Study of the Co-ordination Behaviour of the Thiocyanate and Cyanate Ions in some Platinum(II) Complexes by Heteronuclear Resonance Spectroscopy

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The isomers present in solutions of [Pt(CNS)$_2$L$_2$] (L = NMe$_3$, PMe$_3$, PMe$_2$Et, PMeEt$_2$, PEt$_3$, AsMe$_3$, AsMe$_2$Et, AsMeEt$_2$, AsEt$_3$, SbMe$_3$, SMe$_2$, and SeMe$_2$) have been identified by ^{1}H-{^{195}Pt} INDOR and ^{31}P n.m.r. measurements. The mode of co-ordination of the thiocyanate ion is shown to be sensitive to the size of the *cis* ligands. Some related cyanate complexes have been prepared and are shown to be entirely N-bonded. Some representative infrared and Raman spectra are reported and the shortcomings of such measurements as a means of establishing stereochemistry are discussed.

FOR discussion of the relative stabilities of S- and N-bonded forms of the thiocyanate group in metal complexes, and the factors which determine them, it is important that the observed mode of bonding is thermodynamically controlled. Results from structural studies of solids may be of dubious significance since the form isolated may merely reflect relative solubilities, and studies of solutions are to be preferred.

Whilst most published work in this field has assumed that only one type of thiocyanate co-ordination is present, recent *X*-ray crystallographic results have demonstrated that mixed co-ordination types can occur {*e.g.*

[Pd(NCS)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(SCN)] [1]}, and Carty and Jacobson [2] showed that in solution all the linkage isomeric forms of *cis*-[Pd(CNS)$_2${P(OPh)$_3$}$_2$] * may be present together in equilibrium. The mode of co-ordination of the thiocyanate group has mainly been determined by *X*-ray crystallography or infrared spectroscopy,[3] and whilst the latter can be usefully applied to solutions it is unlikely to provide conclusive or quantitatively significant results when several isomers are present together. Carty and Jacobson [2] used ^{31}P n.m.r. in examining the isomeric composition of solutions of *cis*-[M(CNS)$_2$L$_2$] (M = Pd or Pt, L = a phosphorus donor), but since the method relies on the coupling between ^{31}P and ^{14}N of a *trans*-NCS group its applicability is very limited.

TABLE 1

N.m.r. parameters of some neutral thiocyanate complexes of platinum(II)

Complex	Isomer [a]	τ_{Me}	^3J(PtH)/Hz	δ_{Pt} [b]	^1J(PtN)/Hz	δ_N(Pt–N) [c]	Relative proportion
trans-[Pt(CNS)$_2$(NMe$_3$)$_2$]	NN	7.31	33.5	2 309	504 ± 2	−288 ± 1	1.0
trans-[PtCl(NCS)(NMe$_3$)$_2$]		7.32	31.1	2 443	460 ± 10		
trans-[Pt(AsMe$_3$)$_2$(CNS)$_2$]	SS	8.37	18.4	38			1.0
	NS	8.42	19.0	374	330 ± 5	−288 ± 5	0.4
	NN	8.45	19.8	800	370 ± 10		0.06
trans-[Pt(AsMe$_2$Et)$_2$(CNS)$_2$]	SS	8.43	18.9	36			1.0
	NS	8.48	19.2	370	330 ± 5		0.7
	NN	8.52		796			0.08
trans-[Pt(AsMeEt$_2$)$_2$(CNS)$_2$]	SS	8.48	18.8	39			0.6
	NS	8.55	19.4	371	310 ± 10		0.6
	NN	8.60	20.6	794	390 ± 10		1.0
trans-[Pt(AsEt$_3$)$_2$(CNS)$_2$]	NS			386			*ca.* 0.2
	NN			819	395 ± 10		1.0
$\left.\begin{matrix}cis\\trans\end{matrix}\right\}$-[Pt(CNS)$_2$(SbMe$_3$)$_2$] [d]	SS	8.51		−417			
	SS			−37			
trans-[Pt(CNS)$_2$(SMe$_2$)$_2$]	SS	7.37	46.1	387			1.0
	NS	7.41	45.8	807	373 ± 2	−271 ± 1	0.7
	NN	7.47	46.5	1 335	451 ± 2	−308 ± 1	0.2
trans-[Pt(CNS)$_2$(SeMe$_2$)$_2$] [e]	SS	7.51	39.7	170			1.0
	NS	7.52	39.8	636	375 ± 2	−275 ± 1	0.8
	NN	7.56	40.9	1 195	440 ± 2	−313 ± 1	0.4

[a] SS indicates [Pt(SCN)$_2$L$_2$]; NS, [Pt(NCS)(SCN)L$_2$]; NN, [Pt(NCS)$_2$L$_2$]. [b] In p.p.m. to high frequency of 21.4 MHz (when SiMe$_4$ resonates at 100 MHz). [c] In p.p.m. to high frequency of [NO$_3$]$^-$. [d] At *ca.* 270 K. [e] At *ca.* 240 K.

In a preliminary report,[4] we demonstrated that ^{1}H-{^{195}Pt} INDOR spectroscopy provides a new means of studying and identifying the mode of co-ordination of the thiocyanate ion to platinum in solution which is not restricted to phosphine complexes. Here we have used it to examine a series of complexes, [Pt(CNS)$_2$L$_2$] (L = a S, Se, N, P, As, or Sb donor), in order to evaluate the effect of the neutral ligand on the mode of co-ordination of the thiocyanate group. We have also investigated some related cyanate derivatives.

RESULTS

The ^{1}H n.m.r. spectrum of [Pt(CNS)$_2$(SMe$_2$)$_2$] exhibited three resonances each with ^{195}Pt satellites. The ^{1}H-{^{195}Pt} INDOR spectra of these were: (*i*) a typical multiplet due to ^3J(PtH); (*ii*) a 1 : 1 : 1 triplet of such multiplets; and (*iii*) a 1 : 2 : 3 : 2 : 1 quintet of multiplets. On the basis that the additional splitting is due to the ^{14}N nucleus ($I = 1$) of N-bonded thiocyanate, the species can be assigned as [Pt(SCN)$_2$(SMe$_2$)$_2$], [Pt(NCS)(SCN)(SMe$_2$)$_2$], and [Pt(NCS)$_2$(SMe$_2$)$_2$] respectively. The ^{1}H resonances of the corresponding dimethyl selenide complex were broad at room temperature but well resolved at *ca.* 240 K when it gave similar results to the dimethyl sulphide complex (Table 1). Platinum-195–nitrogen-14 coupling is also observed in the ^{1}H-{^{195}Pt} INDOR spectra of complexes [Pt(AsR$_3$)$_2$(CNS)$_2$] (AsR$_3$ = AsMe$_3$, AsMe$_2$Et, AsMeEt$_2$, and AsEt$_3$), although the Pt–H coupling is not resolved, as a consequence of the relaxation of ^{195}Pt by ^{75}As.[5] The complexes [Pt(NCS)(SCN)L$_2$] (L = SMe$_2$, SeMe$_2$, and AsMe$_3$) must have the *trans* configuration since only one type of proton resonance was observed. The other two isomers of each complex are also presumably *trans* in view of the similarity in the values of ^3J(PtH) and, for the dimethyl selenide complexes, ^1J(PtSe) (Table 2).

TABLE 2

Selenium-77 n.m.r. parameters

	δ_{Se} [a]	^2J(SeH)/ Hz	^1J(PtSe)/ Hz
trans-[Pt(SCN)$_2$(SeMe$_2$)$_2$]	134	9.4	+270 ± 10
trans-[Pt(NCS)(SCN)(SeMe$_2$)$_2$]	142	9.6	+270 ± 10
trans-[Pt(NCS)$_2$(SeMe$_2$)$_2$]	139	9.8	+250 ± 10
cis-[Pt(NCO)$_2$(SeMe$_2$)$_2$]	92	9.4	615 ± 5
cis-[PtCl(NCO)(SeMe$_2$)$_2$]	118 [b]	*ca.* 10	480 ± 10
	92	*ca.* 10	630 ± 10
trans-[PtCl(NCO)(SeMe$_2$)$_2$]	134	9.4	345 ± 10

[a] In p.p.m. to high frequency of SeMe$_2$. [b] *trans* to Cl.

The ^{1}H n.m.r. spectra of complexes *cis*-[Pt(CNS)$_2$L$_2$] (L = PMe$_3$ and PMe$_2$Et) in nitromethane or dimethyl sulphoxide were broad at room temperature but gave a single Me(P) doublet with ^{195}Pt satellites at *ca.* 340 K. In contrast, the ^{1}H-{^{195}Pt} INDOR spectrum of each complex gave two sets of resonances corresponding to *cis*-[Pt(NCS)$_2$L$_2$] and

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* CNS is used where the mode of co-ordination of the thiocyanate group is unspecified.

[1] G. Baran and G. J. Palenik, *Chem. Comm.*, 1970, 1354.

[2] A. J. Carty and S. E. Jacobson, *J.C.S. Chem. Comm.*, 1975, 175.

[3] A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 231.

[4] S. J. Anderson and R. J. Goodfellow, *J.C.S. Chem. Comm.*, 1975, 443.

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

cis-[Pt(NCS)L$_2$(SCN)], which suggests that the rate of equilibration between these species was sufficiently rapid to cause coalescence of the ^{1}H resonances but not of the ^{195}Pt resonances where the separation in chemical shifts is much greater. The complex [Pt(CNS)$_2$(PMeEt$_2$)$_2$] behaved similarly in dichloromethane solution at room temperature. Values of J(PtP), from the ^{1}H-{^{195}Pt} spectra, are typical of *cis*-platinum(II) complexes (Table 3), being somewhat less when *trans* to SCN than when *trans* to NCS. Furthermore, values of ^1J(PtN) are considerably lower than for the *trans* complexes above, reflecting the *trans* influence of the phosphine. The ^{1}H-decoupled ^{31}P Fourier-transform spectra of these complexes had resonances that, following Carty and Jacobson,[2] could be assigned to *cis*-[Pt(NCS)$_2$L$_2$] and *cis*-[Pt(NCS)L$_2$(SCN)] but there was no indication of *cis*-[Pt-L$_2$(SCN)$_2$]. These ^{31}P resonances were also identified by ^{1}H-{^{31}P} INDOR.

TABLE 3

N.m.r. parameters of [Pt(CNS)$_2$(PR$_3$)$_2$] (R = Me or Et)

Complex	Isomer [a]	δ_P [b]	^1J(PtP)/Hz	^2J(PP)/Hz	δ_{Pt} [c]	^1J(PtN)/Hz	Proportion NS/NN
cis-[Pt(CNS)$_2$(PMe$_3$)$_2$] [d]	NS	15.5 [e]	3 029	24	69 [f]		0.39 [d]
		32.9	3 273				
	NN	28.0	3 333		161		
cis-[Pt(CNS)$_2$(PMe$_2$Et)$_2$] [d]	NS	3.7 [e]	3 021	23	14 [g]	205 ± 5	0.3 [d] (0.46 [h])
		20.9	3 299				
	NN	16.3	3 331		110 [g]	220 ± 10 [g]	
cis-[Pt(CNS)$_2$(PMeEt$_2$)$_2$] [h]	NS	−6.0 [e]	3 001	21	−11	245 ± 5	0.28 [d] (0.42 [h])
		9.9	3 346				
	NN	6.0	3 350		91	220 ± 5	
cis-[Pt(CNS)$_2$(PEt$_3$)$_2$] [h]	NS	−14.9 [e]	2 996	20			0.3 [h]
		1.1	3 348				
	NN	−3.1	3 354		99		
trans-[Pt(CNS)$_2$(PEt$_3$)$_2$] [h]	NN	−17.7	2 216	+404	663	424 ± 2	

[a] and [c] As in Table 1. [b] In p.p.m. to high field of H_3PO_4. [d] In $(CD_3)_2SO$. [e] *trans* to S. At 340 K. [g] In CD_3NO_2 at 340 K. [h] In CH_2Cl_2.

We were able to obtain separately the *cis* and *trans* isomers of [Pt(CNS)$_2$(PEt$_3$)$_2$] and, for both, the ^{1}H-{^{195}Pt} INDOR spectra showed only the all N-bonded configuration. However, the ^{31}P Fourier-transform spectrum of the *cis* isomer also contained the resonances of *cis*-[Pt(NCS)(PEt$_3$)$_2$(SCN)]; that of the *trans* isomer had *ca.* 3% of a second *trans* species [δ_P 15.9 p.p.m., ^1J(PtP) 2 252 Hz] which may be *trans*-[Pt(NCS)(PEt$_3$)$_2$(SCN)]. (Because of the complexity of the methylene proton resonances, ^{1}H-{^{195}Pt} INDOR experiments are not very satisfactory for triethylphosphine complexes.) Small amounts of *trans* species with similar parameters to these occurred in the spectra of *cis* complexes with PEt$_3$, PMeEt$_2$, and PMe$_2$Et.

From the effect of halides on δ_{Pt}, we may expect the replacement of N-bonded by S-bonded thiocyanate to cause a significant shift to low frequency.[6] Thus for the complexes *trans*-[PtX$_2$L$_2$] above, δ_{Pt} decreases according to X in the order (NCS)$_2$ > Cl$_2$ > BrCl > (NCS)(SCN) > Br$_2$ > (SCN)$_2$. This is further illustrated by the ^{195}Pt chemical shifts of *trans*-[Pt(AsMe$_3$)$_2$(CNS)X] in Table 4. For the *cis*-phosphine complexes, the order is slightly different, (NCS)$_2$ > Cl$_2$ > (NCS)(SCN) > BrCl. The effect on δ_{Pt} of going from N-bonded to S-bonded thiocyanate is apparently reduced even more by a *trans*-phosphine ligand than replacing chloride by bromide.[6]

Although the ^{1}H spectrum of [Pt(CNS)$_2$(SbMe$_3$)$_2$] showed only one type of methyl resonance, the corresponding ^{1}H-{^{195}Pt} INDOR spectrum had two resonances at −38 and −417 p.p.m. respectively, the former predominating. The platinum resonances of trimethylstibine complexes are very broad because of the relaxation by the quadrupolar antimony nuclei (*cf.* ref. 6) and this precluded the observation of Pt–N coupling. Although the platinum shift of −38 p.p.m. is greater than that of *cis*-[PtCl$_2$(SbMe$_3$)$_2$],[6] it is unlikely to relate to *cis*-[Pt(NCS)$_2$(SbMe$_3$)$_2$] because the integrated absorbance of the CN stretching vibration in the i.r. precludes any significant amount of N-bonded forms (see below). Since the solution of [PtBr$_2$(SbMe$_3$)$_2$] showed no trace of the *trans* isomer we were unable to measure its ^{195}Pt chemical shift, but using the results of Goggin *et al.*[6] we estimate it as 99 p.p.m. from which it is reasonable to assign the shift of −38 p.p.m. to *trans*-[Pt(SCN)$_2$(SbMe$_3$)$_2$]. From the partial sequence of δ_{Pt} for *cis*-[Pt(CNS)$_2$(PMe$_3$)$_2$], it seems likely that the shift of *cis*-[Pt(SCN)$_2$L$_2$] could lie above that of the analogous bromide so that the shift of −417 p.p.m. does not seem unreasonable for *cis*-[Pt(SCN)$_2$-(SbMe$_3$)$_2$].

TABLE 4

Platinum-195 chemical shifts for *trans*-[Pt(AsMe$_3$)$_2$-(CNS)X] (X = Cl, Br, or I)

CNS	X	δ_{Pt} *
NCS	Cl	777
SCN	Cl	329
NCS	Br	536
SCN	Br	89
NCS	I	6
SCN	I	−373

* As in Table 1.

The ^{1}H spectrum of [Pt(CNS)$_2$(NMe$_3$)$_2$] contained only one type of methyl group whose ^{195}Pt spectrum approximates to a 1 : 2 : 3 : 2 : 1 quintet [^1J(PtN) *ca.* 500 Hz]. However, this pattern might be due to the ^{14}N nuclei of the two amine ligands. After 2 d, the spectrum of a mixture of this complex with [PtCl$_2$(NMe$_3$)$_2$] was predominantly that of [Pt(CNS)Cl(NMe$_3$)$_2$]. The ^{195}Pt spectrum clearly shows coupling to one N-bonded thiocyanate group [1 : 1 : 1 triplet, ^1J(PtN) *ca.* 460 Hz] as well as the suggestion of quintets due to the amines. The latter coupling (*ca.* 250 Hz) is typical of (trimethylamine)platinum(II) complexes.[7] The coupling seen for [Pt(CNS)$_2$(NMe$_3$)$_2$] must, in view of its magnitude,

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[6] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, B. F. Taylor, and I. R. H. Marshall, *J.C.S. Dalton*, 1976, 459.

[7] 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.

be due to N-bonded thiocyanate. As only one type of methyl group was observed, $[PtCl(NCS)(NMe_3)_2]$ must be the *trans* isomer, and from the n.m.r. parameters there is no reason to suppose that $[Pt(NCS)_2(NMe_3)_2]$ is not the same. In contrast to all the other complexes, δ_{Pt} for these N-bonded complexes lies below that of the analogous chloride. We suggest that this is a consequence of the steric hindrance associated with trimethylamine[8] which destabilises the platinum-to-halogen bond more than that to the slim NCS group.

TABLE 5

N.m.r. parameters for some neutral cyanate complexes of platinum(II)

	τ_{Me}	^3J(PtH)/Hz	δ_{Pt} [a]	^1J(PtN)/Hz
trans-$[Pt(NCO)_2(NMe_3)_2]$	7.37	33.1	2 479	420 ± 20
trans-$[PtCl(NCO)(NMe_3)_2]$	7.36	30.7	2 558	470 ± 10
cis-$[Pt(NCO)_2(PMe_2Et)_2]$	8.41	35.4	183	200 ± 20 [b]
cis-$[Pt(AsMe_3)_2(NCO)_2]$	8.43	23.1	416	
cis-$[Pt(NCO)_2(SMe_2)_2]$	7.53	47.5	1 205	330 ± 5
cis-$[Pt(NCO)_2(SeMe_2)_2]$	7.64	40.1	1 075	300 ± 5
cis-$[PtCl(NCO)(SeMe_2)_2]$	7.58 [c]	44.4	953	300 ± 10
	7.62	38.4		
trans-$[PtCl(NCO)(SeMe_2)_2]$	7.68	38.8	953	305 ± 10

[a] As in Table 1. [b] δ_P 18.3 p.p.m., ^1J(PtP) 3 381 Hz. [c] *trans* to Cl.

The ^1H n.m.r. spectra of all the cyanate complexes that we have prepared showed only one species to be present in solution (Table 5). The ^1H-$\{^{195}Pt\}$ INDOR spectra, although not as well resolved as for the thiocyanate complexes, indicated that this was $[Pt(NCO)_2L_2]$. In the case of trimethylamine we studied $[PtCl(NCO)(NMe_3)_2]$ to confirm the origin of the Pt–N coupling and this also established the *trans* configuration. For $[Pt(NCO)_2(PMe_2Et)_2]$, the value of ^1J(PtP) indicates that it is the *cis* isomer. The large Pt–Se coupling constant observed for $[Pt(NCO)_2(SeMe_2)_2]$ would be in keeping with a *cis* structure,[9] but the sensitivity of ^1J(PtSe) to the other ligands present could confuse such an assignment.[10] As a further check, we recorded the spectrum of a mixture of $[PtCl_2(SeMe_2)_2]$ and $[Pt(NCO)_2(SeMe_2)_2]$. Initially, the twin peaks due to *cis*-$[PtCl(NCO)(SeMe_2)_2]$ appeared but were later largely replaced by the single peak of the *trans* isomer. The n.m.r. parameters, especially ^1J(PtSe) and δ_{Se} (Table 2), show that $SeMe_2$ in $[Pt(NCO)_2(SeMe_2)_2]$ is related to that *trans* to cyanate in *cis*-$[PtCl(NCO)(SeMe_2)_2]$ and hence that the former complex is also the *cis* isomer. From a comparison of the n.m.r. results we conclude that the $AsMe_3$ and SMe_2 complexes also have the *cis* structure.

TABLE 6

Vibrations of the CNS group in some thiocyanate complexes of platinum(II) *

	cis-$[Pt(SCN)_2(SbMe_3)_2]$ (I)		*cis*-$[Pt(NCS)_2(PMe_3)_2]$ (II)		*trans*-$[Pt(NCS)_2(PEt_3)_2]$ (III)		*trans*-$[Pt(NCS)_2(SeMe_2)_2]$ (IV)	
	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman
CN str.	2 110(sh)		2 108vs	2 170vs		2 127vs		2 132s
	2 105vs	2 106s	2 096vs	2 089vs	2 118vs		2 116s	2 113s
CS str.	701wm	700wm	851wm			867s	843s	846ms
			846m	845m	857s		702w	698w
			840vw(sh)	840wm(sh)			695w	692w
CNS bend	450m		474w	475w			466w	
	423m		468w	465w	462w		458w	
			464(sh)	442w			420w	
Pt–N or Pt–S str.	280m	280m	268m,bd	271m	305w,bd		294ms	292s
	263s	263m				294w	282s	287(sh)

* Infrared of heavy paraffin mulls, Raman of solids.

As mentioned in our preliminary report,[4] the ^{14}N resonance of nitrogen bound to ^{195}Pt may be observed by ^1H-$\{^{195}Pt^{14}N\}$ triple resonance. The ^{14}N resonances were difficult or impossible to identify when the ^{195}Pt spectra were broad, *e.g.* for arsine complexes (Table 1). The only cyanate complexes to give ^{14}N results were those of SMe_2 and $SeMe_2$ for which δ_N is -370 ± 10 p.p.m. In contrast to all other systems, $[Pt(NCS)_2(NMe_3)_2]$ gave a well defined INDOR spectrum by ^1H-$\{^{14}N\}$ double resonance.

Recently, Norbury[3] critically reviewed the use of i.r. spectra in identifying chalcogenocyanate co-ordination. Hitherto, there has been little application of Raman spectroscopy to this problem, although this technique might provide a better means of discerning chalcogenocyanate vibrations or at least a useful complement to i.r. studies. We measured the Raman and i.r. spectra of the complexes discussed above. In many cases, the solid-state spectra showed a complexity which is consistent with the presence of a mixture of linkage isomers as found by n.m.r. spectroscopy for their solutions. The significant features are illustrated by the spectra of *cis*-$[Pt(SCN)_2(SbMe_3)_2)]$, (I), *cis*-$[Pt(NCS)_2(PMe_3)_2]$, (II), and *trans*-$[Pt(NCS)_2(PEt_3)_2]$, (III), which we are reasonably sure are predominantly one isomer in the solid state, together with those of *trans*-$[Pt(CNS)_2(SeMe_2)_2]$, (IV), as an example of a mixture of linkage isomers (Table 6).

For *cis* complexes, two CN and two CS stretching vibrations, active in both i.r. and Raman, are predicted. In the spectra of (I) a second CN vibration was observed as a

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[8] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J.C.S. Dalton*, 1972, 1298.

[9] W. McFarlane, *Chem. Comm.*, 1968, 755.

[10] P. L. Goggin, R. J. Goodfellow, and S. R. Haddock, *J.C.S. Chem. Comm.*, 1975, 176.

shoulder but otherwise there was no sign of a second feature. Thus CN and CS band multiplicities do not give a reliable guide to the stereochemistry around the metal of S-bonded thiocyanate complexes, although the Pt–S stretching vibrations do give a clear indication of the *cis* structure of (I). Single Raman-active CN and CS bands were found for the *trans* complex, (III), and at significantly higher wavenumbers than the i.r. bands, whereas the expected two features were observed in each case for the *cis* complex, (II). There is, however, poor i.r.–Raman coincidence for the latter, implying solid-state effects which could affect the validity of conclusions as to stereochemistry based on solid-state spectra. Platinum–nitrogen stretching vibrations are not strong in either type of spectra and are often difficult to identify with certainty, rendering them of little use for stereochemistry diagnosis.

The CN-stretching wavenumbers observed for (II) and (III) are above the normal range given by Norbury [3] for N-bonded thiocyanates and, in fact, for (III) lie above those of the S-bonded complex (I) instead of below them. This illustrates the unreliability of CN-stretching frequencies as a determination of linkage type. Although the NCS deformation bands of N-bonded isomers do tend to be higher than those of S-bonded complexes, they do not conform to the wavenumber ranges previously given.[3] The number of such vibrations observed is rarely as great as predicted and they are extremely weak in the Raman spectra.

TABLE 7

Vibrations of the NCO group in some cyanate complexes of platinum(II)

	cis-$[Pt(AsMe_3)_2(NCO)_2]$			*cis*-$[Pt(NCO)_2(PMe_2Et)_2]$		*cis*-$[Pt(NCO)_2(SMe_2)_2]$		*cis*-$[Pt(NCO)_2(SeMe_2)_2]$			*trans*-$[Pt(NCO)_2(NMe_3)_2]$	
	I.r. (mull)	Raman (solid)	I.r. (CH_2Cl_2)	I.r. (mull)	Raman (solid)	I.r. (mull)	Raman (solid)	I.r. (mull)	Raman (solid)	I.r. (CH_2Cl_2)	I.r. (mull)	Raman (solid)
CN str.		2 260(sh)		2 240vs	2 236w,bd	2 240vs	2 234w	2 218vs,bd	2 225w	2 217vs		2 267w
	2 240vs	2 246w		2 220(sh)		2 217vs					2 240vs,bd	
	2 217vs	2 222w	2 225vs	2 200(sh)								
CO str.	1 341s	1 341ms		1 340(sh)		1 340m	1 347s	1 338ms	1 338ms	1 345s		1 353s
	1 334s	1 333ms	1 334s	1 330s	1 335s						1 338m	
NCO bend	*	*		596s	595m	594s	597w	602s(sh)				587w
											580m	
Pt–N str.	350s	352w		348m		365s	369s	360s	357w			360w
	336m(sh)										350m	

* Obscured by ligand modes.

Qualitatively, the Raman intensities of stretching vibrations follow those of the i.r.-active bands. However, because most of the Raman bands arising from organic ligands in the 800—900 cm^{-1} region tend to be weak, Raman spectra may be more helpful than i.r. for the detection of N-bonded thiocyanate groups [ν(CS) at 820—870 cm^{-1}]. Whilst the spectra of (IV) are compatible with the presence of a mixture of forms, the intensity differential between the C–S stretching vibrations of N- and S-bonded groups makes the former much more easily detected even though they are probably in the minority.

Integrated absorbances of the i.r. CN stretches have been used as an empirical distinction between N- and S-bonded forms, and despite the theoretical objections to their application to different stereochemistries they seem to have been reliable as to the predominant mode of co-ordination.[3] We made such measurements for some of our complexes. All the examples showed a single feature in dichloromethane solution, even those which are *cis* (although the band was then rather broad). The values per CN group ($A \times 10^{-4}$ dm^3 mol^{-1} cm^{-2}) were: *cis*-$[Pt(CNS)_2(PEt_3)_2]$, 7.5; *cis*-$[Pt(CNS)_2(PMeEt_2)_2]$, 7.5; *trans*-$[Pt(CNS)_2(PEt_3)_2]$, 6.7; *trans*-$[Pt(AsEt_3)_2(CNS)_2]$, 11.4; and $[Pt(CNS)_2(SbMe_3)_2]$, 1.2. The first four are in the range quoted for N-bonded thiocyanate, and for the triethylphosphine complexes are in excellent agreement with the values obtained by Pecile for butan-2-one solutions.[11] The last value agrees with that for the S-bonded form, and indeed leaves little possibility of any significant contribution from N-bonded forms.

It has been pointed out by Tsivadze *et al.*[12] that there is much greater mixing between stretching vibrations of the cyanate group than of the thiocyanate group. With the parallel to CO_2 in terms of masses it is not too surprising that what might be termed ' CO stretching ' (at *ca.* 1340 cm^{-1}) gives very intense Raman bands, whereas what might be termed ' CN stretching ' gives relatively weak features, The reverse behaviour is, however, not so evident in the i.r. (Table 7). Whilst the ' CN ' and ' CO ' regions of the spectra of solid $[Pt(AsMe_3)_2(NCO)_2]$ are completely compatible with a *cis* structure, the doublets collapse to single bands in solution although there is no change in stereochemistry. Again, in solid $[Pt(NCO)_2(SeMe_2)_2]$ they are singular features yet we are certain of the *cis* structure. In *trans*-$[Pt(NCO)_2(NMe_3)_2]$ there is a significant lack of coincidence between the single i.r. and Raman frequencies which may be a useful indication of a *trans* structure. Overall, the number of ' CN ' and ' CO ' bands observed seems far from reliable as an indication of the stereochemistry. We never observed more than one NCO deformation band in the i.r. (fairly strong) or Raman (fairly weak), and generally only one Pt–N stretching band.

Thus, in general, vibrational spectra seem to be rather limited in their conclusiveness about the stereochemistry and mode of co-ordination of chalcogenocyanate complexes.

DISCUSSION

Since different solutions showed the same isomeric composition and this was invariant with time, we are confident that this composition represents equilibrium. Because S-bonded thiocyanate involves a nearly tetrahedral MSC angle,[13] there will be much more steric interaction with *cis* ligands than for the linearly co-ordinated NCS. The effect is clearly demonstrated by the series *trans*-$[PtL_2(CNS)_2]$ where L goes from $AsMe_3$ to $AsEt_3$ resulting in an almost complete change from S- to N-co-ordination (see Table 1). The effects of successive changes from PMe_3 to PEt_3 in *cis*-$[Pt(CNS)_2L_2]$ are

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rather less (Table 3) as there is only one neutral ligand *cis* to each thiocyanate group. Decreasing steric interaction may also account for the change in bonding in the sequence *trans*-$[Pt(CNS)_2L_2]$ (L = NMe_3, $AsMe_3$, and $SbMe_3$), although there might also be electronic effects related to the period of the donor atom.

The ratio of S- to N-bonded thiocyanate in *trans*-$[Pt(AsMe_3)_2(CNS)X]$ is *ca.* 1 : 0.05 for X = Cl, Br, and I. Comparison with the ratios $[Pt(AsMe_3)_2(NCS)(SCN)]$: $[Pt(AsMe_3)_2(NCS)_2]$ and $[Pt(AsMe_3)_2(SCN)_2]$: $[Pt(AsMe_3)_2(NCS)(SCN)]$ shows that the proportion of S-bonded isomer decreases according to the *trans* ligand in order Cl > NCS > SCN. As judged from ${}^1J$(PtP) or ${}^1J$(PtN), this is the likely order of increasing *trans* influence, *i.e.* strong *trans*-influence ligands destabilise S-bonded thiocyanate more than N-bonded thiocyanate.

TABLE 8

Characterisation of thiocyanate and cyanate complexes

Complex	Colour	M.p. (θ_c/°C)	Analyses (%) C Found	C Calc.	H Found	H Calc.	N Found	N Calc.
$[Pt(CNS)_2(SMe_2)_2]$	Yellow	78—80	16.7	16.6	3.1	2.8	6.4	6.5
$[Pt(CNS)_2(SeMe_2)_2]$	Yellow	84—86	13.4	13.6	2.4	2.3	5.2	5.3
$[Pt(AsMe_3)_2(CNS)_2]$	White	146—148	17.5	17.4	3.5	3.3	5.1	5.1
$[Pt(AsMe_2Et)_2(CNS)_2]$	White	74—76	20.7	20.7	3.9	3.9	4.9	4.8
$[Pt(AsMeEt_2)_2(CNS)_2]$	White	80—83	23.9	23.7	4.5	4.3	4.8	4.6
$[Pt(AsEt_3)_2(CNS)_2]$	White	134—136	26.4	26.5	4.6	4.7	4.4	4.4
$[Pt(NCS)_2(NMe_3)_2]$	White	140 *	22.5	22.4	4.2	4.2	13.0	13.1
$[Pt(SCN)_2(SbMe_3)_2]$	Yellow	167—168	15.1	14.9	2.8	2.8	4.5	4.4
$[Pt(CNS)_2(PMe_3)_2]$	White	226—230	20.9	20.7	4.0	3.9	6.0	6.1
$[Pt(CNS)_2(PMe_2Et)_2]$	White	158—161	24.7	24.5	4.5	4.5	5.6	5.7
$[Pt(CNS)_2(PMeEt_2)_2]$	White	140—142	27.8	27.7	5.2	5.0	5.4	5.4
$[Pt(NCO)_2(SMe_2)_2]$	White	170—172	18.0	17.9	3.2	3.0	7.0	6.9
$[Pt(NCO)_2(SeMe_2)_2]$	White	140—142	14.6	14.5	2.4	2.4	5.6	5.6
$[Pt(AsMe_3)_2(NCO)_2]$	White	224—226	18.7	18.5	3.6	3.5	5.4	5.4
$[Pt(NCO)_2(NMe_3)_2]$	White	170 *	24.2	24.1	4.7	4.5	14.1	14.1
$[Pt(NCO)_2(PMe_2Et)_2]$	White	189—191	26.2	26.2	4.8	5.1	6.1	6.2

* Decomposed without melting.

The proportion of S-bonded thiocyanate present for *cis*-$[Pt(CNS)_2(PR_3)_2]$ (Table 3) is markedly more in dichloromethane solution than in dimethyl sulphoxide. This is the reverse of the trend observed by Burmeister *et al.*[14] for some palladium complexes. We were unable to investigate the effects of solvent on *trans*-$[Pt(AsMe_3)_2(CNS)_2]$ as it decomposed in the more polar solvents such as acetone or acetonitrile.

EXPERIMENTAL

Phosphorus-31 n.m.r. spectra were recorded on a JEOL PFT100 Fourier-transform spectrometer, using an internal deuterium lock. Vibrational and INDOR spectral measurements were made as previously described.[8,15,16] Dichloromethane solutions were used for the n.m.r. spectral measurements and were examined at ambient magnet temperature (*ca.* 300 K) except where otherwise stated. Measurements of the mixed halogenothiocyanate species were made as described in ref. 6.

Preparation of Complexes.—The complexes $[Pt(CNS)_2L_2]$ (L = SMe_2, $SeMe_2$, $AsMe_3$, $AsMe_2Et$, $AsMeEt_2$, $AsEt_3$, NMe_3, $SbMe_3$, PMe_3, PMe_2Et, and $PMeEt_2$) were prepared by metathesis between the corresponding chloro-complex [6] and K[SCN]. The chloro-complex was stirred with an excess of K[SCN] for 2—3 h in acetone. The residual potassium salts were filtered off and the extract evaporated to dryness under reduced pressure. The crude product was extracted into dichloromethane, taken to dryness, and recrystallised from a suitable solvent. The complexes $[Pt(CNS)_2L_2]$ (L = $SeMe_2$ or SMe_2) were recrystallised from benzene containing a small proportion of the appropriate ligand. The complexes *trans*- and *cis*-$[Pt(CNS)_2(PEt_3)_2]$ have been described previously.[17] The cyanate complexes were prepared similarly from the corresponding chloro-complex and K[OCN] in acetone (6—8 h). Analytical data are given in Table 8.

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