resulting proton spectrum shows six different dimethyl sulphide environments. The three resonances at highest field can be identified as $[PtCl_3SMe_2]^-$, *trans*- and *cis*-$PtCl_2(SMe_2)_2$ respectively from the values of τ_{Me} and $^3J_{PtH}$.[4] However, the best proof is the platinum chemical shift, obtained from ^1H $\{^{195}Pt\}$ INDOR measurements, which is within 3 p.p.m. of the value for an authenticated sample[6] in each case. The ^{195}Pt satellites of the remaining three (see ref. 7) indicate that they belong to sulphide groups that are terminal, bridging between two equivalent metal atoms, and bridging between two different platinum atoms respectively (in order to low field). The corresponding reaction with $Pt_2Br_4(SMe_2)_2$ gives $[PtBr_3SMe_2]^-$ as the major product, but *cis*- and *trans*-$PtBr_2(SMe_2)_2$ are also present together with one species containing bridging dimethyl sulphide (bonded to two equivalent metal atoms). When the reactions are carried out with a five-fold excess of $[Ph_4P]X$, $[PtX_3SMe_2]^-$ is the sole product. These experiments suggested that sulphide-bridged anions existed but as we were unable to isolate any from the mixtures formed, we have tried alternative routes.

The preparation of $[Pr^n_4N][PtCl_3SMe_2]$ by the reaction of dimethyl sulphide with $[Pr^n_4N]_2[Pt_2Cl_6]$ yields only 40% of the desired product.[4] The remainder analyses as, and has ^1H n.m.r. integrals consistent with, $[Pr^n_4N]_2[Pt_2Cl_6SMe_2]$. The relative intensities of the ^{195}Pt satellites of the methyl protons indicate that the sulphide is bridging so structure (III) is proposed.

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

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

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

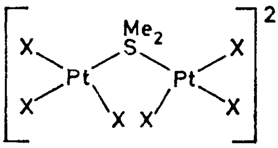
[4] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, F. J. S. Reed, J. G. Smith, and K. M. Thomas, *J.C.S. Dalton*, 1972, 1904.

[5] D. A. Duddell, J. G. Evans, P. L. Goggin, R. J. Goodfellow, A. J. Rest, and J. G. Smith, *J. Chem. Soc.* (*A*), 1969, 2134.

[6] R. J. Gooffellow and B. F. Taylor, unpublished work.

[7] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J. Chem. Soc.* (*A*), 1971, 2031.

Although there are other examples of complexes where metal atoms are linked by a single ligand atom, *e.g.* $[Cr_2O_7]^-$ and $[Al_2Cl_7]^-$,[8] cases where the bridging group is a neutral ligand are almost unknown. One example[9] is $[(\pi\text{-}C_6H_5)Fe(CO)_2]\cdot SO_2\cdot[(\pi\text{-}C_6H_5)Fe(CO)_2]$, whilst the trimeric complex $[Pt(CH_2SiMe_3)_2SMe_2]_3$ presumably consists of a ring of single Pt–S–Pt bridges.[10] The reaction of $[Pr^n{}_4N]_2[Pt_2Br_6]$ and 2 mol equiv. of $[Pr^n{}_4N][PtBr_3SMe_2]$ in dimethylformamide yielded a very insoluble product which could not be satisfactorily separated from starting material. Using the more soluble $[Bu^n{}_4N]$ salt, the ^1H n.m.r. spectrum showed about one sixth conversion into a sulphide-bridged species after equilibration for one week in dichloromethane. The values of $^3J_{PtH}$ and δ(Pt) (see Table 1) suggest that it is the singly bridged anion $[Pt_2Br_6SMe_2]^-$. The reaction of dimethyl sulphide with $[Pr^n{}_4N]_2[Pt_2Br_6]$ yields only the monomeric anion even if only 1 mol equiv. of SMe_2 is used.



(III)

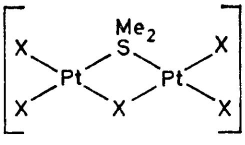
TABLE 1

N.m.r. parameters of dimethyl sulphide bridged anions

	τ_{Me}	$^3J_{PtH}$	δ_{Pt} [a]
$[Pr^n{}_4N]_2[Pt_2Cl_6SMe_2]$	6·92	35·8	−1776
$[Bu^n{}_4N]_2[Pt_2Br_6SMe_2]$	6·74	35·8	−1146
$[Pr^n{}_4N][Pt_2Cl_5SMe_2]$	6·97	37·8	−2336
$[Pr^n{}_4N][Pt_2Br_5SMe_2]$	6·89	38·2	−1583

[a] P.p.m. upfield of 21·4 MHz when corrected to Me_4Si = 100 MHz, values ±2 p.p.m.

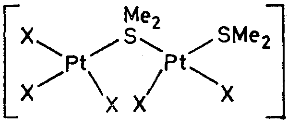
Since dimethyl sulphide and halide ions can act as bridging groups, it should be possible to prepare complexes containing both bridging groups simultaneously which would be structurally similar to the monomethylthio-derivatives $Pt_2X_3SMeL_2$ ($L = PMe_3$ or $AsMe_3$).[7] Platinum(II) chloride under acetone slowly reacts with $[Pr^n{}_4N][PtCl_3SMe_2]$ to yield $[Pr^n{}_4N][Pt_2Cl_5SMe_2]$, the ^1H n.m.r. spectrum of which supports structure (IV). The same method can be used to produce the bromo-analogue in good yield.



(IV)

The addition of 1 mol equiv. of $[Pr^n{}_4N]X$ to these mixed bridged anions in dichloromethane provides another route to the singly bridged anions and this is the only convenient way of preparing pure $[Pr^n{}_4N]_2[Pt_2Br_6SMe_2]$ which precipitates as sparingly soluble red crystals. The ^1H n.m.r. spectrum of an equimolar mixture of $Pt_2Cl_4(AsMe_3)_2$ and $[Pr^n{}_4N]Cl$ in dichloromethane showed that only $[PtCl_3AsMe_3]^-$ and $Pt_2Cl_4(AsMe_3)_2$ were present, indicating that a similar partial opening of twin halide bridges does not occur. Attempts to open the chloride bridge in $Pt_2Cl_3(SMe)(PMe_3)_2$ to leave a singly bridging SMe group were also unsuccessful. The n.m.r. parameters of the binuclear anionic complexes are given in Table 1. It seems that the proton resonances of bridging dimethyl sulphide characteristically occur to low field of those of terminal dimethyl sulphide.[4]

Returning to the mixture formed when $[Ph_4P]Cl$ reacts with $Pt_2Cl_4(SMe_2)_2$, the dimethyl sulphide group which is bridging between equivalent platinum atoms could be either $[Pt_2Cl_5SMe_2]^-$ or $[Pt_2Cl_6SMe_2]^{2-}$ from the proton parameters. However, the ^{195}Pt shift of −2339 p.p.m. clearly identifies it as $[Pt_2Cl_5SMe_2]^-$. The remaining two unassigned methyl resonances had equal intensities in each of several experiments. The terminal SMe_2 group is bonded to a platinum atom with shift −1007 p.p.m. whilst the bridging group is co-ordinated to platinum nuclei whose shifts are −1008 and −1710 p.p.m. In view of the range of ^{195}Pt chemical shifts, −1007 and −1008 p.p.m. must refer to the same platinum atom. The ^{195}Pt shift of $[PtCl_3SMe_2]^-$ is only 3 p.p.m. from that of $[Pt_2Cl_6SMe_2]^-$ suggesting that δ_{Pt} is not greatly affected by the co-ordination of the sulphide ligand to a second platinum atom. If this also applies to our unknown species, then the low-field ^{195}Pt resonance belongs to the unit $PtCl_3SMe_2$ whilst the other is similar to *cis*- or *trans*-$PtCl_2(SMe_2)_2$ (−983 and −1109 p.p.m. respectively). From the value of $^3J_{PtH}$ of the terminal sulphide, we favour the *cis*-configuration leading to structure (V) and formulation $[Pt_2Cl_5(SMe_2)_2]^-$. The ^1H n.m.r. parameters are τ_{Me} (terminal) 7·42, $^3J_{PtH}$ 48·8 Hz, τ_{Me} (bridging) 6·76, $^3J_{PtH}$ 36·8 and 34·5 Hz. Formation of such a species can be readily understood since it is the result of one Pt–S bond being broken by incoming halide. In an effort to obtain this complex for complete characterisation we investigated the following reactions:



(V)

(i) $[Pr^n{}_4N]_2[Pt_2Cl_6] + 2\ cis\text{-}PtCl_2(SMe_2)_2 \xrightarrow[\text{1 week}]{CH_2Cl_2}$

(ii) $[Pr^n{}_4N][PtCl_3C_2H_4] + cis\text{-}PtCl_2(SMe_2)_2 \xrightarrow[\text{24 h}]{\text{boiling } CH_2Cl_2}$

(iii) $[Pr^n{}_4N]_2[Pt_2Cl_6SMe_2] + AgNO_3SMe_2 \xrightarrow[\text{24 h}]{CH_2Cl_2}$

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[8] T. W. Couch, D. A. Lokken, and J. D. Corbett, *Inorg. Chem.*, 1972, **11**, 357.

[9] M. R. Churchill, B. G. DeBoer, K. L. Kalra, P. Reich-Rohrwig, and A. Wojcicki, *J.C.S. Chem. Comm.*, 1972, 981.

[10] B. Wozniak, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 3116.

Whilst it was formed in all three cases, only in (i) was it a major product and even then we were unable to separate it from the other products ($[PtCl_3SMe_2]^-$ and $[Pt_2Cl_5SMe_2]^-$).

Neutral Complexes containing bridging Dimethyl Sulphide.—In general, the dimeric complexes, $Pt_2X_4(SR_2)_2$ (X = Cl or Br, R = Me or Et) can be prepared by the reaction of Na_2PtX_4 and $PtX_2(SR_2)_2$ in ethanol, but with $PtCl_2(SMe_2)_2$ the product is reported to be $Pt_2Cl_4(SMe_2)_3$.[11] Chatt and Venanzi prepared $Pt_2Cl_4(SMe_2)_2$ by the reaction of SMe_2 on $Pt_2Cl_4(C_2H_4)_2$.[11] We find that heating $PtCl_2$ and $PtCl_2L_2$ in xylene (a method applicable to a range of systems [12]) gives the complex but the yield is rather low and the product difficult to purify because of its low solubility. Stirring the same reactants in acetone for a week gives a higher yield but the solution above the precipitate remains dark red and the n.m.r. spectrum (in [$^2H_6$]acetone) shows only $[Pt_2Cl_5SMe_2]^-$. A product of more lustrous appearance is obtained by the action of an approximately stoicheiometric quantity of methyl fluorosulphonate [13] on $[Pr^n{}_4N][PtCl_3SMe_2]$ in dry dichloromethane. $Pt_2Cl_4(SMe_2)_2$ crystallised slowly from the medium in which all other products (presumably mainly MeCl and $[Pr^n{}_4N][FSO_3]$) are soluble. (Our hope in trying this reaction had been to prepare $PtCl_3SMe_3$, a zwitterion isoelectronic with $[PtCl_3PMe_3]^-$.) The same reaction yields good samples of the bromo-analogue. We have not found a solvent in which these complexes are sufficiently soluble to give ^1H n.m.r. spectra even with spectrum accumulation. However, vibrational measurements alone (*vide infra*) are sufficient to show that all have structure (II) as actually derived for $Pt_2Br_4(SEt_2)_2$ by *X*-ray crystallography.[3]

The light yellow, insoluble, complex $Pt_2Cl_4(SMe_2)_3$ may be prepared by stirring stoicheiometric amounts of K_2PtCl_4 and $PtCl_2(SMe_2)_2$ in water and evaporating the resulting red solution to dryness. It is also formed by the reaction of methyl fluorosulphonate with $PtCl_2(SMe_2)_2$ but either preparative method applied to the corresponding bromide yields only $Pt_2Br_4(SMe_2)_2$.

TABLE 2

Vibrational spectra (below 800 cm^{-1}) of $[Pr^n{}_4N][Pt_2X_5SMe_2]$ (X = Cl or Br)

	$[Pr^n{}_4N][Pt_2Cl_5SMe_2]$				$[Pr^n{}_4N][Pt_2Br_5SMe_2]$			
	I.r. (mull)	I.r. (CH_2Br_2)	R (solid)	R (CH_2Br_2)	I.r. (mull)	I.r. (CH_2Br_2)	R (solid)	R (CH_2Br_2)
Pt_2S str sym	340 [a]		337m,bd	348sh,bd	344m	339m	344wm	339m,p
asym	413m	414m			406ms	406m		
$(PtX)_2$ (*trans* to X) sym	*358*ms	*352*sh	*362*s	*357*s,p			*239*m,sh	*243*s,p
asym	*348*	*343*vs		*348*sh,bd	*238*s	*241*s		
$(PtX)_2$ (*trans* to S) sym	*325* } *a*				*225*sh	*224*sh	*229*s	*224*vs,p
	314							
asym	*334*	*334*sh	*337*m,bd	*336*sh,bd	*228*vs	*230*vs		*232*sh,dp?
Pt_2X str sym	*303*vw		*305*m	*300*m,bd,p	*199*vw	*201*vw	*199*s	*202*vs,p
asym	*290*s	*288*ms	*291*wm		*190*m		*194*sh	*193*ms,dp
	*283*sh							
SC_2 str sym	690vw	†	688m	†	691w	†	691wm	688m,p
asym		†	729m	†		†	732wm	729vw,dp
SC_2 bend	236m	237m	234s	230m,p	246m	248m	250m	252m,p
SC_2 rock, wag, or twist	245m		240sh	236sh,dp				
Skeletal deformations and lattice modes	153w		164m	166m,p?	104w		119s	
	136w,bd							
	102w			112m,dp	95m		80sh	
	75w,bd							
Cation	755m				750m			
	610w						308w	309w,p
	514w							
Unassigned					578vw			
					472vw			
Limit of study	(40)	(195)	(140)	(90)	(40)	(195)	(75)	(110)

† Not investigated or obscured by solvent.
[a] Strong-broad multicomponent feature.

Vibrational Spectra

Mixed Bridged Anions $[Pt_2X_5SMe_2]^-$.—The similarity of the solid and solution spectra (Table 2) shows that the sulphide bridge persists in the solid state. To judge from $[Pt_2Br_6]^{2-}$ (ref. 14) and $[PtBr_3SMe_2]^-$ (ref. 4), the energies of the PtBr stretches should fall in the order PtBr (terminal, *trans* to Br) > PtBr (terminal, *trans* to S) > PtBr (bridging). Thus the three intense polarised Raman bands of $[Pt_2Br_5SMe_2]^-$ at 243, 224, and 202 cm^{-1} are assigned as the symmetric modes of these three types of bond, respectively. The depolarised band at 193 cm^{-1} (190 cm^{-1} in the infrared) must be the asymmetric bridging vibration. The values of

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[11] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1955, 2787.

[12] R. J. Goodfellow and L. M. Venanzi, *J. Chem. Soc.*, 1965, 7533.

[13] M. G. Ahmed, R. W. Alder, G. H. James, M. L. Sinnott, and M. C. Whiting, *Chem. Comm.*, 1968, 1533.

[14] (*a*) D. M. Adams, P. J. Chandler, and R. G. Churchill, *J. Chem. Soc.* (*A*), 1967, 1272; (*b*) P. L. Goggin and J. Mink, *J.C.S. Dalton*, submitted for publication.

the PtBr (terminal) stretching modes of $[Pt_2Br_6]^{2-}$ suggest[14] that such asymmetric and symmetric vibrations are not much separated in energy and we assign the two strong infrared bands at **241** and **230** cm^{-1} accordingly.

In addition to PtS (bridging) stretching vibrations, the only other motion that might occur in the region **300—450** cm^{-1} is the SC_2 bend. However, as this is of symmetric type, it is likely to be one of the polarised Raman bands (**339** or **252** cm^{-1}) leaving the infrared band at **406** cm^{-1} as the asymmetric Pt_2S stretch. It could not be found in the Raman spectrum but weak bands in this region are difficult to identify on our spectrometer because of a broad grating ghost. The much the same in the two cases. Following the reasoning for $[Pt_2Br_5SMe_2]^-$, the band at **254** cm^{-1} for $[Pt_2Br_6SMe_2]^{2-}$ is assigned as the SC_2 bend and **394** cm^{-1} as the characteristic asymmetric Pt_2S stretch. The symmetric counterpart is more difficult to assign and **322** cm^{-1} is chosen as it is the only infrared frequency which does not correspond to a cation band. In the Raman spectrum, this band probably occurs at **316** cm^{-1} although this does correspond to a cation band.[4] The bands at **228** and **230** cm^{-1} may arise from $PtSC_2$ deformations.

Two significant features are seen close to **330** cm^{-1} in both the Raman and infrared spectra of the chloro-analogue. Whilst these might be assigned as the two $PtCl_2$ stretching vibrations, this does not agree with the usual partition of the symmetric and asymmetric vibrations of $[PtCl_3L]^-$ between Raman and infrared.[15] It seems better to assume that the two vibrations are almost coincident and doubled in both cases due to the coupling between the ends of the dimer or solid-state effects. In any case this complication seems to be removed in the $[Me_4N]^+$ salt. The band which appears at **330** cm^{-1} under the polarised condition for the Raman spectrum of a nitromethane solution might be $PtCl_2$ (asym) or the symmetric Pt_2S stretch.

TABLE 3

Vibrational spectra (below 800 cm^{-1}) of $[Pt_2X_6SMe_2]^{2-}$ (X = Cl or Br)

	$[Pr^n_4N]_2[Pt_2Cl_6SMe_2]$			$[Me_4N]_2[Pt_2Cl_6SMe_2]$		$[Pr^n_4N]_2[Pt_2Br_6SMe_2]$	
	I.r. (mull)	R (solid)	R ($MeNO_2$)	I.r. (mull)	R (solid)	I.r. (mull)	R (solid)
Pt_2S str sym			330m?	325sh		322w	316m
asym	401m			408m		394m	
PtX_2 str sym	*338*vs	*336*s	*333*s,p	*337*sh	*329*s	*201*m	*202*vs
asym	*330*vs	*332*ms	*330*m?	*330*vs		*241*m	
PtX str	*316*s	*316*s	*314*m,p	*314*s	*314*m	*221*vs	*219*s
SC_2 str sym	680vw	680wm	683w,p	683vvw	685wm	678vw	678m
asym		726w	728vw,dp		731w		719w
SC_2 bend	246m,bd			250m		254wm	
SC_2 rock, wag, or twist	225w			238m 226sh		228sh	230m
Skeletal deformations and lattice modes	169w	163s	166m,dp	170wm	169s	120w	120sh
	162w						
	144w			143m		109vw	109vs
	131ms	129sh		138sh	135sh	97m	96m
	56m,bd			79s,bd		54s,bd	
Cation	749m	767vw			755wm,bd	749m	
						612vw	
	516w	515vw		456w		517wm	
			372vw,p	374vw		342vw	344w,bd
Limit of study	(40)	(110)	(150)	(40)	(110)	(40)	(80)

depolarised band at **236** cm^{-1} in the chloride (obscured by PtBr vibrations in the bromide) is presumably associated with CSPt bending (*cf.* 220 cm^{-1} for terminal SMe_2 complexes [4]).

For $[Pt_2Cl_5SMe_2]^-$ the intensity, energy, and strongly polarised nature of the band at **357** cm^{-1} identify it as the terminal Pt–Cl (*trans* to Cl) symmetric stretching mode. The Pt_2Cl (bridging) vibrations are obvious. However, assignments of the various features that constitute the broad infrared band at *ca.* **330** cm^{-1} are somewhat arbitrary in view of the similarity in energy of the remaining Pt–S and Pt–Cl vibrations.

Singly Bridged Anions $[Pt_2X_6SMe_2]^{2-}$.—There is little reason to expect more than a few wavenumbers difference for Pt–X motions differing only as to phase on the two platinum atoms. The Pt–Br stretches of $[Pt_2Br_6SMe_2]^{2-}$ are assigned on the assumption that the Br–Pt–Br vibrations should be similar to those[4] of $[PtBr_3SMe_2]^-$, as should also be the Pt–Br (*trans* to S) mode provided that the *trans*-influence of sulphur is

Neutral Complexes $[Pt_2X_4(SR_2)_2]$ (R = Me or Et).—The chloride and bromide complexes have structure (II) with D_{2h} symmetry and hence exclusion between Raman and infrared spectra. The infrared spectra of the diethyl sulphide complexes have been previously reported by Adams and Chandler;[16] our results agree largely with theirs and are detailed in reference 17. In triethylphosphine complexes of nickel, palladium, and platinum, bands around **400** cm^{-1}, although reliable

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

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

[17] F. J. S. Reed, Ph.D. Thesis, University of Bristol, 1972.

indicators of stereochemistry,[18] have been shown to have no significant metal–ligand stretching contribution in the case of the first two metals.[19] As diethyl sulphide is likely to have similar vibrations (due to CCS motions) in this region, the assignment by Adams and Chandler[16] of the infrared active Pt_2S stretching vibrations to two bands above 400 cm^{-1} must be regarded as suspect.

The asymmetric Pt_2S stretch of $[Pt_2X_5SMe_2]^-$ will have two counterparts in $Pt_2X_4(SMe_2)_2$ (B_{1g} and B_{3g} if the skeletal plane is xy and the sulphur atoms lie on the y axis), and likewise there will be two Pt_2S stretching vibrations of symmetric type (A_g and B_{2u}). For $Pt_2Br_4(SMe_2)_2$ there are two infrared and two Raman features, with no coincidences, between 430 and 300 cm^{-1} (Table 4). Relating these to the vibrations of $[Pt_2Br_5SMe_2]^-$, the infrared band of higher energy must be B_{3u}. The Raman bands are assigned in the same order. Parallel assignments can be made for the chloride except that the B_{2u} vibration lies under the much more intense PtCl stretching bands.

TABLE 4

Vibrational spectra (below 800 cm^{-1}) of $Pt_2X_4(SMe_2)_2$ (X = Cl or Br)

	$Pt_2Cl_4(SMe_2)_2$		$Pt_2Br_4(SMe_2)_2$	
	I.r. (mull)	R (solid)	I.r. (mull)	R (solid)
Pt_2S_2 str. A_g		359m		354m
B_{1g}		374w		369wm
B_{2u}			322m	
B_{3u}	422m		414m	
PtX_2 str. A_g		*342*s		*240*vs
B_{1g}		*330*s		*231*vs
B_{2u}	*327*sh		*230*m	
B_{3u}	*338*vs		*241*m	
SC_2 str. sym	690vw	699wm	686vw	695wm
asym		738w		736w
SC_2 bend, rock,	244m	234s	235sh	227vs
twist, or wag	230m	216w	214s	207w
		182wm	169w	175m
Skeletal deformations and	163wm	170w		134s
	150w		103w	107sh
lattice modes		136sh		96wm
		121vs	85vw,bd	87vvs
	116w,bd	113sh		
	95sh	96sh		
	87m	84m	71wm	
	74wm		59wm	64sh
Limit of study	(20)	(75)	(20)	(60)

The region of PtBr stretching vibrations (200—250 cm^{-1}) also contains SC_2 and PtSC modes for the SMe_2 complexes but is completely free in $Pt_2Cl_4(SEt_2)_2$ (we see no sign of the medium band previously reported[17] at 238 cm^{-1}). Thus, $Pt_2Br_4(SEt_2)_2$ gives a clear identification of the PtBr stretching modes (242vs and 232s in the Raman, 235vs and 230vs cm^{-1} in the infrared). Without Raman polarisation data there is no certain way of assigning these but comparison with the terminal PtBr vibrations[14] of $[Pt_2Br_6]^{2-}$ suggests that the higher frequency, more intense, Raman band is the A_g mode. The higher frequency infrared band is most probably the related motion which is opposite phase on the two ends (B_{3u}). Parallel assignments can then be made for $Pt_2Br_4(SMe_2)_2$ and $Pt_2Cl_4(SMe_2)_2$. For $Pt_2Cl_4(SEt_2)_2$, Pt–Cl stretches are: (in cm^{-1}) A_g, 349vs; B_{1g}, 335s; B_{2u}, 334sh; B_{3u}, 345vs + 349sh.

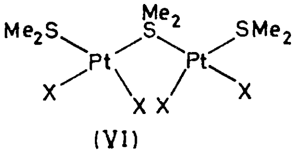
The Neutral Complex $Pt_2Cl_4(SMe_2)_3$.—Although this complex has been known for 80 years,[20] there has been no previous investigation of its structure. As it was too insoluble for n.m.r. measurements and no equivalent bromide complex could be prepared, we have only the vibrational results for the chloride (Table 5) on which to base a structure. The infrared band at 403 cm^{-1} indicates a bridging dimethyl sulphide group which could be part of a singly bridged neutral species or a doubly bridged (two sulphides or sulphide plus chloride) cation with chloride as anion. The Pt–Cl stretching vibrations would agree well with the singly bridged structure (VI) where both ends have a *cis*-configuration. Not all possible cationic structures can be excluded on the basis of the vibrational spectra but since for the anionic complexes the singly bridged structure (III) seems more stable than the mixed bridged structure (IV) in the presence of halide anions and since we have been unable to isolate cationic systems involving bridging sulphide (*vide infra*), we favour the neutral structure (VI). The very low solubility of the complex would be expected of structure (VI) in view of the insolubility of the complexes of structure (II) whereas

TABLE 5

Vibrational spectra (below 800 cm^{-1}) of $Pt_2Cl_4(SMe_2)_3$

	I.r. (mull)	R (solid)
PtS str		357wm
Pt_2S str sym	330sh *	
asym	403m	
PtCl str	*337*vs	*338*vs
	*330*sh *	
	*317*vs	*316*ms,bd
	*310*sh *	
SC_2 sym str	680vw,bd	683wm,bd
SC_2 asym str		729wm
SC_2 deformations, rock and wag	310sh *	
	262s	
	257sh	256m
	244vw,sh	
	228vw,sh	224m
	219m	
Skeletal deformations and lattice modes	174m	170ms
		160wm
	137m	134m
	127sh	
	104sh	
	96w	
	63m,bd	
Limit of study	(40)	(110)

* Alternative assignments.



(VI)

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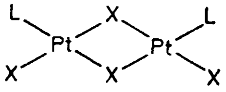
[18] P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc.* (*A*), 1966, **1462**.

[19] K. Nakamoto, *Angew. Chem. Internat. Edn.*, 1972, **11**, 666.

[20] G. W. Blomstrand and C. Enebuske, *J. prakt. Chem.*, 1888, **38**, 345.

salts of cations with small anions such as chloride are usually more soluble. Finally, the complex reacts cleanly with two molecules of $[Pr^n_4N]Cl$ yielding *cis* $PtCl_2(SMe_2)_2$ and $[Pr^n_4N][PtCl_3SMe_2]$ in 1 : 1 ratio as might be expected for the neutral structure and in contrast to the behaviour of $Pt_2X_4(SMe_2)_2$. The assignments in Table 5 assume structure (VI).

The Structures of some other Dimethyl Sulphide Complexes.—As iodide bridges are more readily formed and less readily ruptured than chloride or bromide bridges,[14b] the dimeric complex $Pt_2I_4(SMe_2)_2$ might have the halide bridging structure (I). The reaction of $PtI_2(SMe_2)_2$ with Na_2PtI_4 in ethanol produced a small quantity of a rather insoluble purple material which analyses as intermediate between $Pt_2I_4(SMe_2)_2$ and $PtI_2(SMe_2)_2$. However, the reaction of methyl fluorosulphonate with $[Bu^n_4N][PtI_3SMe_2]$ yielded $Pt_2I_4(SMe_2)_2$ as a crystalline purple solid. The proton n.m.r. spectrum indicates three SMe_2 species, one of which is identified as *trans*-$PtI_2(SMe_2)_2$ and which grows with time at the expense of the others whilst a precipitate, presumably of platinum(II) iodide, is formed. The other two resonances which always occur in the same ratio (*ca.* 2 : 1) have parameters τ_{Me} 7·44, $^3J_{PtH}$ 58·4 Hz, δ_{Pt} +294 p.p.m., and τ_{Me} 7·46, $^3J_{PtH}$ 55·9 Hz, δ_{Pt} +262 p.p.m. The ^{195}Pt satellites show them to be terminal groups and the n.m.r. parameters of both are reasonable for structure (I). The small difference in the parameters, especially δ_{Pt}, suggests that there is no major difference in the co-ordination arrangement and the most reasonable possibilities are the *cis*- and *trans*-iodide bridged structures (VII) and (I) although all previous halide-bridged dimeric complexes have the *trans*-structure (I).[21]



(VII)

The Raman spectrum of $Pt_2I_4(SMe_2)_2$ could not be obtained as the compound decomposed even in a 10 mW beam of 725·5 nm. We were able to obtain a spectrum of the analogous SPr^n_2 complex which is the same colour and has a closely comparable infrared spectrum. The results for this compound in the region of interest, *i.e.* below 300 cm^{-1}, are given in Table 6 together with the infrared data for $Pt_2I_4(SMe_2)_2$. There are three strong bands in the PtI stretching region of the Raman spectrum of $Pt_2I_4(SPr^n_2)_2$ which have related, but not necessarily coincident, prominent infrared features. Comparison of the terminal stretching frequencies of $Pt_2X_4(SMe_2)_2$ (X = Cl or Br) with those of $[Pt_2X_6]^{2-}$ (X = Cl, Br, or I) [14] suggests that the higher two bands might be the PtI vibrations of the sulphide-bridged structure (II) but the band at 150 cm^{-1} cannot be explained on this basis. The latter frequency is typical of the symmetric vibration of a linear PtI_2 unit either as in *trans*-PtI_2L_2 or as the partially bridging unit in $Pt_2I_4L_2$ of structure (I) [16] or $[Pt_2I_6]^{2-}$.[14] Thus, the vibrational spectra favour an iodide-bridged structure in agreement with the n.m.r. results and purple colour. The band at 190 cm^{-1} is much stronger in the infrared spectrum than is usual for complexes of structure (I).[15] This might be a feature of the *cis*-structure (VII) which would probably have similar stretching frequencies to those of the *trans*-structure (I), but without an authenticated example of structure (VII) we cannot say more. The *cis*-isomer of MX_2L_2 is more favoured in the solid state than in solution and if this applied to $M_2X_4L_2$, then a solid of structure (VII) dissolving to give a mixture of structures (I) and (VII) would fit the n.m.r. results. All bands in the region 350—200 cm^{-1} of the infrared spectrum of $Pt_2I_4(SMe_2)_2$ are extremely weak so we cannot be very confident of the assignment of the band at 335 cm^{-1} as PtS stretching.

TABLE 6

Vibrational spectra of $Pt_2I_4(SR_2)_2$ (R = Me and Pr^n) [a]

	$Pt_2I_4(SMe_2)_2$	$Pt_2I_4(SPr^n_2)_2$	
	I.r. (mull)	I.r. (mull)	R (solid)
PtS str	335vvw,bd		
PtI (*trans* to I) str	*190*s	*191*vs	*193*w
Pt_2I (*trans* to I) str	*151*ms	*152*s	*149*vs
Pt_2I (*trans* to S) str	*176*s	*177*s	*171*m
SC_2 str sym	680vw		
asym	732vw		
Other bands	232vw	247w	248vw
	167vw		
	130vw,bd	126w	
	117m		
	103m		98wm
	91w		81w
	65m	46m	72s

[a] 800—40 cm^{-1} for R = Me but only 300—40 cm^{-1} for R = Pr^n.

As we reported recently,[4] when *trans*-$PtBr_2(SMe_2)_2$ is dissolved in boiling water only *ca.* 50% of the precipitate formed on cooling is soluble in benzene, *i.e.* is the *trans*-isomer. The residue has the same apparent stoicheiometry but the weak infrared bands at 441 and 376 cm^{-1} suggested the presence of a bridging dimethyl sulphide group. When dissolved in cold dichloromethane, the main species is *cis*-$PtBr_2(SMe_2)_2$ which largely isomerises to *trans* when brought to room temperature. There are, however, two other resonances in the proton n.m.r. spectrum (τ_{Me} 6·42, J_{PtH} 23·5 Hz and τ_{Me} 7·37, J_{PtH} 51·6 Hz) which are not changed after 10 days. Each represents *ca.* 3% of the total methyl intensity and the ^{195}Pt satellites show both to be terminal. They give the same $^1H\{^{195}Pt\}$ resonance (δ_{Pt} −673 p.p.m.) and can therefore be assigned to the same compound. This shift is close to that of *cis*-$PtBr_2(SMe_2)_2$ and $^3J_{PtH}$ of the high-field resonance also resembles that of the latter complex. The platinum shift of *cis*-$PtCl_2Me_2SO{\cdot}SMe_2$ is close

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[21] J. Chatt, *J. Chem. Soc.*, 1951, 652.

to that of *cis*-$PtCl_2(SMe_2)_2$.[22] The parameters of *cis*-$PtBr_2(Me_2SO)_2$ are τ_{Me} 6·40, $^3J_{PtH}$ 23·5 Hz and δ_{Pt} -755 p.p.m. (in CD_3NO_2 solution)[23] from which we may identify our impurity as *cis*-$PtBr_2Me_2SO{\cdot}SMe_2$ presumably formed by oxidation of the dimethyl sulphide complex in hot water. For S-bonded dimethyl sulphoxide, the intense infrared S–O stretching absorption occurs near to 1150 cm^{-1}.[24] Dimethyl sulphide complexes do not normally have any absorptions in this region but '*cis*-$PtBr_2(SMe_2)_2$' has a weak band at 1134 cm^{-1}. *cis*-$PtBr_2(Me_2SO)_2$ has strong infrared bands at 444, 429, and 377 cm^{-1} and for $[Pr^n{}_4N][PtBr_3(Me_2SO)]$ the equivalent bands are at 438 and 375 cm^{-1}.[23] Thus the weak bands at 441 and 376 cm^{-1} in the spectrum of '*cis*-$PtBr_2(SMe_2)_2$' are almost certainly due to the *cis*-$PtBr_2Me_2SO{\cdot}SMe_2$ present and not to bridging dimethyl sulphide. The bands at 216s and 195m cm^{-1} in the Raman spectrum and 222m and 196vs cm^{-1} in the infrared spectrum are, no doubt, the PtBr stretching vibrations of *cis*-$PtBr_2(SMe_2)_2$ but in view of the contamination by *cis*-$PtBr_2Me_2SO{\cdot}SMe_2$ we will not describe the spectra further.

TABLE 7

MX stretching frequencies and ^1H n.m.r. parameters of some methyl phenyl sulphide and diphenyl sulphide complexes

	M–X stretching vibrations (cm^{-1})		τ_{Me}	$^3J_{PtH}$
$[Pr^n{}_4N][PtCl_3SMePh]$	I.r.	328vs, 313s	7·40	47·2
$[Pr^n{}_4N][PtBr_3SMePh]$	I.r.	239s, 223ms, 204w	7·30	49·0
cis-$PtCl_2(SMePh)_2$	I.r.	328s, 318s	7·23	48·1
	R	323vs, 309sh		
cis-$PtCl_2(SPh_2)_2$	I.r.	334s, 322s, 318sh		
	R	330s, 318s		
cis-$PtBr_2(SMePh)_2$			7·15	48·0
trans-$PtCl_2(SMePh)_2$	I.r.	341s	7·34	43·8
	R	332s		
trans-$PtCl_2(SPh_2)_2$	I.r.	344s		
	R	332s		
trans-$PtBr_2(SMePh)_2$	I.r.	238s	7·19	44·6
	R	206s, 201s		
trans-$PtBr_2(SPh_2)_2$	I.r.	256s		
	R	209s		
$Pt_2Cl_4(SPh_2)_2$	I.r.	357s, 349sh, 320s, 314sh, 294s		
$Pt_2Br_4(SPh_2)_2$	I.r.	253s, 212s, 207sh		
$[Pr^n{}_4N][Pt_2Cl_5SMePh]$	I.r.	356m,sh, 346s, 336sh, 320m, 303vw, 287ms, 281sh		

The cations $[Pt_2Cl_2(SMe_2)_2L_2]^{2+}$ where L is SMe_2 or some other neutral ligand might be sulphide bridged and hence relevant to this study. Complexes of this type can usually be prepared by the action of silver fluoroborate on $PtCl_2L_2$[15,25] but with the dimethyl sulphide complex, the result was an insoluble, inseparable, mixture. A parallel reaction with the mixed complex $PtCl_2(SMe_2)(PMe_3)$ lead to rapid decomposition and no characterisable product was obtained. The reaction of $AgNO_3,PMe_3$ with $Pt_2Cl_4(SMe_2)_2$ might have given $[Pt_2Cl_2(SMe_2)_2(PMe_3)_2]^{2+}$ but in fact produced a complicated mixture whose n.m.r. spectrum defied analysis. The reverse approach, $AgNO_3,SMe_2$ with $Pt_2Cl_4(PMe_3)_2$ gave $[PtCl(SMe_2)_2(PMe_3)]^+$, identified by its n.m.r. spectrum.

Related Complexes containing SPh_2 *and* SMePh.—Complexes $Pt_2X_4(SPh_2)_2$ were formed in low yield by the method of Goodfellow and Venanzi[12] and are sparingly soluble in dichloromethane. The chloride is deep orange and the bromide dark brown, suggesting that unlike the dimethyl sulphide analogues, these complexes have the halogen-bridged structure (I). The pattern of infrared-active M–X stretching frequencies (Table 7) is quite different from that of $Pt_2X_4(SMe_2)_2$ but similar to that of other complexes of structure (I),[15] confirming that the diphenyl sulphide complexes are halide not sulphide bridged. Analogous attempts to prepare dimeric SMePh complexes resulted in extensive decomposition and none of the desired product could be isolated. No reaction occurred between $PtCl_2(SMePh)_2$ and $PtCl_2$ in acetone in contrast to the behaviour of the SMe_2 complexes. The reaction of methyl fluorosulphonate with $[Pr^n{}_4N][PtCl_3SMePh]$ instead of giving $Pt_2Cl_4(SMePh)_2$ produces a small yield of an insoluble red crystalline material, with the composition $[Pr^n{}_4N][Pt_2Cl_5(SMePh)]$. The n.m.r. spectrum of the supernatant liquid was predominantly that of $[PtCl_3(SMePh)]^-$. The equivalent reaction with the bromide did not give a precipitate.

We have examined the infrared and, where colour allowed, Raman spectra of the complexes prepared. The spectra are more complicated than those of SMe_2 but the M–X stretching vibrations have been assigned by comparison with assignments of the equivalent SMe_2 complexes and are recorded in Table 7 together with the ^1H n.m.r. parameters of the soluble SMePh complexes. (Full details of the vibrational spectra may be found in ref. 17.)

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

[23] B. F. Taylor, Ph.D. Thesis, University of Bristol, 1973.

[24] J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, *Inorg. Chem.*, 1972, **11**, 1280.

[25] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, 1968, **90**, 2259.

DISCUSSION

It is clear that where both possibilities exist, bridging dialkyl sulphide is preferred to bridging halide or chloride and bromide but not for iodide, which is in keeping with the expected stabilities of the halide bridges, *e.g.* $[PtX_4]^{2-}$ *vs.* $[Pt_2X_6]^{2-}$.[14b] Previously,[2] we have suggested that the stability of bridging sulphide compared to terminal sulphide may arise because the second lone pair, which is bonded to platinum in the bridging arrangement, has an antibonding (repulsive) interaction with filled metal *d*-orbitals in the terminal arrangement. In this case, increasing the electronegativity of the substituents on the sulphur atom should decrease the tendency to form bridging sulphide isomers. The behaviour of diphenyl sulphide complexes agrees with this but could be due to difficulties of accommodating the bulk of the phenyl ring in the more rigid bridging arrangement. Increasing the formal positive charge on the metal should improve the relative stability of the terminal arrangement but, in the absence of results for cationic species, the situation is not clear. Oxidation would have a similar result but the action of halogen on the bridged anions resulted in decomposition although we were able to obtain n.m.r. results for $[Pt_2Cl_9SMe_2]^-$. The ratio of $^3J_{PtH}$ of this complex to that of its platinum(II) analogue is 0·62 which is lower than for any terminal dimethyl sulphide complex but similar to the ratio for trimethylarsine complexes which would be in keeping with an antibonding interaction for the terminal sulphide complexes.[26]

A surprising feature of SMe_2-bridged complexes is the occurrence of singly bridged species particularly as these do not seem to occur for halide or methylthio-bridges. The last two bridging groups differ from dialkyl sulphides in still having an unco-ordinated lone pair. Since this is likely to have a relatively large *s*-orbital contribution, the co-ordinate bonds can have a high *p*-orbital component so that the angle between them will approach 90°. For a dialkyl sulphide, the hybridisation is likely to be much nearer to tetrahedral which should imply significant strain in the formation of a Pt_2S_2 ring where the ideal angles are presumably 90°. Crystallographic data seems to bear this out. In the absence of results for a dialkyl sulphide in an unstrained bridge we note that the MSM angle in $[(\pi\text{-}C_6H_5)Fe(CO)_2]_2SO_2$ is 118°[9] whilst in $Pt_2Br_4(SEt_2)_2$ it is 98°.[3] The latter is higher than for halogeno-bridged complexes, *e.g.* $Pt_2Cl_4(AsMe_3)_2$ (96°)[27] or alkylthio-bridges, *e.g.* *cis*-$Pt_2Cl_2(SEt)_2(PPr^n_3)_2$ (90 and 85°).[28] Similar angular strain should occur with bridging $[PR_2]^-$ groups, *e.g.* in $[FeIPMe_2(CO)_3]_2$ the FePFe angle is 102·6° reducing the angle at octahedral iron to 77·6°.[29] Such strain will be more severe when the atom opposite sulphur in the four-membered ring is small.

We have previously discussed the difficulty of describing any particular band in the vibrational spectra of trimethylphosphine complexes as an M–P stretching mode, due to the interaction with a symmetric PC_3 deformation.[15,26] Similarly, in terminal SMe_2 complexes, the M–S stretch may mix with the SC_2 bend or M–SC_2 wag. However, in contrast to PMe_3 complexes, bands may usually be assigned to SC_2 bending vibrations at energies similar to that of the free ligand, implying that the mixing is much less.[4] For bridging SMe_2, only the symmetric M–S–M vibrations may mix with the SC_2 bend whilst the asymmetric vibration is related to the M_2SC_2 wag. The situation is mechanically nearer to that of PMe_3 than for terminal SMe_2 and now an SC_2 vibration cannot be assigned in the region of that of the free ligand. Thus, comparison of ' M–S stretching ' energies in terminal and bridging environments will be liable to particularly severe uncertainties. Again, the span of the four stretching vibrations of the Pt_2A_2 ring is 22 cm⁻¹ in $[Pt_2Cl_6]^{2-}$,[14] 35 cm⁻¹ in $[Pt_2Cl_2(PMe_3)_4]^{2+}$ ($A = Cl^-$),[15] 56 cm⁻¹ in $[Pt_2(SMe)_2(AsMe_3)_4]^{2+}$ ($A = SMe^-$), and 92 cm⁻¹ in $Pt_2Br_4(SMe_2)_2$ ($A = SMe_2$). It is plausible to ascribe the increase in span to changes in the nature of the normal co-ordinates caused by the increasing number of substituent methyl groups although changes in bonding related to the electronegativity and angle strain might be responsible. In Table 8 some relevant bond lengths are compared with the mean of the related stretching energies, using values from complexes with closely related ligands where necessary. In view of the vibrational complications mentioned above, the differences between the nature of the vibrations and the different effective masses of the ligands, there is an amazing agreement between bond length and vibrational energy, and the wavenumber increment per unit change in bond length

TABLE 8

Comparison of bond lengths with their stretching frequencies

Bond [a]	Length [b]	Mean of stretching frequencies	Antibonding [d] interactions
Pt–PR_3	223 [e]	393	0
Pt–SR_2 (br)	223 [f]	370	0
Pt–SR (br)	227 [g]	361	2
Pt–Cl (t)	228 [e]	344	3
Pd–SR_2 (t)	230 [h]	340	1
Pt–Cl (br)	232 [e]	327	4

[a] br = Bridging, t = terminal. [b] In pm. [c] In cm⁻¹, for the complex with R = Me. [d] Number of free lone pairs on ligand × number of metal atoms. [e] $Pt_2Cl_4(PPr^n_3)_2$, M. Black, R. H. B. Mais, and P. G. Owston, *Acta Cryst.*, 1969, **B25**, 1760. [f] $Pt_2Br_4(SEt_2)_2$, ref. 3. [g] *cis*-$Pt_2Cl_2(SEt)_2(PPr^n_3)_2$, M. C. Hall, J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *J.C.S. Dalton*, 1972, 1544. [h] $Pd_2Br_4(SMe_2)_2$, ref. 3.

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[26] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, J. R. Knight, F. J. S. Reed, and B. F. Taylor *J.C.S. Dalton*, 1974, 523.

[27] S. F. Watkins, *J. Chem. Soc.* (*A*), 1970, 168.

[28] M. C. Hall, J. A. Jarvis, B. T. Kilbourn, and P. G. Owston, *J.C.S. Dalton*, 1972, 1544.

[29] G. R. Davies, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc.* (*A*), 1968, 1251.

(pm) is similar to that for M–Cl bonds in some octahedral complexes.[30] The order is that of decreasing possible lone pair/filled metal *d*-orbital interactions if the neutral and anionic ligands are regarded as separate series; the anionic ligands form the stronger bonds for a given number of interactions.

The Pt–S stretching energies are higher in the mixed sulphide/halide-bridged complexes $[Pt_2X_5SMe_2]^-$ than in the singly sulphide-bridged complexes $[Pt_2X_6SMe_2]^{2-}$, in keeping with the general lowering of metal–ligand bond strengths on increasing overall negative charge.

TABLE 9

Characterisation of compounds

	M.p. (t/°C)	Analyses (%) [c] C	H	N	X	S
$[Pr^n{}_4N]_2[Pt_2Cl_6SMe_2]$	182—183 [d]	30·05 (30·1)	6·15 (6·0)	2·8 (2·7)	20·7 (20·5)	3·35 (3·1)
$[Me_4N]_2[Pt_2Cl_6SMe_2]$	>190 [d]	15·5 (14·75)	3·6 (3·7)	3·35 (3·45)	26·2 (26·15)	3·85 (3·95)
$[Pr^n{}_4N]_2[Pt_2Br_6SMe_2]$	240—243 [a,d]	24·15 (23·95)	4·55 (4·8)	2·1 (2·15)	37·15 (36·75)	2·55 (2·45)
$[Pr^n{}_4N][Pt_2Cl_5SMe_2]$	>140 [d]	20·5 (20·6)	4·1 (4·2)	1·8 (1·7)	21·05 (21·7)	3·8 (3·9)
$[Pr^n{}_4N][Pt_2Br_5SMe_2]$	240—242 [b,d]	16·45 (16·2)	3·2 (3·3)	1·35 (1·35)	39·1 (38·5)	3·3 (3·1)
$Pt_2Cl_4(SMe_2)_2$	>200 [d]	7·6 (7·3)	1·75 (1·85)		21·7 (21·6)	9·65 (9·75)
$Pt_2Cl_4(SEt_2)_2$	>214 [d]	13·8 (13·5)	2·9 (2·85)			
$Pt_2Br_4(SMe_2)_2$	190—195 [d]	6·2 (5·75)	1·35 (1·4)		38·9 (38·3)	7·7 (7·7)
$Pt_2Br_4(SEt_2)_2$	221—223 [d]	10·9 (10·75)	2·2 (2·25)			
$Pt_2I_4(SMe_2)_2$	176—177	4·7 (4·7)	1·2 (1·2)		49·4 (49·65)	6·4 (6·25)
$Pt_2I_4(SPr^n{}_2)_2$	162—163	13·0 (12·7)	2·55 (2·5)			
$Pt_2Cl_4(SMe_2)_3$	203—205 [d]	10·55 (10·05)	2·15 (2·5)		19·55 (19·75)	13·8 (13·4)
$Pt_2Cl_4(SPh_2)_2$	212—216	32·05 (31·85)	2·1 (2·2)			
$Pt_2Br_4(SPh_2)_2$	245—247 [d]	27·05 (26·6)	1·85 (1·85)			
$[Pr^n{}_4N][Pt_2Cl_5SMePh]$	180—182	26·1 (26·0)	4·05 (4·1)	1·5 (1·55)		

[a] Darkens >215°. [b] Appears to change ~160°. [c] Calculated values in parentheses. [d] Decomposition (> indicates decomp. without melting).

The metal–halide stretches *trans* to bridging dimethyl sulphide in $Pt_2X_4(SMe_2)_2$ and $[Pt_2X_6SMe_2]^{2-}$ occur at higher wavenumbers than for the structurally related terminal sulphide cases, *cis*-$PtX_2(SMe_2)_2$ and $[PtX_3SMe_2]^-$, implying a higher *trans*-influence for terminal SMe_2. This is opposed to the usual trend that the stronger Pt–L bond has the higher *trans*-influence. However, if the terminal SMe_2–Pt bond does involve an antibonding interaction with the filled metal *d*-orbitals, then this will distort those *d*-orbitals in the direction of the *trans*-halide and cause increased repulsion with the halide lone-pairs resulting in a higher *trans*-influence. Alternatively, the greater electronegativity of bridging sulphide will increase the positive charge on platinum and hence the Pt–X bond strength.

EXPERIMENTAL

Infrared, Raman, and ^1H n.m.r. measurements were made as described in reference 26. The experimental arrangement for $^1H\{^{195}Pt\}$ INDOR has been previously described.[31] The shifts are given in p.p.m. from 21·4 MHz after correction such that tetramethylsilane would resonate at 100 MHz exactly: positive shifts are to low frequency. Where reactions were studied *in situ* by n.m.r. spectroscopy 1/20 mmol of each reactant was normally used in a total of 0·5 ml of dichloromethane.

Preparation of Complexes.—Details of elemental analyses and melting points are given in Table 9 (yields are based on platinum).

$[Pr^n{}_4N]_2[Pt_2Cl_6SMe]$. Dimethyl sulphide and $[Pr^n{}_4N]_2[Pt_2Cl_6]$ (mol ratio 2·2 : 1) were stirred in dimethylformamide for 3 h. The crude product was precipitated with ether and extracted twice with cold acetone to remove $[Pr^n{}_4N][PtCl_3SMe_2]$. The residue was dissolved in dichloromethane, dried over $MgSO_4$, and crystallised as orange-yellow needles by slow addition of ether; yield 35%.

$[Me_4N]_2[Pt_2Cl_6SMe_2]$. $[Me_4N]Cl$ (0·005 mol) and $PtCl_2$ (0·005 mol) were stirred with dimethylformamide (100 ml) for 5 h. The solution was filtered and dimethyl sulphide (0·003 mol) in dimethylformamide added. An orange precipitate slowly formed (2 h). It was recrystallised from boiling water; yield 40%.

$[Pr^n{}_4N][Pt_2Cl_5SMe_2]$. $[Pr^n{}_4N][PtCl_3SMe_2]$ and $PtCl_2$ (0·002 mol each) were stirred with acetone (20 ml) for a day, after which time the solution had turned red and most of the $PtCl_2$ dissolved. The solvent was removed on a rotary evaporator and the product recrystallised from dichloromethane as dark orange crystals by slow addition of ether; yield 80%.

$[Pr^n{}_4N][Pt_2Br_5SMe_2]$ was prepared in the same way, as dark red crystals; yield 65%.

$[Pr^n{}_4N]_2[Pt_2Br_6SMe_2]$ was precipitated as small dark red crystals by slow addition of a stoicheiometric quantity of $[Pr^n{}_4N]Br$ in dichloromethane to $[Pr^n{}_4N][Pt_2Br_5SMe]$ in the same solvent; yield 100%.

$Pt_2Cl_4(SMe_2)_2$. (*a*) $PtCl_2(SMe_2)_2$ (1 g) and $PtCl_2$ (0·75 g) were heated with xylene (2 ml) at 140° for 1½ h. The solid was washed into an extraction thimble with light petroleum (b.p. 60—80°) and continuously extracted with this solvent for 20 min. It was then extracted with a portion of dichloromethane for 10 min and with a fresh portion of the same solvent for 12 h. The product separated out as a slightly dull yellow-green solid; yield 16%.

(*b*) $[Pr^n{}_4N][PtCl_3SMe_2]$ and $MeSO_3F$ (mol ratio 1 : 1·1) were dissolved in dry dichloromethane. During 4 days a bright yellow-green solid deposited; it was washed with ether to give a yield of 40% of product.

$Pt_2Cl_4(SEt_2)_2$. $PtCl_2(SEt_2)_2$ (1·5 g) and $Na_2PtCl_4,4H_2O$

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[30] P. L. Goggin and J. R. Knight, *J.C.S. Dalton*, 1973, 1489.

[31] P. L. Goggin, R. J. Goodfellow, J. R. Knight, M. G. Norton, and B. F. Taylor, *J.C.S. Dalton*, 1973, 2220.

(1·7 g) were heated in ethanol (50 ml) at 45° for 8 h and then allowed to cool and stand overnight. The precipitate formed was filtered off and washed with ethanol, water, ethanol, and ether. It was purified by continuous extraction with dichloromethane. Yellow crystals were deposited; yield 35%.

$Pt_2Br_4(SMe_2)_2$. (*a*) Disodium tetrabromoplatinate(II) was prepared *in situ* in ethanol by addition of sodium bromide (2·0 g) to $Na_2PtCl_4,4H_2O$ (1·0 g) in ethanol (100 ml). To the filtered solution was added $PtBr_2(SMe_2)_2$ (1·0 g) and the mixture was stirred for 16 h. The solution was evaporated to dryness on a rotary evaporator and the residue was washed with dichloromethane before being continuously extracted with the same solvent for 10 days. The product separated as a yellow solid, which was washed with ether; yield 44%.

(*b*) From $[Pr^n_4N][PtBr_3SMe_2]$ and $MeSO_3F$ (mol ratio (1 : 1·1) in dry dichloromethane, the product separated as bright yellow crystals; yield 25%.

$Pt_2Br_4(SEt_2)_2$ was prepared by the same method as the chloride analogue, but was obtained as bright yellow crystals after extraction for only 1 day; yield 80%.

$Pt_2I_4(SMe_2)_2$ was prepared from $[Bu^n_4N][PtI_3SMe_2]$ and $MeSO_3F$ (2 days), as outlined above for the chloro- and bromo-analogues, as dark purple crystals; yield 50%.

$Pt_2I_4(SPr^n_2)_2$ was prepared by stirring aqueous K_2PtI_4, prepared *in situ* from K_2PtCl_4 and KI, with di-n-propyl sulphide (mol. ratio 1 : 1) for 2 weeks. The orange precipitate formed initially was slowly converted into a red-brown colour; it recrystallised from dichloromethane as deep purple crystals; yield 25%.

$Pt_2Cl_4(SMe_2)_3$. $PtCl_2(SMe_2)_2$ and $MeSO_3F$ (mol. ratio 1 : 2) in dichloromethane deposited the product as light yellow crystals during 4 days; yield 60%.

$Pt_2Cl_4(SPh_2)_2$. $PtCl_2$ and $PtCl_2(SPh_2)_2$ (each 0·01 mol) were heated at 180° in *o*-dichlorobenzene for 30 min. After being cooled, the mixture was washed into an extraction thimble with ether. It was continuously extracted with dichloromethane for 5 min and then with a second portion of dichloromethane for 24 h during which time dark orange crystals deposited; yield 10%.

The dark brown $Pt_2Br_4(SPh_2)_2$ was obtained in an analogous way.

$[Pr^n_4N][Pt_2Cl_5SMePh]$. $[Pr^n_4N][PtCl_3SMePh]$ and $MeSO_3F$ (mol. ratio 1 : 1·1) in dry dichloromethane produced a small amount of dark orange crystals during 2 days; yield 20%.

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