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^{13}C Nuclear Magnetic Resonance Spectra of Coordinated Thiocyanate

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Although a variety of physical techniques [1, 2] have been utilized to determine the bonding mode of the coordinated thiocyanate group, infrared spectroscopy has continued to be the most widely used method [3]. Recent studies have also shown INDOR [4] and ^{14}N NQR [5] spectroscopy to be useful diagnostic tools, but they are not always efficacious. The results described herein are intended to demonstrate the diagnostic potential which is found in the use of ^{13}C NMR data for the thiocyanate.

With the exception of three ^{14}N NMR studies [6–8] and some ^{13}C NMR data for alkyl and ionic thiocyanates [9], NMR spectroscopy has primarily been used to establish the bonding mode of thiocyanate only in an indirect manner via the resonances of nuclei in other ligands present in the complex [10–12]. In this study, the ^{13}C chemical shifts of some metal-thiocyanate complexes of known bonding mode have been obtained using a pulsed Bruker HFX-90 spectrometer. The ^{13}C chemical shifts were measured at natural abundance, and therefore compounds with good solubility in either deuterochloroform or deuterium oxide were chosen. Either tetramethylsilane (TMS) or dioxane was used as an internal reference for the deuterochloroform and deuterium oxide solutions, respectively. The ^{13}C chemical shifts obtained in the latter solutions were converted to the TMS reference by adding 67.4 ppm to their values.

From the results shown in the Table for the solutions containing ionic SCN^-, it can be inferred that the cation present exerts very little effect on the value of the ^{13}C chemical shift. The values are also in good agreement with a recently reported value [13] for NaSCN in D_2O solution.

The values of the ^{13}C chemical shifts for the three mononuclear S-bound complexes are all upfield from the ionic values. The results of earlier infrared [14] and Raman [15] spectral studies on respectively, $[Co(CN)_5NCS]^{3-}$ and $[Zn(NCS)_4]^{2-}$ have shown the thiocyanates in these complexes to be stable N-bonded species in the solvents used. This indicates that the ^{13}C thiocyanate chemical shifts observed for these complexes, while being close to those exhibited by ionic thiocyanate, are in fact due to complexed isothiocyanates. Thus, whereas the thiocyanate ^{13}C resonances of the remaining N-bound complexes shown in the Table are indicative of significant deshielding, relative to the ionic values, this need not always be true. This trend is comparable to that observed for S- and N-bound alkyl thiocyanates [9], *i.e.*, the ^{13}C resonances of the S-bound isomers are shifted upfield from the ionic resonances, whereas those of the N-bound isomers may either be found at comparable values or may be shifted downfield.

The greater amount of deshielding in the N-bound isomers may be a consequence of a greater degree of C≡N multiple bonding, while the greater amount of shielding in the S-bound isomers could be due to a synergistic effect. The study of additional complexes is, of course, needed to further substantiate the generality of the trend and the validity of these conclusions.

The wider range exhibited by the ^{13}C chemical shifts of the alkyl thiocyanates, relative to that exhibited by the chemical shifts of the metal thiocyanate complexes, may be attributed to the different degrees of covalency involved in the carbon–thiocyanate and metal–thiocyanate interactions. Likewise, the observed greater range of the ^{14}N thiocyanate chemical shift values [6, 7], relative to that of the ^{13}C values, is to be expected, since the nitrogen atom of the thiocyanate will be more strongly affected by linkage isomerization than will the carbon atom.

A direct comparison of the thiocyanatopentacyanocobaltate(III) linkage isomers could not be made in the same solvent because a solvent which is suitable for the stability of one isomer causes the isomerization or decomposition of the other [14]. The ^{13}C resonances of the cyanides were observed in each case as a single line, with that of the N-bound isomer being at 136.3 ppm relative to TMS and that of the S-bound isomer at 141.8 ppm. While some of this shift may be due to a solvent effect, it would appear that most of the shift is due to the different electronic properties of the two isomeric forms. It should be noted that the ^{13}C resonance for $[Co(CN)_6]^{3-}$ is found [16] at 139.8 ppm.

The copper(I) metal cluster complex deserves special mention. Whereas all of the other compounds listed in the Table are known compounds, this compound is a new addition to the class of compounds represented by tetrakis[iodo(tri-n-butylphosphine)-copper(I)] [17, 18]. The sulfur atom of the SCN^- presumably bridges (as does the iodide) three copper metal centers. As such, it represents the first report of this type of bonding involving the thiocyanate. Infrared data indicate that the tetramer undergoes partial

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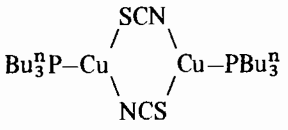
TABLE. ^{13}C Chemical Shift Data for Various Thiocyanate-containing Compounds.

Compound	Solvent	δ,[a] ppm	Structure	Bonding Mode of Thiocyanate
CH_3CH_2SCN	Neat	112.1	Tetrahedral	S
$K_2[Hg(SCN)_4]$	D_2O	124.8	Tetrahedral	S
$K_3[Co(CN)_5SCN]$	D_2O	127.9	Octahedral	S
$K_2[Pd(SCN)_4]$	D_2O	128.4	Square Planar	S
$[Cu(PBu^n_3)SCN]_4$	$DCCl_3$	130.7	Metal Cluster	S-bridging
$Ca(NCS)_2$	D_2O	133.0	Ionic	–
$Mg(NCS)_2$	D_2O	133.7	Ionic	–
KNCS	D_2O	133.7	Ionic	–
NH_4NCS	D_2O	133.8	Ionic	–
$Ba(NCS)_2$	D_2O	134.0	Ionic	–
LiNCS	D_2O	134.0	Ionic	–
$[Bu^n_4N]_3[Co(CN)_5NCS]$	$DCCl_3$	132.3	Octahedral	N
$K_2[Zn(NCS)_4]$	D_2O	134.1	Tetrahedral	N
$[Zn(t\text{-}Bu\text{-}py)_2(NCS)_2]$	$DCCl_3$	138.7	Tetrahedral	N
$[Co(NH_3)_5NCS](C_2H_3O_2)_2$	D_2O	140.5	Octahedral	N
$[Ni(PBu^n_3)_2(NCS)_2]$	$DCCl_3$	146.0	*Trans*-square Planar	N
$[Ni(PEt_3)_2(NCS)_2]$	$DCCl_3$	146.4	*Trans*-square Planar	N

[a] All values ± 0.2 ppm.

dissociation into a dimeric species in solution, wherein the thiocyanates bridge in a conventional end-on manner:



The structural isomerization between the two forms is too rapid to observe via ^{13}C, ^{31}P or ^{1}H NMR. The value of the ^{13}C resonance shown in the Table therefore represents a time-average of the two forms, with the tetramer being the predominant form [19].

Further conclusions regarding such effects as different metal ions and/or geometries cannot be drawn without additional data. Wider application of ^{13}C NMR data would be facilitated by the use of ^{13}C labeled thiocyanate and possible by employing a small amount of a relaxation agent, such as $[Cr(acac)_3]^{3-}$ [20].

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References

1 J. L. Burmeister, in "The Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives", A. A. Newman, Ed., Academic Press, London (1975) pp. 68–130.
2 A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, *17,* 231 (1975).
3 R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coordin. Chem. Rev.*, *6,* 407 (1971).
4 S. J. Anderson and R. J. Goodfellow, *Chem. Comm.*, 443 (1975).
5 C. P. Cheng, T. L. Brown, W. C. Fultz and J. L. Burmeister, *Chem. Comm.*, 599 (1977).
6 O. W. Howarth, R. E. Richards and L. M. Venanzi, *J. Chem. Soc.*, 3335 (1964).
7 H. Boehland and E. Mühle, *Z. Anorg. Allg. Chem.*, *379,* 273 (1970).
8 A. H. Zeltmann and L. O. Morgan, *Inorg. Chem.*, *9,* 2522 (1970).
9 G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley–Interscience, New York (1972) p. 133.
10 L. G. Marzilli, R. C. Stewart, L. A. Epps and J. B. Allen, *J. Am. Chem. Soc.*, *95,* 5796 (1973).
11 S J. Anderson and A. H. Norbury, *Chem. Comm.*, 48 (1975).
12 A. J. Carty, *Inorg. Chem.*, *15,* 1956 (1976).
13 A. D. James and R. S. Murray, *Inorg. Nucl. Chem. Letters*, *12,* 739 (1976).
14 J. P. Melpolder and J. L. Burmeister, *Inorg. Chim. Acta*, *15,* 91 (1975).
15 K. A. Taylor, T. V. Long and R. A. Plane, *J. Chem. Phys.*, *47,* 138 (1967).
16 M. Hirota, Y. Koike, H. Ishizuka, A. Yamasaki and S. Fujiwara, *Chem. Lett.*, 853 (1973).
17 F. G. Mann, D. Purdie and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).
18 G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, *7,* 9 (1963).
19 This work will be described in detail at a later date.
20 R. C. Stewart amd L. G. Marzilli, *Inorg. Chem.*, *16,* 425 (1977).