Identification of the Mode of Co-ordination of Thiocyanate Ion to Platinum by Heteronuclear Magnetic Multiple Resonance Spectroscopy

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Summary The linkage isomers of $[Pt(CNS)_2(SMe_2)_2]$† are identified by the coupling patterns of the $^1H\{^{195}Pt\}$ INDOR spectra and it is suggested that the ^{195}Pt chemical shift provides a further distinction; the chemical shifts of the ^{14}N nuclei coupled to ^{195}Pt (from $^1H\{^{195}Pt^{14}N\}$ triple resonance measurements) are typical of N-bonded thiocyanate species.

Whilst i.r. spectroscopy is the most widely used method for determining the mode of co-ordination of the thiocyanate ion in metal complexes, it is not always reliable.[1] In particular, it is unlikely to be able to distinguish between a complex with mixed co-ordination such as $[Pt(SCN)(NCS)L_2]$ (where L is a neutral ligand) and a mixture of the S- and N-bonded forms, $[Pt(SCN)_2L_2]$ and $[Pt(NCS)_2L_2]$. Under these circumstances, the only reliable method of characterisation is *X*-ray crystallography which is not very applicable to such solutions. We have explored the possibility of using $^1H\{^{195}Pt\}$ INDOR spectroscopy to study the co-ordination of the thiocyanate ion to platinum, since the ^{195}Pt chemical shift can provide an easy means of identifying the species in a mixture of similar complexes.[2]

The ^1H n.m.r. spectrum of $[Pt(CNS)_2(SMe_2)_2]$ exhibits three resonances each with ^{195}Pt satellites (Table). The $^1H\{^{195}Pt\}$ INDOR spectra of the three species (see Figure) are consistent with the presence in solution of the three isomers, $[Pt(SCN)_2(SMe_2)_2]$ (I), $[Pt(SCN)(NCS)(SMe_2)_2]$ (II), and $[Pt(NCS)_2(SMe_2)_2]$ (III) in the approximate proportions 1:0.7:0·2. Thus (I) gives a multiplet due to Pt–H coupling, similar to those observed for other dimethyl sulphide complexes of platinum, (II) gives a pattern of three such multiplets with approximate relative intensity 1:1:1, as expected when ^{195}Pt is coupled to one ^{14}N nucleus, and (III) gives an approximate 1:2:3:2:1 quintet corresponding to coupling to two ^{14}N nuclei. Since (II) must be the *trans* isomer because only one type of SMe_2 proton is observed, the other two isomers are, presumably, also *trans* isomers in view of the similarity of the values of $^3J_{PtH}$.

The ^{195}Pt chemical shifts show a large increase on replacement of SCN by NCS. For related complexes of different

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

TABLE. N.m.r. parameters for the isomers of $[Pt(CNS)_2(SMe_2)_2]$

		τ_H	$^3J_{PtH}$/Hz	δ_{Pt}[b]	δ_N(Pt-N)[c]	$^1J_{PtN}$/Hz
(I)	*trans*-$[Pt(SCN)_2(SMe_2)_2]$	7·37	46·1	387	—	—
(II)	*trans*-$[Pt(SCN)(NCS)(SMe_2)_2]$	7·41	45·8	807	−271	373
(III)	*trans*-$[Pt(NCS)_2(SMe_2)_2]$	7·47	46·5	1335	−308	451

[a] 0·1 M solution in dichloromethane. [b] In p.p.m. to high frequency of 21·4 MHz when corrected to Me_4Si = 100 MHz. [c] In p.p.m. to high frequency of NO_3^-.

halides, δ_{Pt} decreases with increasing 'softness' of the halide.[2] For $[PtX_2(SMe_2)_2]$, δ_{Pt} decreases according to X in the order $(NCS)_2 > Cl_2 >$ (SCN)(NCS) $> Br_2 > (SCN)_2$, demonstrating the difference in 'softness' character between the N and S ends of the thiocyanate group as compared with chloride and bromide. Accordingly, it seems clear that the mode of co-ordination of the thiocyanate ion can be identified from the ^{195}Pt chemical shift.

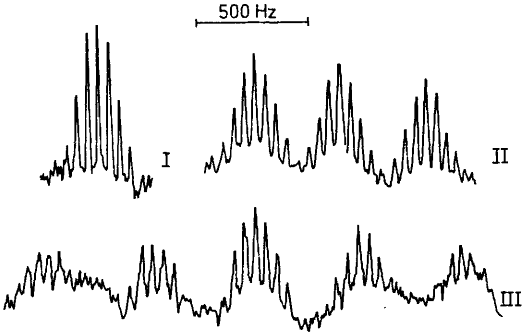

FIGURE. $^1H\{^{195}Pt\}$ INDOR spectrum of isomers of $[Pt(CNS)_2(SMe_2)_2]$.

Furthermore, the ^{14}N chemical shifts of the N-bonded thiocyanate species can be measured by triple resonance, since both ^1H and ^{14}N are coupled to ^{195}Pt (*cf.* McFarlane and Rycroft[3]), although such measurements are not possible by $^1H\{^{14}N\}$ double resonance because of the absence of ^{14}N–^1H coupling. Thus, when a ^{195}Pt satellite in the ^1H n.m.r. spectrum of (II) [or (III)] is monitored and the ^{14}N region swept, whilst simultaneously irradiating the centre of the ^{195}Pt resonances, the platinum satellites of the ^{14}N spectrum can be observed as a doublet, separation $^1J_{PtN}$. The ^{14}N chemical shifts, which increase from (II) to (III), are well to low frequency of that of the free thiocyanate ion (−170 p.p.m.), consistent with the chemical shifts of N-bonded thiocyanate complexes determined by direct ^{14}N n.m.r. measurements.[1] The value of $^1J_{PtN}$ also increases from (II) to (III) in keeping with the likely *trans* influences of -SCN and -NCS.

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