Effects of some Neutral Ligands on the Co-ordination of the Thiocyanate Ion in some Anionic Platinum(II) Complexes

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The isomers present in solutions of $[Pt(CNS)_3L]^-$ [L = NMe_3, $PMe_{(3-n)}Et_n$ (n = 0—3), $AsMe_3$, $AsMe_2Et$, $SbMe_3$, SMe_2, $SeMe_2$, or $TeMe_2$] have been identified by means of ^1H-$\{^{195}Pt\}$ and ^{31}P n.m.r. spectroscopy. *N*-Bonding of the thiocyanate ion is favoured when L contains a light donor atom, when the *trans* ligand has a high *trans* influence, or when a *cis* ligand is bulky.

RECENTLY [1] we reported the results of our investigations into the co-ordination isomers of $[Pt(CNS)_2L_2]$.† Using ^1H-$\{^{195}Pt\}$ INDOR we were able to identify the isomers present [2] and hence the position of the equilibria between *N*- and *S*-bonded forms. From the set of *trans* complexes studied, clear evidence was found for the promotion of *N*-bonding by steric interaction with the *cis* ligands. Because only phosphines and trimethylstibine gave *cis* isomers, no definite conclusions could be reached on the role of a neutral ligand in the *trans* position. The relative effects of a neutral ligand on the co-ordination behaviour of *cis*- and *trans*-thiocyanate groups may be assessed simultaneously in the anionic complexes, $[Pt(CNS)_3L]^-$, which we have now investigated using ^1H-$\{^{195}Pt\}$ INDOR and ^{31}P Fourier-transform spectroscopy.

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

RESULTS

There are six possible isomers of $[Pt(CNS)_3L]^-$. In the proton spectrum of $[NBu^n_4][Pt(CNS)_3(PMe_3)]$ four doublets could be readily identified. The form of the related ^1H-$\{^{195}Pt\}$ INDOR resonances (*cf.* ref. 2) showed them to be $[Pt(SCN)_3(PMe_3)]^-$, the two isomers of $[Pt(NCS)(SCN)_2(PMe_3)]^-$ and one isomer of $[Pt(NCS)_2(SCN)(PMe_3)]^-$. The

[1] S. J. Anderson, P. L. Goggin, and R. J. Goodfellow, *J.C.S. Dalton*, 1976, 1959.
[2] S. J. Anderson and R. J. Goodfellow, *J.C.S. Chem. Comm.*, 1975, 443.

values of ^1J(PtN) and ^1J(PtP) (Tables 1 and 2) clearly distinguished the two mono-*N*-bonded forms (*cf.* ref. 1). The lack of resolution of the ^{195}Pt resonances of the doubly *N*-bonded form might be expected if there were two values of ^1J(PtN) and the magnitude of ^1J(PtP) suggested nitrogen *trans* to the phosphine, *i.e. cis*-$[Pt(NCS)_2(SCN)(PMe_3)]^-$. The Fourier-transform ^{31}P spectrum (Figure) has the features of all the six isomers. Using the changes in ^{1}H chemical shifts resulting from the replacement of *S*- by chain. The spectra were assigned by comparison with that of the trimethylphosphine complex.

For the complexes of $AsMe_3$, $AsMe_2Et$, SMe_2, $SeMe_2$, and $TeMe_2$, the number of *N*-bonded thiocyanate groups could usually be found from the multiplicity of the ^{14}N coupling pattern in the ^{1}H-{^{195}Pt} INDOR spectrum. The isomers of $[Pt(NCS)_2(SCN)L]^-$ can be distinguished by the values of ^1J(PtN) when L is an arsine, but the *trans* influences of the chalcogen ligands are too close to that of SCN to make

TABLE 1

N.m.r. parameters of some anionic complexes, $[Pt(CNS)_3L]^-$

L	Isomer [a]	τ(Me)	^3J(PtH) Hz	δ(Pt) [b]	^1J(PtN) Hz	Relative proportion
NMe_3	NSN	7.25	33.2	1 928(q)	460 ± 5	1.0
	NNN	7.32	*ca.* 31	2 445(bd)		0.2
PMe_3	SSS	8.25	32.3	179(s)		
	NSS	8.34	32.4	538(t)	355 ± 5	
	NSN	8.40	*ca.* 33	955(q)	439 ± 5	*c*
	SNS	8.40	32.2	439(t)	205 ± 5	
	NNS	8.43	32.8	703(bd)		
	NNN	8.45	*ca.* 34	1 014(bd)		
PMe_2Et	SSS	8.30	*ca.* 32	164(s)		
	NSS	8.39	*ca.* 33	518(t)	340 ± 10	*c*
	SNS	8.47	*ca.* 33	415(t)	215 ± 5	
	NNS	8.50	*ca.* 33	675(bd)		
$AsMe_3$	SSS	8.33	21.4	228(s)		1.0
	NSS	8.41	22.3	642(t)	353 ± 5	0.4
	SNS	8.46	22.6	576(t)	290 ± 10	0.2
	NNS	8.48	*ca.* 22	897(bd)		0.04
$AsMe_2Et$	SSS	8.40	21.6	215(s)		1.0
	NSS	8.46	21.6	627(t)	360 ± 5	0.3
	SNS	8.54	22.1	551(t)	270 ± 5	0.2
	NNS	8.55		*d*		0.03
$SbMe_3$	SSS	8.57	*d*	159(v.bd)		1.0
	NSS	8.62	*d*	598(v.bd)		0.05
SMe_2	SSS	7.38	45.6	466(s)		1.0
	NSS	7.43	45.3	931(t)	370 ± 5	0.4
	NSN	7.50	45.2	1 498(q)	450 ± 30	0.08
	SNS	7.53	47.1	944(t)	360 ± 10	0.1
	NNS	7.55	*ca.* 46	1 302(bd)		0.02
$SeMe_2$	SSS	7.52	38.4	359(s)		1.0
	NSS	7.55	38.9	857(t)	375 ± 5	0.4
	NSN	7.59	39.0	1 446(q)	438 ± 5	0.1
	SNS	7.67	*ca.* 39	851(t)	368 ± 10	0.06
$TeMe_2$ [e]	SSS	7.75	33.6	92(s)		1.0
	NSS	7.76	35.7	605(t)	367 ± 5	0.3
	NSN	7.80	*ca.* 35	1 190(bd)		0.04
	SNS	7.86		*d*		0.006

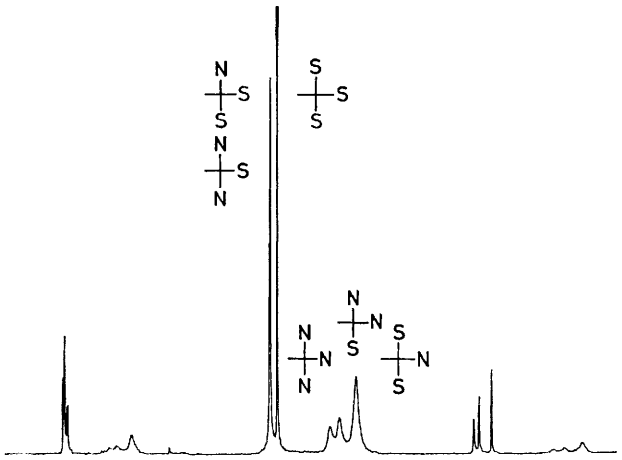
[a] The co-ordinated atoms of the thiocyanate groups are given in order around the metal starting with the group next to L, *e.g.* SNS indicates NCS *trans* to L. [b] In p.p.m. to high frequency of 21.4 MHz (when $SiMe_4$ resonates at 100 MHz). Multiplicity due to Pt–N coupling: s = singlet, t = 1 : 1 : 1 triplet, q = 1 : 2 : 3 : 2 : 1 quintet, bd = broad unresolved resonance. [c] See Table 2. [d] Not observed. [e] At 240 K.

N-bonded thiocyanate as a guide, the ^{1}H resonances of the last two isomers were then identified. The nature of all the features was confirmed by ^{1}H-{^{31}P} and ^{1}H-{^{195}Pt} INDOR experiments. The ^{31}P resonances of a phosphine are broad when *trans* to *N*-bonded thiocyanate due to partially relaxed coupling to ^{14}N (*cf.* ref. 3). The resonances of a phosphine *trans* to *S*-bonded thiocyanate broaden a little with increasing number of *cis*-NCS groups. We have studied the ^{31}P Fourier-transform spectra of the series $[NBu^n_4][Pt(CNS)_3L]$ (L = PMe_2Et, $PMeEt_2$, or PEt_3) to provide an assessment of the steric effects of the alkyl such a distinction reliable. The resonances of *trans*-$[Pt(NCS)_2(SCN)L]^-$ can be identified by the large value of ^1J(PtN) (*ca.* 450 Hz) for ^{14}N *trans* to NCS.[1] The remaining isomers are assigned so that there is a regular upfield shift of the proton resonances when *S*- is replaced by *N*-bonded thiocyanate in the position *cis* to the neutral ligand and a rather larger upfield shift for the *trans* position.

As found for $[Pt(CNS)_2L_2]$,[1] there is a large decrease in δ(Pt) when NCS is replaced by SCN. For the anions

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

studied here, the ^{195}Pt resonances of $[Pt(SCN)_3L]^-$ lie well below those of $[PtBr_3L]^-$,[4] whilst those of the mono-*N*-bonded species lie close to it. The two ^{195}Pt signals of $[Pt(CNS)_3(SbMe_3)]^-$ were very broad because of the relaxation caused by the quadrupolar antimony nucleus (*cf.*



Phosphorus-31 spectrum (^1H decoupled) of $[NBu^n_4][Pt(CNS)_3(PMe_3)]$

TABLE 2

Phosphorus-31 n.m.r. parameters of $[Pt(CNS)_3L]^-$ [L = $PMe_{3-n}Et_n$ (n = 0—3)]

L	Isomer [a]	δ(P) [b]	^1J(PtP) Hz	Relative proportion
PMe_3	SSS	19.1	3 229	1.0
	NSS	17.8	3 143	0.9
	NSN	17.7	3 075	0.9
	SNS	33.7	3 401	1.5
	NNS	30.6	3 369	0.7
	NNN	28.9	3 348	0.5
PMe_2Et	SSS	8.3	3 219	1.0
	NSS	6.9	3 141	1.2
	NSN	6.8	3 081	1.3
	SNS	22.1	3 391	1.7
	NNS	19.2	3 373	0.9
	NNN	17.4	3 353	0.7
$PMeEt_2$	SSS	−2.8	3 215	1.0
	NSS	−4.2	3 139	1.5
	NSN	−4.4	3 082	2.0
	SNS	10.4	3 395	1.9
	NNS	7.4	3 380	1.2
	NNN	5.8	3 360	1.1
PEt_3	SSS	−11.8	3 213	1.0
	NSS	−13.4	3 141	1.9
	NSN	−13.9	3 092	2.7
	SNS	1.1	3 402	2.4
	NNS	−2.0	3 389	1.7
	NNN	−3.7	3 375	1.9

[a] As in Table 1. [b] In p.p.m. to high field of H_3PO_4.

ref. 4) which precluded the observation of Pt–N coupling. One species has a shift *ca.* 450 p.p.m. below that of $[PtBr_3(SbMe_3)]^-$ (ref. 4) and is therefore assigned to $[Pt(SCN)_3(SbMe_3)]^-$ whilst the other is close to that of the bromo-anion and the proton shift suggests *cis*-$[Pt(NCS)(SCN)_2(SbMe_3)]^-$. Two species were observed for $[Pt(CNS)_3(NMe_3)]^-$, the most abundant of which gave a well resolved quintet in the ^1H-{^{195}Pt} INDOR spectrum. The magnitude of ^1J(PtN) is much greater than for the nitrogen of NMe_3 (ref. 1) and must therefore belong to a *trans*-SCN–Pt–NCS group. The relative proton and ^{195}Pt chemical shifts of the other isomer are *in* accord with $[Pt(NCS)_3(NMe_3)]^-$.

DISCUSSION

In our study of the neutral complexes, $[Pt(CNS)_2L_2]$, we identified a significant enhancement of the amount of *N*-bonded isomers when the bulk of a *cis* neutral ligand increased.[1] The consequences of the size of the neutral ligand in the present anionic complexes may be assessed from our measurements on $[Pt(CNS)_3L]^-$ [L = $PMe_{(3-n)}Et_n$ (n = 0—3)]. The thiocyanate group *trans* to the phosphine would not be expected to be directly affected by the bulk of the phosphine. Whilst the ratios of *N*- to *S*-bonded thiocyanate *trans* to the phosphine are essentially unaffected (Table 3) when the

TABLE 3

Ratios of *N*- to *S*-bonded thiocyanate in $[NBu^n_4][Pt(CNS)_3(PMe_{(3-n)}Et_n)]$ (n = 0—3)

	L = PMe_3	PMe_2Et	$PMeEt_2$	PEt_3
L–Pt(N)(S) : L–Pt(S)(S)	0.9	1.2	1.5	1.9
L–Pt(N)(S) : L–Pt(N)(S)	0.9	0.9	1.3	1.4
L–Pt(N)(N) : L–Pt(S)(S)	0.5	0.5	0.6	0.7
L–Pt(N)(N) : L–Pt(N)(S)	0.7	0.8	0.9	1.1
L–Pt(N)(S) : L–Pt(S)(S)	1.5	1.7	1.9	2.4
L–Pt(N)(N) : L–Pt(S)(S)	0.7	0.8	0.8	0.9
L–Pt(N)(N) : L–Pt(N)(N)	0.5	0.6	0.5	0.7

cis groups are $(NCS)_2$ or (NCS)(SCN), there is a marked steric effect when they are $(SCN)_2$. We suggest that the increasing size of the phosphine causes the *cis*-*S*-bonded thiocyanate groups to interfere more with the thiocyanate *trans* to L, *i.e.* the steric effect of the phosphine is 'transmitted' by the sterically demanding SCN groups. As expected, *N*-bonding in the *cis* position increases with the number of ethyl groups in the phosphine. This effect is greater when the other positions are *S*-bonded, *i.e.* when the system is most sterically crowded.

For the neutral complexes we noted that the degree of *N*-bonding increased with the increasing *trans* influence

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

of the *trans* anionic groups in the order $Cl^- < [NCS]^- < [SCN]^-$. The considerably enhanced amount of *N*-bonding when *trans* to a phosphine compared to other neutral ligands (Table 4) suggests a similar process for neutral ligands. The *trans* influence of NMe_3 (ref. 5) should be much lower than that of $AsMe_3$, *e.g.* ^1J(PtP) in *trans*-$[PtCl_2L(PMe_3)]$ is **3 674** (L = Cl),[6] **3 299** (NMe_3),[7] **2 796** ($AsMe_3$),[7] and **2 379** Hz (PMe_3).[6] Thus, the similar degree of *N*-bonding *trans* to NMe_3 and $AsMe_3$ is not in accord with their *trans* influences, neither is the very low amount of *N*-bonding *trans* to $SbMe_3$ and $TeMe_2$ as these ligands should have a significant *trans* influence. The ratios in Table 4 imply a tendency for light donors to promote *N*-bonding whilst heavy donors encourage *S*-bonding, *i.e.* the ' symbiosis ' referred to by Jørgensen [8] for cobalt(III) systems. Such an effect should be non-directional and equally affect the *cis* position. The change from *N*- to *S*-bonding with increasing atomic numbers of a *cis* Group 5 donor in both $[Pt(CNS)_3L]^-$ and *trans*-$[Pt(CNS)_2L_2]$ may therefore be due to a ' symbiotic ' effect in addition to the reduction of steric interactions as the bonds between the methyl groups and the donor atom lengthen. Such a change *cis* to the neutral ligand is much less marked for the chalcogen ligands, which may be a consequence of the steric effects of the additional unco-ordinated lone pair present in these ligands.

TABLE 4

Ratios of *N*- to *S*-bonded thiocyanate in $[Pt(CNS)_3L]^-$

	L = NMe_3	PMe_3	PEt_3	$AsMe_3$	$SbMe_3$	SMe_2	$SeMe_2$	$TeMe_2$
N S / L–Pt–S : L–Pt–S / S S		0.8	1.9	0.4	0.05	0.4	0.4	0.3
S S / L–Pt–N : L–Pt–S / S S	0.2 *	1.4	2.4	0.2	*ca.* 0	0.1	0.05	0.005

* For NMe_3, ratio of $[Pt(NCS)_3(NMe_3)]^-$: *trans*-$[Pt(NCS)_2(SCN)(NMe_3)]^-$.

We have examined $[Pt(CNS)_3(PMe_3)]^-$ in chloroform, dichloromethane, acetone, acetonitrile, and dimethyl sulphoxide to assess the effect of solvent on the equilibria between *N*- and *S*-bonded thiocyanate. The proportion of *N*-bonded thiocyanate both *cis* and *trans* to PMe_3 increased according to the solvent in the above order, *i.e.* with increasing dielectric constant. This is in agreement with the behaviour of $[Pt(CNS)_2(PR_3)_2]$ (R = Me or Et) [1] but contrasts with the trend observed by Burmeister *et al.*[9] for some palladium systems.

EXPERIMENTAL

The n.m.r. measurements were made as for the neutral complexes $[Pt(CNS)_2L_2]$,[1] using 0.2—0.5 mol dm^{-3} solutions in dichloromethane (with the addition of CD_2Cl_2 to provide a ' lock ' for the Fourier-transform measurements). Several days were required to achieve equilibrium between the isomers especially where isomerisation involved a group *cis* to the neutral ligand. The relative concentrations were estimated by integration of the Fourier-transform spectra of the phosphine complexes and by weighing the area under the ^1H peaks of the others since there was frequently interference from cation features. Because of the similarity of the environments of ^{31}P nuclei in the various isomers of $[Pt(CNS)_3(PR_3)]^-$, the relaxation rates should not differ much and their effect on the observed ratios is likely to be much less than other possible errors especially those resulting from the overlap of signals.

The complexes $[NBu^n_4][Pt(CNS)_3L]$ (L = $AsMe_3$, $AsMe_2Et$, PMe_3, PMe_2Et, and PEt_3) were prepared by metathetic substitution of the corresponding chloro-complexes using K[NCS] in acetone solution. After removal of the solvent and extraction with dichloromethane, the complexes of $AsMe_3$, $AsMe_2Et$, and PMe_3 were obtained as yellow crystals from acetone–diethyl ether: $[NBu^n_4][Pt(CNS)_3(AsMe_3)]$, m.p. 83—85 °C [Found (Calc.): C, 36.3 (36.1); H, 6.3 (6.2); N, 7.6 (7.7)]; $[NBu^n_4][Pt(CNS)_3(AsMe_2Et)]$ [Found (Calc.): C, 37.0 (37.0); H, 6.0 (6.3); N, 7.4 (7.5)]; $[NBu^n_4][Pt(CNS)_3(PMe_3)]$, m.p. 62—64 °C [Found (Calc.): C, 38.4 (38.4); H, 6.7 (6.6); N, 8.0 (8.1)%]. The complexes of PMe_2Et, $PMeEt_2$, and PEt_3 were only obtained as yellow oils. The complexes $[NBu^n_4][PtCl_3L]$ were prepared as in ref. 10.

Metathetical replacement with K[NCS] tended to displace NMe_3, SMe_2, $SeMe_2$, $TeMe_2$, or $SbMe_3$. However, solutions containing $[NBu^n_4][Pt(CNS)_3L]$ could be obtained for these ligands by equilibration of $[Pt(CNS)_2L_2]$ with $[NBu^n_4]_2[Pt(SCN)_4]$. Formation of $[Pt(CNS)_3L]^-$ was essentially complete except for trimethylamine where the ^1H spectrum indicated an *ca.* 1 : 1 mixture of $[Pt(CNS)_3(NMe_3)]^-$ and $[Pt(NCS)_2(NMe_3)_2]$. The complex $[NBu^n_4][Pt(SCN)_4]$ was prepared by metathetic reaction between $[NBu^n_4][PtCl_4]$ and K[NCS] as above and was obtained as orange crystals, m.p. 91—93 °C [Found (Calc.): C, 47.45 (47.4); H, 8.1 (7.95); N, 8.9 (9.2)%].

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