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### **Application of Isotopic Labelling to the Infrared Spectra of the Linkage Isomers Pyridine(isothiocyanato)cobaloxime and Pyridine(thiocyanato)cobaloxime**

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APPLICATION OF ISOTOPIC LABELLING TO THE INFRARED SPECTRA OF  
THE LINKAGE ISOMERS PYRIDINE(ISOTHIOCYANATO)COBALOXIME AND  
PYRIDINE(THIOCYANATO)COBALOXIME

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ABSTRACT

The infrared spectra of the isomeric complexes  $[\text{Co}(\text{DH})_2(\text{py})(\text{NCS})]$  and  $[\text{Co}(\text{DH})_2(\text{py})(\text{SCN})]$  (DH = dimethylglyoximate anion, py = pyridine) and their  $\text{py-}^{15}\text{N-}$ ,  $\text{py-}d_5\text{-}$  and  $^{15}\text{NCS-}$ labelled derivatives have been determined. Band assignments are based on the shifts incurred by labelling and on previous labelling studies applied to the complexes  $[\text{Co}(\text{DH})_2(\text{py})\text{X}]$  (X = CH<sub>3</sub>, Cl, Br, I).  $\nu \text{Co-N(py)}$  occurs at  $464 \text{ cm}^{-1}$  in both complexes with an additional band at  $450 \text{ cm}^{-1}$  in the isothiocyanate complex, while  $\nu \text{Co-N(DH)}$  appears at  $513 \text{ cm}^{-1}$  in both complexes.  $\nu \text{Co-NCS}$  occurs at  $377 \text{ cm}^{-1}$  in the isothiocyanate complex while  $\nu \text{Co-SCN}$  appears at  $356 \text{ cm}^{-1}$  in the thiocyanate complex.

INTRODUCTION

Both N- and S-bonded forms of the complex  $[\text{Co}(\text{DH})_2(\text{py})(\text{CNS})]$  may be isolated in the solid state<sup>1</sup>. Existence of the two linkage

isomers has been confirmed by consideration of the integrated intensities of the C-N band which yielded values of  $10.24 \times 10^4 \text{ M}^{-1}\text{cm}^{-2}$  for the N-bonded and  $1.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-2}$  for the S-bonded forms<sup>1,2</sup>. These compounds are of interest in being the first reported examples of isothiocyanate-thiocyanate linkage isomers involving cobalt(III). We now report a study of their infrared spectra over the range 4000 - 150  $\text{cm}^{-1}$ .

#### EXPERIMENTAL

The compounds were prepared by the reported methods<sup>1</sup>. The py-<sup>15</sup>N- and <sup>15</sup>NCS-labelled analogues were similarly prepared from pyridine-<sup>15</sup>N of 95% isotopic purity and NaSC<sup>15</sup>N of 97% isotopic purity supplied by Merck, Sharp and Dohme (Canada) Ltd., while the py-d<sub>5</sub>-labelled analogue was obtained from pyridine-d<sub>5</sub> of 99% isotopic purity supplied by BOC Prochem Ltd. Spectra were determined on nujol mulls between caesium iodide plates (or, below 250  $\text{cm}^{-1}$ , on nujol mulls between polyethylene plates) on Beckman IR-12 and Perkin-Elmer 180 spectrophotometers.

#### RESULTS AND DISCUSSION

The frequencies and isotopically-induced shifts are reported in Table 1. In a previous paper<sup>4</sup>, we reported the application of <sup>15</sup>N-labelling to the assignment of infrared bands in the complexes  $[\text{Co}(\text{DH})_2(\text{py})\text{X}]$  (X = CH<sub>3</sub>, Cl, Br, I). Similar techniques are employed here except that <sup>15</sup>N-labelling of the dimethylglyoximate anion has been omitted, assignment of the internal vibrations of this moiety now being made by direct comparison with the earlier work. In the present work,

TABLE 1

Vibrational frequencies ( $\text{cm}^{-1}$ ), isotopic shifts ( $\Delta\nu$ ,  $\text{cm}^{-1}$ , in the sequence  $^{15}\text{NCS}$ ,  $\text{py-}^{15}\text{N}$ ,  $\text{py-}d_5$ ) and band assignments for the linkage isomers  $[\text{Co}(\text{DH})_2(\text{py})(\text{NCS})]$  and  $[\text{Co}(\text{DH})_2(\text{py})(\text{SCN})]^a$

[Co(DH) <sub>2</sub> (py)(NCS)]		[Co(DH) <sub>2</sub> (py)(SCN)]		py		Assignment <sup>b</sup>
$\nu$	$\Delta\nu$	$\nu$	$\Delta\nu$	$\nu$	$\Delta\nu$	
2122	30,0,0	2112	29,0,0			$\nu\text{N}=\text{CS}$
		2028	26,0,0			$\nu\text{N}=\text{CS}$
1606	0,2,39	1606	0,0,48	1606	58	$\nu$ ring(py) (6a)
				1590	54	$\nu$ ring(py) (8a)
				1581		$\nu$ ring(py) (8a)
1564	0,0,0	1556	0,0,0			$\nu\text{C}=\text{N}(\text{DH})$
1495	0,3,173	1492	0,2,169	1481	162	$\nu$ ring(py) (19a)
1449	0,5,127	1449	0,6,126	1436	138	$\nu$ ring(py) + $\nu\text{C}=\text{N}(\text{DH})$ (19b)
1370	0,0,0/44 <sup>c</sup>	1370	0,0,1/47 <sup>c</sup>	1374	147	$\nu$ ring(py) + $\delta\text{CH}_3$ (14)
				1291	251	$\delta\text{C-H}(\text{py})$
1273	0,0,0					$\nu\text{C-CH}_3(\text{DH})$
1242	0,0,0	1238	0,0,1			$\nu\text{C-C}(\text{DH})$ + $\nu\text{N-O}(\text{DH})$
1231	0,0,134	1224	1,2,127	1215	208	$\delta\text{C-H}(\text{py})$ (3,9a)
		1156	3,0,329	1145	183	$\delta\text{C-H}(\text{py})$ (15)
1094	0,0,0	1093	0,1,0			$\nu\text{N-O}(\text{DH})$
1070	0,4,160	1067	0,4,167	1067	182	$\delta\text{C-H}(\text{py})$ (18b)
1052	0,2,5	1049	1,5,3	1029	197	$\nu$ ring(py) (12)
1019	0,11,15	1025	1,10,19	990	168	$\nu$ ring(py) (1)
982	0,0,1	979	0,0,1			$\nu\text{N-O}(\text{DH})$
		957	0,0,173	940	34	
				882	193	$\gamma\text{C-H}(\text{py})$ (10b)
833	11,0,0					$\nu\text{NC-S}$
				818		
761	0,4,143	766	0,4,139	748	168	$\gamma\text{C-H}(\text{py})$ (11)
$\sim 735$	tb,tb,tb	$\sim 735$	tb,tb,tb			skel. def. (DH)
694	0,2,155	694	0,2,157	702	168	$\gamma\text{C-H}(\text{py})$ (4)
651	0,8,13	649	0,5,11	675		$\delta$ ring(py) (6a)
645	0,2,22			653	29	$\delta$ ring(py) (6a)
				602	72	$\delta$ ring(py) (6a)
513	0,0,0	513	0,0,0			$\nu\text{Co-N}(\text{DH})$
481	0,1,4	464	0,0,0			$\delta\text{NCS}$
464	3,0,26	464	0,0,19			$\nu\text{Co-N}(\text{py})$
456	sh,0,1	424	0,0,0			$\delta\text{NCS}$
450	0,3,12					$\nu\text{Co-N}(\text{py})$
423	0,0,22	424	0,0,21	404	37	$\gamma$ ring(py) (16b)
397	0,0,-					
377	0,0,0					$\nu\text{Co-NCS}$
		356	0,0,1			$\nu\text{Co-SCN}$
292	1,1,0	309	o,sh,0			$\tau\text{CH}_3(\text{DH})$
$\sim 260$	2,0,2	$\sim 250$	tb,tb,tb			$\tau\text{CH}_3(\text{DH})$
217	0,0,5	232	0,0,12			$\delta\text{L-Co-L}$
195	1,0,0					$\delta\text{L-Co-L}$
169	0,0,3	168	0,0,2			$\delta\text{L-Co-L}$

<sup>a</sup> - All shifts cited are to lower wavenumber. Abbreviations: sh - shoulder (shift masked by adjacent band), tb - band too broad and/or weak for shift to be determined.

<sup>b</sup> - Figures in parentheses following assignments of pyridine vibrations are the band numbers in the notation of Kline and Turkevich<sup>3</sup>.

<sup>c</sup> - Extra band observed in the spectrum of  $\text{py-}d_5$  complex.

$^{15}\text{N}$ -labelling of the NCS groups has been adopted in order to assist with the assignment of the internal NCS and metal-isothiocyanate (or thiocyanate) modes. However,  $^{15}\text{NCS}$ -labelling does not always induce significant shifts in metal-ligand vibrations<sup>5</sup>. Three reasons may be advanced for the small shifts observed. Firstly, the small increase in mass relative to the unlabelled isothiocyanate yields<sup>6</sup> an unfavourable reduced mass ratio  $\mu/\mu^2$ . Secondly, where M-SCN bonding occurs, the labelled nitrogen atom is too far removed from the coordination site. Thirdly, vibrational coupling may serve to attenuate the mass effect. Thus, empirical methods are relied upon considerably in assigning the M-NCS modes.

*Ligand vibrations associated with the isothiocyanate and thiocyanate groups*

The spectrum of NaSCN yields four bands within the range 4000 - 150  $\text{cm}^{-1}$ . Each of these bands exhibits significant  $^{15}\text{NCS}$ -sensitivity. The band at 2074  $\text{cm}^{-1}$ , assigned to  $\nu\text{N-CS}$  appears as a relatively broad band in the spectrum of the isothiocyanate complex and exhibits a large  $^{15}\text{NCS}$ -induced shift (30  $\text{cm}^{-1}$ ). In the thiocyanate complex,  $\nu\text{N-CS}$  is split into two bands at 2112 and 2028  $\text{cm}^{-1}$ , also with large  $^{15}\text{NCS}$ -sensitivities. The  $\nu\text{NC-S}$  band occurs at 757  $\text{cm}^{-1}$  in the spectrum of NaSCN and at 747  $\text{cm}^{-1}$  in the spectrum of  $\text{NaSC}^{15}\text{N}$ . In the isothiocyanate complex it appears at 833  $\text{cm}^{-1}$  (characteristic of M-NCS coordination). It is apparently absent from the spectrum of the thiocyanate complex, where it is probably obscured by the broad skeletal deformation of the dimethylglyoximate ion around 735  $\text{cm}^{-1}$ . (It is expected<sup>7</sup> to occur somewhere near 700  $\text{cm}^{-1}$ . The bending mode,  $\delta\text{NCS}$ , occurring at 481  $\text{cm}^{-1}$  in the spectrum of NaSCN, is split into two bands in the spectra of the complexes. Although they show no  $^{15}\text{NCS}$ -shift, they are assigned to  $\delta\text{NCS}$  by comparison with the spectra of  $[\text{Co}(\text{DH})_2(\text{py})\text{X}]$ .

The overtone of the  $\delta\text{NCS}$  mode (at  $960\text{ cm}^{-1}$  in the  $\text{NaSCN}$  spectrum) is absent from the spectra of the complexes. A similar phenomenon was noted in the spectra of *bis*(aniline)metal(II) isothiocyanate complexes<sup>5</sup>.

*Skeletal vibrations of the chelated dimethylglyoximate anion*

All assignments were based on comparison with the spectra of the complexes  $[\text{Co}(\text{DH})_2(\text{py})\text{X}]$  where they were firmly based on  $^{15}\text{N}$ -labelling of the dimethylglyoximate nitrogen atoms<sup>4</sup>. There is generally a band-for-band correspondence between the DH-vibrations of the two linkage isomers and usually they appear at similar frequencies. One exception, the band at  $1273\text{ cm}^{-1}$ , which is unique to the spectrum of the isothiocyanate complex, is assigned to  $\nu\text{C-C}$  of dimethylglyoxime. The bands near  $1240\text{ cm}^{-1}$ , assigned by Norbury and Sinha<sup>1</sup> to a pyridine ring vibration are shown here by their insensitivity to  $\text{py-}^{15}\text{N}$ - and  $\text{py-}d_5$ -labelling, to be due to  $\nu\text{C-C}$  of the dimethylglyoximate anion.

*Metal-ligand vibrations*

The metal-ligand stretching modes  $\nu\text{Co-N}(\text{DH})$  and  $\nu\text{Co-N}(\text{py})$ , being relatively insensitive to variation of the axial ligand, are expected to occur at frequencies similar to those in  $[\text{Co}(\text{DH})_2(\text{py})\text{X}]$ . The strong band at  $513\text{ cm}^{-1}$  is confirmed as  $\nu\text{Co N}(\text{DH})$  by its lack of sensitivity towards pyridine or isothiocyanate labelling. In the isothiocyanate complex, the split band near  $460\text{ cm}^{-1}$  is assigned to  $\nu\text{Co-N}(\text{py})$ . Both components are sensitive to labelling of pyridine. In the thiocyanate complex,  $\nu\text{Co-N}(\text{py})$  occurs at  $464\text{ cm}^{-1}$  as a single band masking a  $\delta\text{NCS}$  band. It is sensitive to both  $^{15}\text{N}(\text{py})$ - and  $\text{py-}d_5$ -labelling whereupon it shifts to lower frequency, revealing the  $\delta\text{NCS}$  band which remains insensitive to labelling. As expected,  $\nu\text{Co-NCS}$  is considerably

sensitive to the mode of thiocyanate coordination. The bands occurring at  $377\text{ cm}^{-1}$  in the spectrum of the isothiocyanate complex and at  $356\text{ cm}^{-1}$  in the spectrum of the thiocyanate complex, are assigned to  $\nu\text{Co-NCS}$  and  $\nu\text{Co-SCN}$ , respectively. Although neither of these bands exhibits sensitivity to  $^{15}\text{NCS}$ -labelling, they are the only vibrations sufficiently sensitive to change of the bonding mode in the isomers, to be so assigned. Furthermore, they occur in the same region of the spectrum as  $\nu\text{Co-X}$  in  $[\text{Co}(\text{DH})_2(\text{py})\text{X}]$ .<sup>4</sup>

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