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A Double Isotopic Labelling Study of the Infrared Spectra of the Linkage Isomers [Pd(bipy)(SCN)₂], [Pd(bipy)(NCS)₂] and Related Complexes

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**A DOUBLE ISOTOPIC LABELLING STUDY OF THE INFRARED SPECTRA OF
THE LINKAGE ISOMERS $[\text{Pd}(\text{bipy})(\text{SCN})_2]$, $[\text{Pd}(\text{bipy})(\text{NCS})_2]$ AND
RELATED COMPLEXES**

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ABSTRACT

The IR spectra of the linkage isomers $[\text{Pd}(\text{bipy})(\text{SCN})_2]$ and $[\text{Pd}(\text{bipy})(\text{NCS})_2]$ have been determined in the $\text{C}\equiv\text{N}$ stretching region ($2200\text{-}2000\text{ cm}^{-1}$) and below 500 cm^{-1} . The band shifts resulting from deuteration of the 2,2'-bipyridine (bipy) ring and ^{15}NCS -labelling are shown to provide a ready means for distinguishing between the internal ligand modes, the $\nu\text{Pd-N}(\text{bipy})$ and $\nu\text{Pd-SCN}/\nu\text{Pd-NCS}$ vibrations. The assignment technique has been further extended to the complexes $[\text{Pt}(\text{bipy})(\text{SCN})_2]$ and $[\text{Pd}(\text{phen})(\text{SCN})_2]$ (phen = 1,10-phenanthroline). Finally, a comparison between the IR spectra of $[\text{Pd}(\text{bipy})(\text{NCO})_2]$, $[\text{Pd}(\text{bipy})(\text{NCS})_2]$ and $[\text{Pd}(\text{bipy})(\text{SCN})_2]$ reveals that the frequencies $\nu\text{M-NCO}$, $\nu\text{M-NCS}$ and $\nu\text{M-SCN}$ decrease in the sequence $\text{NCO} > \text{NCS} > \text{SCN}$.

INTRODUCTION

The IR spectra of metal thiocyanate(M-SCN) and isothiocyanate(M-NCS) complexes have been widely studied,¹⁻⁷ much of the attention being given to the question of distinction between the two modes of bonding. Further attention has been given to the difficult problem of distinguishing between the two types of metal-nitrogen stretching modes in the isothiocyanate complexes of heterocyclic nitrogenous bases such as pyridine, 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen).

In this paper we report on the application of ¹⁵N-labelled sodium thiocyanate and fully deuterated bipy-*d*₈ and phen-*d*₈ to these problems. As examples for study by the double isotopic labelling technique, we have selected the linkage isomers [Pd(bipy)(SCN)₂] and [Pd(bipy)(NCS)₂]. The S-bonded complexes: [Pt(bipy)(SCN)₂] and [Pd(phen)(SCN)₂] (for which N-bonded isomers have not been reported) are also included in the study which incorporates the νC≡N region (2200 - 2000 cm⁻¹) and the far-IR range 500 - 50 cm⁻¹.

EXPERIMENTAL

The complexes [Pd(bipy)(NCS)₂] and [Pd(bipy)(SCN)₂] were prepared by reported methods^{2,8}. The complex [Pd(phen)(SCN)₂] was prepared as follows. An ethanolic solution of 1,10-phenanthroline (0.5 mMole) was added to an aqueous solution of K₂PdCl₄ (0.5 mMole in 5 ml H₂O). The yellow precipitate which immediately resulted, was treated with an excess of a concentrated aqueous solution of NaSCN. The colour changed to orange-yellow. After 30 minutes, the precipitate was

collected by filtration, washed with water followed by ethanol and dried under reduced pressure over silica gel. The complex $[\text{Pt}(\text{bipy})(\text{SCN})_2]$ was prepared as follows. An aqueous solution of K_2PtCl_4 (0.5 mMole) and KSCN or NaSCN (2 mMole) was heated on a water-bath for 10 minutes. An ethanolic solution of 2,2'-bipyridine (0.5 mMole) was added, followed by dilute HCl to bring the pH to 1.5. The resulting orange-red precipitate was allowed to stand overnight and was collected by filtration. The product was washed with water followed by ethanol and dried under reduced pressure over silica gel.

The labelled complexes were similarly prepared from 2,2'-bipyridine- d_8 , 1,10-phenanthroline- d_8 and sodium thiocyanate- ^{15}N of >98% isotopic purity supplied by Merck Frosst (Canada) Ltd. The labelled complexes were washed, after filtration, with D_2O followed by EtOD (Aldrich). The S-bonded complexes were stored at reduced temperature ($\sim 0^\circ\text{C}$). Composition and purity of all complexes were determined by microanalysis.

Infrared spectra were determined on nujol mulls between CsI plates ($2200 - 2000$ and $600 - 250 \text{ cm}^{-1}$) or polyethylene plates ($500 - 50 \text{ cm}^{-1}$) on a Perkin-Elmer 983 spectrophotometer and a Digilab FTS 16B/D interferometer.

RESULTS AND DISCUSSION

The spectra of the complexes and their ^{15}NCS - and $\text{bipy-}d_8$ (or $\text{phen-}d_8$) analogues are depicted in Fig. 1 and the frequencies and assignments are reported in Table 1.

The internal ligand modes

The $\nu\text{C}\equiv\text{N}$ region of the spectrum was useful for distinguishing between the linkage isomeric pair of palladium

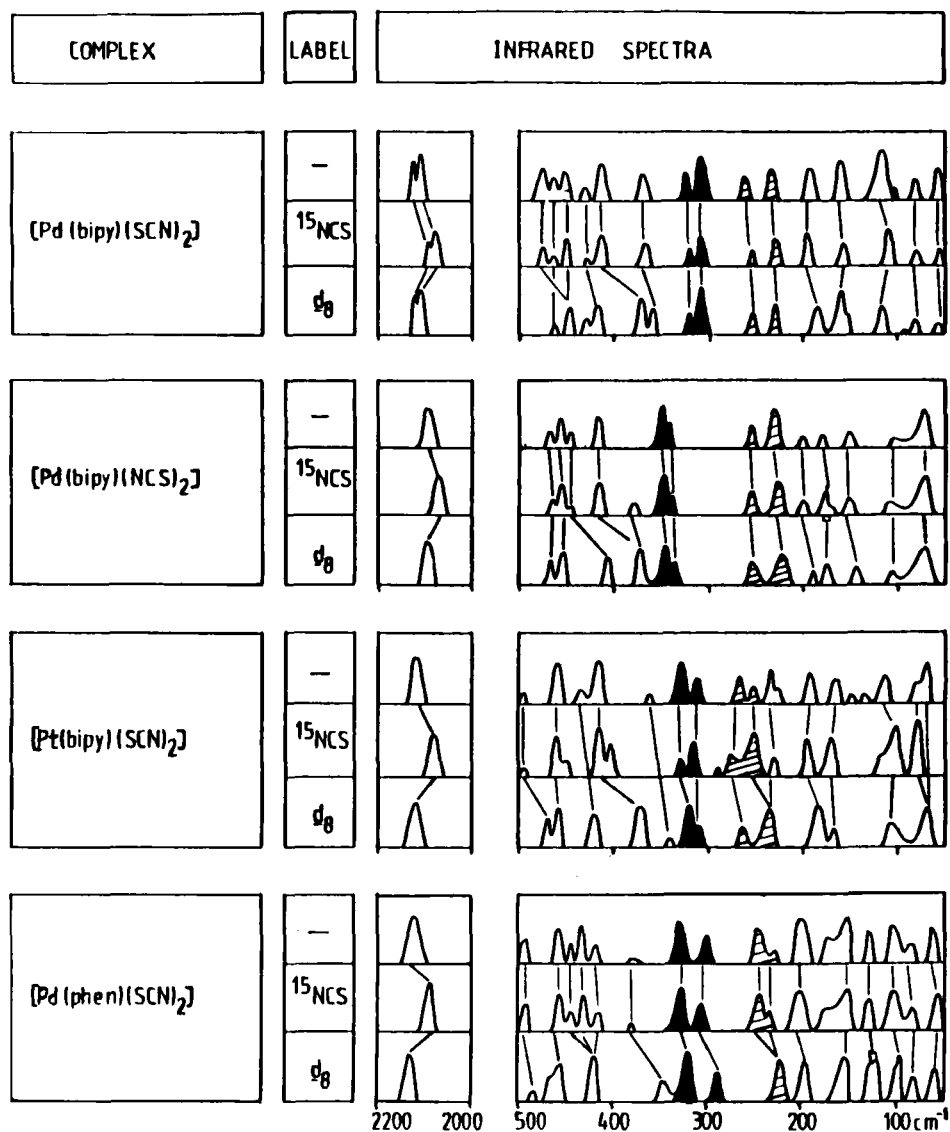


Fig. 1. Infrared spectra of thiocyanate and isothiocyanate complexes. Solid bands: $\nu\text{M}-\text{SCN}$ or $\nu\text{M}-\text{NCS}$; shaded bands: $\nu\text{M}-\text{N}$.

Table 1. Frequencies, ^{15}NCS and bipy/phen- d_8 shifts ($\Delta\nu$), previous and present assignments for IR bands in thiocyanate/isothiocyanate complexes.

[Pd(bipy)(SCN) ₂]				[Pd(bipy)(NCS) ₂]				[Pt(bipy)(SCN) ₂]				[Pd(phen)(SCN) ₂]				Assignment
Freq.	^{15}NCS	$\Delta\nu$	d_8	Freq.	^{15}NCS	$\Delta\nu$	d_8	Freq.	^{15}NCS	$\Delta\nu$	d_8	Freq.	^{15}NCS	$\Delta\nu$	d_8	
2120 ^a	29	2	2	2100 ^b	28	0	0	2115	27	+2		2116 ^c	28	0		$\nu\text{C}\equiv\text{N}$
2112	29	2										495	0	11		γ ring(phen) ring scis.(bipy) $\delta\text{SCN}/\delta\text{NCS}$
475	0	29						493	0	20		460 ^d	1	5		
464	1	0	0	469	5	0	0	464 ^d	4	7		418	3	+1		
454	1	0	0	456 ^e	4	0	0					443	1	41		
430	0	7	40	447	0	40	40	438	n.o.	23		418	3	1		γ ring(bipy/phen)
414	0	43	1	417	1	46	46	418	1	45		432	0	15		ν ring(bipy/phen)
370	0	12	0		0	10	10	366	n.o.	24		378	1	28		γ ring(phen)
322 ^f	2	1						331	2	6		328 ^g	0	4		$\nu\text{M}-\text{SCN}$
309 ^h	1	1						311	0	0		302 ^g	0	12		$\nu\text{M}-\text{NCS}$
				349 ^j	2	5	5									
				340 ^k	2	1	1									
264	2	7	7	257 ^l	1	6	6	275	2	5		247 ^m	0	23		$\nu\text{M}-\text{N}(\text{bipy}/\text{phen})$
231 ⁿ	3	4	227	227	2	6	6	258	2	20		234	1	9		
								238 ⁿ	4	7						
194 ^o	1	9	200	200	2	9	9	190	+4	8		204	0	7		$\delta\text{N}-\text{M}-\text{N}$ $\delta\text{N}(\text{bipy})-\text{M}-\text{NCS}$
			178	178	6	3	3									
			151	151	1	7	7									$\delta\text{S}-\text{M}-\text{S}$
158	2	0						166	+2	0		152	0	0		
115	5	+1														
								113	11	11		130	0	6		$\delta\text{S}-\text{M}-\text{N}(\text{bipy}/\text{phen})$
83	0	2	107	107	0	1	1					104	1	4		lattice
59	0	1	72	72	0	2	2	80	0	7		84	2	0		
								72	n.o.	0		60	3	2		

^a Previously reported at 2117, 2108² and assigned to $\nu\text{C}\equiv\text{N}$
^b Previously reported at 2100^{3,7} and 2099⁷ and assigned to $\nu\text{C}\equiv\text{N}$
^c Previously reported at 2116^{3,7} and assigned to $\nu\text{C}\equiv\text{N}$
^d Coupled with γ ring
^e Previously reported at 458^{3,7} and assigned to δNCS
^f Previously reported at 316⁵ and 319⁶ and assigned to $\nu\text{M}-\text{SCN}$
^g Coupled with ν ring(phen)
^h Previously reported at 304⁵ and assigned to $\nu\text{M}-\text{SCN}$
ⁱ Previously reported at 305⁵ and assigned to $\nu\text{M}-\text{SCN}$
^j Previously reported at 332⁵ and assigned to $\nu\text{M}-\text{NCS}$
^k Previously reported at 335⁵ and assigned to $\nu\text{M}-\text{NCS}$
^l Previously reported at 261⁶ and assigned to $\nu\text{M}-\text{NCS}$
^m Coupled with γ ring
ⁿ Coupled with $\nu\text{M}-\text{SCN}$
^o Coupled with $\delta\text{N}-\text{M}-\text{S}$

complexes in that the *S*-bonded form exhibited sharp splitting into a doublet at 2120, 2112 cm^{-1} while the *N*-bonded isomer yielded a single band at 2100 cm^{-1} . However, the remaining two complexes studied, which both have *S*-bonded thiocyanato ligands, yielded single rather than multiple $\nu\text{C}\equiv\text{N}$ peaks. Isotopic labelling is not suitable for distinguishing between *N*- and *S*-bonded species in this region because the shifts on ^{15}NCS -labelling are identical ($\Delta\nu = 29 \text{ cm}^{-1}$) for both isomers. In all four complexes examined, the shifts were between 27 and 29 cm^{-1} which is comparable with the effect of ^{15}N -labelling on the $\nu\text{C}\equiv\text{N}$ band of KSCN ($\Delta\nu = 25 \text{ cm}^{-1}$)⁹ and with that previously observed for the complexes $[\text{M}(\text{py})_2(\text{NCS})_2]$ ($\text{M} = \text{Mn, Co, Ni, Cu, Zn}$)¹⁰.

The internal ring modes of the heterocycles are readily identified by their high frequency shift of approximately 30 cm^{-1} on complexation and their generally large low frequency shifts on deuteration. These have an average value of 23 cm^{-1} over fifteen observed shifts compared with a mean shift of 10 cm^{-1} in the $\nu\text{M-N}(\text{bipy or phen})$ modes. The bands occur near 490, 440, 420 and 370 cm^{-1} and have the assignments indicated in Table 1. They are, as expected, practically insensitive to ^{15}NCS -labelling.

The only other IR bands within the range 500 - 350 cm^{-1} are the $\delta\text{SCN}/\delta\text{NCS}$ modes, generally observed near 450 cm^{-1} . These have previously been proposed as diagnostic of *S*- or *N*-bonding in that *N*-bonded complexes supposedly yield one band near 475 cm^{-1} while *S*-bonded compounds yield one or more bands near 420 cm^{-1} ⁴. However, in the absence of isotopic labelling, these bands are difficult to distinguish from the neighbouring ring modes and some erroneous assignments have been made in the past on an empirical basis.¹⁻⁷ The bands are identified here by their isotopic shifts which range between 1 and 5 cm^{-1} on ^{15}NCS -labelling (mean shift: 3 cm^{-1}) and

are generally unaffected by ring deuteration (mean shift : 1 cm^{-1}). Two bands are observed for both the *N*- and *S*-bonded linkage isomers and the criterion of position (given above) is not obeyed.

Metal-ligand modes

In terms of the square planar C_{2v} symmetry of these molecules, two $\nu\text{M-SCN}$ (or $\nu\text{M-NCS}$) and two $\nu\text{M-N(bipy or phen)}$ modes are expected. The double isotopic labelling technique serves to distinguish the two types of $\nu\text{M-L}$ mode very well, although there is evidence of some vibrational coupling between them. The $\nu\text{M-SCN}$ (or $\nu\text{M-NCS}$) absorption occurs as a pair of neighbouring bands within the range 330 - 300 cm^{-1} for $\nu\text{M-SCN}$ and 350 - 340 cm^{-1} for $\nu\text{M-NCS}$. These ranges are apparently diagnostic of M-S or M-N bonding although the sensitivities of the bands towards $^{15}\text{NCS-}$ and d_8 -labelling are not very distinctive, especially where vibrational coupling with a ring mode causes the $\nu\text{Pd-SCN}$ bands in the phenanthroline complex to acquire some *d*-sensitivity.

It is noteworthy that the isomerisation process of the *S*-bonded complex can be directly followed from the infrared spectra. The spectrum of a freshly prepared sample of $[\text{Pd}(\text{bipy})(\text{SCN})_2]$ shows only two $\nu\text{Pd-SCN}$ bands (at 322 and 309 cm^{-1}) whereas no band is observed in the $\nu\text{Pd-NCS}$ region at about 350 cm^{-1} . After storage (for over 12 months at room temperature) the spectra of the same sample displays two strong bands at 349 and 340 cm^{-1} (assigned to $\nu\text{Pd-NCS}$) whereas the two $\nu\text{Pd-SCN}$ bands at about 320 cm^{-1} have decreased considerably in intensity. Complete isomerisation to the pure *N*-bonded species is achieved on heating the sample to 150°C for 45 minutes. The spectrum then shows only the two $\nu\text{Pd-NCS}$ bands while the two $\nu\text{Pd-SCN}$ bands have disappeared.

The ν M-N(bipy or phen) bands are distinguished as a band pair (three bands for the Pt complex) within the range 280 - 230 cm^{-1} . The assignment is based on the observed shifts (mean value of $\Delta\nu$: 10 cm^{-1}) caused by ring-deuteration and the position, which is characteristic of ν M-N bands in the complexes of heterocyclic N-bonded ligands in general^{10,11}. These bands generally also exhibit some ^{15}NCS -sensitivity, indicating the existence of vibrational coupling between the two types of metal-ligand stretching modes.

The metal-ligand bending modes occur within the range 200 - 100 cm^{-1} . We have made some attempt to distinguish between the various bending modes on the basis of the observed isotopic shifts (Table 1) but these assignments remain tentative.

A comparison between the frequencies of ν Pd-NCO, ν Pd-NCS and ν Pd-SCN bands is of interest. In the isocyanate complex $[\text{Pd}(\text{bipy})(\text{NCO})_2]$, ν Pd-NCO has been reported at 380 cm^{-1} ¹² while we observe ν Pd-NCS in $[\text{Pd}(\text{bipy})(\text{NCS})_2]$ at 349 and 340 cm^{-1} . The lower frequency of ν Pd-NCS may be attributed to the higher mass of the NCS-ligand. Likewise, we find ν Pd-SCN at a lower frequency than ν Pd-NCS which may be attributed to the higher mass of the sulphur donor atom. This is, however, contrary to the assignments of Keller *et al.*⁶ for the linkage isomers of the complexes $[\text{Pd}(\text{bipy})\text{X}_2]$ and $[\text{Pd}(\text{Ph}_3\text{As})_2\text{X}_2]$ ($\text{X} = \text{NCS}, \text{SCN}$) but supports those given by Goodgame and Malerbi⁵ for $[\text{Pd}(\text{bipy})\text{X}_2]$ ($\text{X} = \text{NCS}, \text{SCN}$) and by workers in this laboratory for *trans*- $[\text{Co}(\text{DH})_2(\text{py})\text{X}]$ ($\text{DH} = \text{dimethylglyoximate anion}$; $\text{X} = \text{NCS}, \text{SCN}$) in which the assignments were also based on the multiple isotopic labelling technique¹³.

CONCLUSION

The double isotopic labelling technique (^{15}N -labelling of the thiocyanate/isothiocyanate ligand and perdeuteration of

bipy or phen) enables a clear distinction to be made between the metal-thiocyanate/isothiocyanate stretching modes ($\nu\text{M-SCN}$ or $\nu\text{M-NCS}$) on the one hand and the metal-bipyridine/phenanthroline stretching modes ($\nu\text{M-N(bipy)}$ or $\nu\text{M-N(phen)}$) on the other, in the far-IR spectra of the complexes. However, for the purposes of distinguishing between the $\nu\text{M-SCN}$ bands of the thiocyanate complexes and the $\nu\text{M-NCS}$ bands of the isothiocyanate complexes, the isotopic labelling technique is rather less distinctive because of vibrational coupling between each of these modes and $\nu\text{M-N(bipy or phen)}$. For distinguishing between two linkage isomers, a combination of the isotopic labelling technique and the more traditional methods for IR distinction based on the nature and position of the $\nu\text{C}\equiv\text{N}$, $\nu\text{C-S}$ and δSCN bands¹⁻⁷ is to be recommended.

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