

## INFRARED SPECTRA OF COMPLEXES OF THE THIOCYANATE AND RELATED IONS

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### CONTENTS

A Introduction	407
B. Theoretical considerations	408
C Empirical criteria	411
D Discussion	417
(i) Thiocyanate and isothiocyanate complexes	417
(ii) Selenocyanate and isoselenocyanate complexes	424
(iii) Cyanate complexes	427
(iv) Fulminate complexes	432
(v) Intensity considerations	434
(vi) Far infrared data	439
(vii) Mixed thiocyanate complexes	442
References	443

### A. INTRODUCTION

Complexes of the thiocyanate ion are known for most of the complex-forming metal ions<sup>1</sup>. One aspect of these compounds which has been of interest is the mode of bonding of this ligand; either the nitrogen or the sulfur atom may be bonded to the metal ion (isothiocyanate and thiocyanate, to be designated  $\text{NCS}^-$  or  $\text{SCN}^-$  respectively; it is conventional to use  $\text{CNS}^-$  for the free ion or an unspecified bonding mode). According to the concepts of Pearson<sup>2</sup>, the nitrogen end of this ion is a hard, and the sulfur end a soft, base. Consequently, N-bonding is expected with the hard (class a) metal ions while S-bonding should take place with those of the soft category (class b). Since many systems are intermediate, and behavior can be influenced by other coordinated ligands or even non-coordinated ions, the bonding to be expected in a given case is not always obvious. Further, bridging of two metal ions in the form  $\text{M}-\text{NCS}-\text{M}'$ , is well known, while alternate types of bridging,  $>\text{SCN}^-$  or  $>\text{NCS}^-$ , are possible. The former has been confirmed in a few cases, for example<sup>3</sup>,  $\text{Co}(\text{NCS})_6\text{Hg}_2\cdot\text{C}_6\text{H}_6$  and<sup>4</sup>  $\text{Ag}(\text{CNS})(\text{P}(\text{C}_3\text{H}_7)_3)_3$ . These actually show three-way bridging,  $\text{M} \xrightarrow{\text{M}'} \text{SCN}-\text{M}'$ . Oki et al.<sup>5</sup> further suggest the possibility of an interaction between the  $\pi$ -bonding electrons of the thiocyanate ion as a whole and a metal ion, but evidence in favor of this mode is not convincing. A review of the structures of thiocyanate complexes is available<sup>6</sup>. It includes some selenocyanate and infrared data.

Various analogues of the thiocyanate ion exist and are of interest. Selenocyanate is most similar, and in recent years a considerable coordination chemistry has been developed for it, although its complexes are not nearly as common as those of thiocyanate. Its bonding behavior is similar to thiocyanate. The same nomenclature ( $M-NCS$ , isoselenocyanate,  $M-SeCN$ , selenocyanate, and  $CNSe^-$  for the free ion) will be used. The third ligand to be considered, the cyanate ion, is rather different in its coordination behavior. Both bonding sites can be considered hard and most of the known complexes bond through nitrogen (isocyanates) although a few have been reported as oxygen bound (cyanates). The only form of bridging established<sup>7</sup> is of the type  $>NCO^-$ .

The fulminate ion is an isomer of the cyanate ion, having the structure  $CNO^-$ . (This formulation will not be used for free cyanate.) Comparatively little is known of fulminate complexes. Coordination is generally assumed to be through the C atom, although  $M-CNO-M'$  bridges are proposed and isofulminates ( $M-ONC$ ) are possible in principle.

The thiocyanate ion has been studied widely by infrared spectroscopy, which provides a means of establishing the bonding mode. In tetrahedral or octahedral compounds only three vibrational modes are expected for  $CNS^-$  in the near infrared region. These can be assigned approximately as the C-N and C-S stretches, and the NCS deformation. In lower energy regions, metal-ligand stretching and deformation modes occur. Any of the above bands may be split by deviations of the complex from high symmetry, or by crystal site symmetry in solid samples, and overtones may appear.

The remaining ions considered here are similar to thiocyanate in their spectral behavior, but cyanate shows a Fermi resonance interaction between the first overtone of the deformation mode and the C-O stretching frequency in the free ion and in certain complexes which may complicate interpretation. Differences in mixing of the various vibrational modes also have important consequences.

This article reviews the various infrared criteria which have been developed to establish bonding type, especially for thiocyanate<sup>8-19</sup>, and attempts to intercompare them for a given set of compounds. The thiocyanate systems have been considered in most detail, and some new data are presented here. Metal ions homogeneously complexed by a given pseudohalide have been emphasized and mixed species included only when the former are unknown or as special examples. Organic systems with these ions have been reviewed by Thayer and West<sup>20</sup>.

## B THEORETICAL CONSIDERATIONS

The normal vibrations of a linear triatomic molecule  $NCX$  are

$\begin{array}{c} \overrightarrow{N}-\overrightarrow{C}-\overleftarrow{X} \\ \uparrow \\ N-C-X \\ \downarrow \\ \overleftarrow{N}-\overrightarrow{C}-\overleftarrow{X} \end{array} \nu_1, \text{ pseudo-asymmetric stretch } (\nu_{CN})$

$\begin{array}{c} \overrightarrow{N}-\overrightarrow{C}-X \\ \downarrow \\ \overleftarrow{N}-\overrightarrow{C}-\overleftarrow{X} \end{array} \nu_2, (\delta_{NCX})$

$\begin{array}{c} \overrightarrow{N}-\overrightarrow{C}-\overleftarrow{X} \\ \downarrow \\ \overleftarrow{N}-\overrightarrow{C}-\overleftarrow{X} \end{array} \nu_3, \text{ pseudo-symmetric stretch } (\nu_{CX})$

(For a description of fulminate, C and N, and  $\nu_1$  and  $\nu_3$  should be interchanged.) The designation in parentheses is very commonly used, and approximates the major bond deformation involved in the vibration; in cyanate and fulminate in particular, the modes are appreciably mixed. The infrared spectra of these ions in the potassium salts are

given in Table 1. These are typical "free-ion" values, but small changes with cation and medium can be expected. Splittings are solid state effects

TABLE 1

Infrared spectra of the "free" ions considered here (as  $K^+$  salt)

Ion	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$	$\nu_3(\text{cm}^{-1})$	Ref
$\text{NCO}^-$	2165	637 628	1254 <sup>a</sup>	A
$\text{CNS}^-$	2053	486 471	746	B
$\text{CNSe}^-$	2070	424 416	558	C
$\text{CNO}^-$	1064 1057	473 468	2043	D

<sup>a</sup> Calculated. A Fermi resonance interaction gives two bands, 1301  $\text{cm}^{-1}$  and 1207  $\text{cm}^{-1}$

## REFERENCES TO TABLE 1

- A A. Maki and J.C. Decius, *J. Chem. Phys.*, 31 (1959) 772  
 B P.O. Kinell and B. Strandberg, *Acta Chem. Scand.*, 13 (1959) 1607  
 C H.W. Morgan, *J. Inorg. Nucl. Chem.*, 16 (1961) 367.  
 D W. Beck, *Chem. Ber.*, 95 (1962) 341.

The resonance contributions have been given for some of these ions. For thiocyanate, Jones<sup>21</sup> gives  $\text{N}\equiv\text{C}-\text{S}^-$ , 71%,  $^-\text{N}=\text{C}=\text{S}$ , 12%,  $^2-\text{N}-\text{C}\equiv\text{S}^+$ , 17%. Coordination through S would favor an increased contribution from the first of these, resulting in a decrease in C-S bond order and vibrational frequency and an increase in C-N bond order and frequency. Analogously, N-bonding would be expected to lead to the opposite effects. The remaining ions have similar resonance structures although with different contributions (e.g.,<sup>22</sup> for  $\text{NCO}^-$ ;  $\text{N}\equiv\text{C}-\text{O}^-$ , 75%,  $^-\text{N}=\text{C}=\text{O}$ , 1%;  $^2-\text{N}-\text{C}\equiv\text{O}^+$ , 24%), and the ion should behave in a similar way on coordination. The same resonance contribution has been used to explain that M-N bonding should increase, but M-X bonding decrease the intensity of the  $\nu_{\text{N-C}}$  mode. This has been accounted for on the assumption that the dipole moment and its rate of change during the vibration will increase with the decreased bond order and increased charge on the nitrogen atom which results from N bonding<sup>22,23</sup>. The validity of these various arguments is dependent upon the purity of the modes concerned. Calculations of Forster and Horrocks on zinc complexes<sup>24</sup> indicate that this is fairly good for  $\text{CNS}^-$  and  $\text{CNSe}^-$ , but that  $\text{NCO}^-$  involves a large amount of mixing between the  $\nu_{\text{CO}}$  and  $\nu_{\text{CN}}$  modes.

The atomic charges on these ions have been tabulated by Wagner<sup>25</sup>

	$Q_N$	$Q_C$	$Q_X$
$NCO^-$	-0.7712	-0.0442	-0.1846
$NCS^-$	-0.4826	+0.1943	-0.7108
$NCSe^-$	-0.3941	+0.2345	-0.8404
$CNO^-$	+0.6516	-1.1663	-0.4852

Thiocyanate shows the least charge difference between the two potential donor sites, and on this basis would be anticipated to show the greatest likelihood of ambidentate behavior. Cyanate, by contrast, has a much greater charge density on N and presumably a much greater tendency to coordinate through this atom than through oxygen.

Khantonov et al. have carried out more elaborate theoretical studies which lead to further understanding of the significance of band shifts on coordination for thiocyanate and selenocyanate ligands.<sup>26-28</sup> In the first instance, this involves analysis of the vibrations of coordinated  $CNS^-$  groups, in which they neglected any effects from electron redistribution on coordination, and considered only a single thiocyanate group in  $M-N-C-S$ ,  $M-S-C-N$ , and  $M-NCS-M$  configurations. For the nitrogen-bound case this treatment predicted the following:

- (1) The  $\nu_{CN}$  and the  $\nu_{CS}$  bands should increase in energy with an increase of  $k_{MN}$  (metal-nitrogen bond force constant). Hence,  $\nu_{CN}$  and  $\nu_{CS}$  increase on coordination.
- (2)  $\nu_{CN}$  is almost independent of the mass of the metal ion, and  $\nu_{CS}$  only slightly more influenced by this.  $\nu_{MN}$  is mass-dependent.
- (3) Changes in  $k_{MN,CN}$ , the interaction force constant, have little effect on  $\nu_{CN}$  and almost none on  $\nu_{CS}$  and  $\nu_{MN}$ .
- (4) The  $\nu_{CN}$ ,  $\nu_{CS}$  and  $\nu_{MN}$  bands are not pure vibrations, there is mixing in all cases.
- (5) These effects are in addition to those due to electron redistribution from coordination, such as changes in the CN and CS force constants. These should be small since the effect of  $k_{MN}$  alone gives reasonable correlation with experimental observations.

For the sulfur-bound case they found

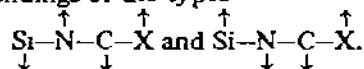
- (1) For unchanged force constants coordination of the  $SCN^-$  group through S has no influence on the frequency of  $\nu_{CN}$ . However,  $\nu_{CS}$  increases relative to the free ion but to a lesser amount than the N-bound case.
- (2)  $\nu_{CN}$  is almost independent of the mass of atom M and  $\nu_{CS}$  and  $\nu_{MS}$  are only slightly affected by it.
- (3)  $\nu_{CN}$  is almost independent of the  $CSM$  angle, but  $\nu_{CS}$  decreases and  $\nu_{MS}$  increases as the angle decreases from  $180^\circ$  to  $90^\circ$ .
- (4)  $\nu_{CN}$  is almost independent of  $k_{MS}$ , but  $\nu_{CS}$  and  $\nu_{MS}$  increase as  $k_{MS}$  increases.
- (5) In order to fit experimental results,  $k_{CN}$  and  $k_{CS}$ , and hence the bond orders must change on coordination (C-S decreasing, C-N increasing).

For the bridged case, their results were

- (1)  $\nu_{\text{CN}}$  and  $\nu_{\text{CS}}$  increase almost linearly with  $k_{\text{MN}}$  and  $k_{\text{SM}}$  (for  $k_{\text{MN}} = k_{\text{SM}}$ ).
- (2) Change in mass of M has almost no effect on  $\nu_{\text{CN}}$  and only a small one on  $\nu_{\text{CS}}$ , the effects appear as increases in  $k_{\text{MN}}$  and  $k_{\text{MS}}$
- (3)  $k_{\text{MS}}$  has almost no effect on  $\nu_{\text{CN}}$ .
- (4)  $\nu_{\text{MS}}$  depends on both  $k_{\text{MN}}$  and  $k_{\text{MS}}$ .
- (5) The high values of  $\nu_{\text{CN}}$  found experimentally are due to the combination of increase for nitrogen bonding and a change in force constants due to S-bonding

The similar treatment of selenocyanate shows that there is a complete analogy between the two groups. The treatment given is approximate, but it is interesting in relation to the correlation of the observed frequencies and does form the basis of a theoretical understanding of the observed shifts.

Carlson<sup>29</sup> and Miller and Carlson<sup>30</sup> have carried out a study of the vibrational spectra of  $\text{Si}(\text{NCS})_4$  and  $\text{Si}(\text{NCO})_4$ , and were able to fit them to species of tetrahedral symmetry with linear  $\text{Si}-\text{N}-\text{C}-\text{X}$  groups. Their results lead to the expectation of six infrared active fundamentals. In addition to the two stretching modes of the  $\text{NCX}$  group, and the  $\text{SiN}_4$  stretching and deformation modes, two bands associated with  $\text{SiNCX}$  deformation are claimed, for thiocyanate these are at  $560\text{ cm}^{-1}$  and  $484\text{ cm}^{-1}$ . These were assigned to bendings of the types



Forster and Goodgame have modified some of these assignments for the cyanate examples<sup>18</sup>. They have also considered square planar and octahedral structures<sup>30a</sup>

A vibrational analysis and force constant calculation for  $[\text{Zn}(\text{NCX})_4]^{2-}$  using the F-G matrix method has been carried out by Forster and Horrocks<sup>24</sup>, also on the basis of  $T_d$  symmetry. While this confirms six infrared active fundamentals, only the first of the three bending modes in  $\text{NCS}$ , described by  $\text{N}-\text{C}-\text{S}$ ,  $\text{Zn}-\text{N}-\text{C}$ , and  $\text{N}-\text{Zn}-\text{Z}$  deformations, falls above  $200\text{ cm}^{-1}$ . (The last is calculated to be below  $40\text{ cm}^{-1}$ ). The spectrum of this ion generally typifies that of tetrahedral N-bonded metal isothiocyanate complexes. These authors concluded that the  $\text{C}-\text{S}$  force constant increases upon coordination, but no significant change in the  $\text{C}-\text{N}$  force constant was observed in the approximations used (cf. the results of Kharitonov et al.<sup>26</sup>). The metal-ligand stretching frequency becomes less purely  $\text{M}-\text{N}$  as the pseudohalogen becomes heavier in the series  $\text{NCO}^-$ ,  $\text{NCS}^-$ ,  $\text{NCSe}^-$ , the force constant appears to be slightly higher than the  $\text{Zn}-\text{C}$  force constant in  $[\text{Zn}(\text{CN})_4]^{2-}$ .

### C EMPIRICAL CRITERIA

Lewis and co-workers<sup>8</sup> have considered the position of the  $\text{C}-\text{S}$  stretching frequency to be characteristic of bonding mode of coordinated thiocyanate. Frequencies near  $700\text{ cm}^{-1}$  are taken as indicative of S-bonding, while those near  $800-830\text{ cm}^{-1}$  indicate N-bonding. As a diagnostic criterion, this band offers the drawback of low intensity. It is often difficult to identify in the presence of organic ligands or counter-ions<sup>31</sup>, and on occasion the overtone of the  $\delta_{\text{NCS}}$  band may be mistaken for it.

The  $\text{C}-\text{N}$  stretching frequency also shifts on coordination and has been considered diagnostic<sup>10,15</sup>. N-bonding generally leads to little change or to a decrease below the "free".

ion value ( $2053\text{ cm}^{-1}$  in KCNS) while S-bonding results in an increase to near  $2100\text{ cm}^{-1}$ . It has been observed<sup>11,12</sup> that bridging ( $-\text{NCS}-$ ) thiocyanate exhibits this band well above  $2100\text{ cm}^{-1}$ .

A third criterion proposed by Lewis et al.<sup>8</sup> and by Sabatini and Bertini<sup>17</sup> is based on the NCS deformation mode. A single, sharp band near  $480\text{ cm}^{-1}$  is taken as indicative of N-bonding, while S-bonding is suggested by several bands of low intensity near  $420\text{ cm}^{-1}$ . The splitting in the second case may be due to the lower symmetry of the non-linear M-S-CN group which removes the degeneracy, while the low values could be explained from greater mixing of  $\delta_{\text{MAC}}$  and  $\delta_{\text{NCS}}$  modes when A is S than when A is N.  $\delta_{\text{MAC}}$  would be expected to be lower for S than for N. The M-NCS group, on the contrary, is more often found to be linear, but not invariably so<sup>6,15,17</sup>. It is also noticed that the first overtone of this band is particularly sharp and intense for N-bonded examples.

The intensity of the  $\nu_{\text{CN}}$  band has been developed as a fourth criterion of bonding mode. This was first suggested by Fronaeus and Larsson<sup>14</sup>, and more fully developed by Pecile<sup>16</sup>. The integrated intensity (i.e., area under the absorption peak) is generally above  $9 \times 10^4 M^{-1}\text{ cm}^{-2}$  per  $\text{CNS}^-$  for N-bonding, but near or below  $2 \times 10^4 M^{-1}\text{ cm}^{-2}$  for S-bonding, representing an increase and decrease, respectively, as compared to the "free"-ion values. The N-bonded peak is always much broader. Integrated intensities must be evaluated with some care. Although approximation by peak height times width at half-maximum is quite crude, (often about 1/3 of the true values) the values obtained may still be much different for S- and N-bonded cases. However, this is not reliable if the peak is irregular. The measurements required are discussed further below. This is a solution technique, and the possibility of partial dissociation must be considered. This would be suggested by a component peak near  $2050\text{ cm}^{-1}$ .

Bonding criteria based on the far infrared regions of the spectra ( $< 400\text{ cm}^{-1}$ ) have also been proposed<sup>9,19</sup>. Generally,  $\nu_{\text{M-N}} > \nu_{\text{M-S}}$ , the former usually above  $\nu_{\text{M-Cl}}$  of the analogous chloride. This is considered in more detail later.

It is known that some of the above criteria are disobeyed. In particular, examples can be cited where the C-N frequency does not fall in the proper range for the bonding actually found<sup>8,32-34</sup>. The deformation band and intensity criteria are fairly recent and have not been tested frequently, and, in addition, there are few general comparisons available for all of these approaches for a given set of compounds.

Bonding mode criteria for the selenocyanate ion have been proposed by Cotton et al.<sup>35</sup>, and Pecile et al.<sup>16,36,37</sup>. These parallel the thiocyanate criteria. In particular, the energy of  $\nu_{\text{CSe}}$  and the intensity of  $\nu_{\text{CN}}$  increase with N-bonding and decrease with Se-bonding relative to the free ion. Values of  $\nu_{\text{CN}}$  well above  $2100\text{ cm}^{-1}$  are also expected for bridging<sup>35</sup>. However, these criteria are based on few results from compounds whose structures are known from X-ray analysis, since less of this information is available than for thiocyanate. More often they are based on analogy and justified by expected chemical behavior, ligand field spectral calculations, etc.

Criteria for cyanate are even more difficult to set up empirically, since not only are structure determinations lacking but greater mixing of the stretching modes makes any analogy with the heavier members of the series less reliable. The same basic arguments of decreased  $\nu_{\text{CO}}$  frequency with oxygen bonding but an increase with N-bonding have been put forward<sup>38,39</sup>.

TABLE 2

Near infrared spectra of thiocyanate complexes<sup>a</sup>

Complex	$\nu_{\text{CN}}(\text{cm}^{-1})$	$2\delta_{\text{NCS}}(\text{cm}^{-1})$	$\nu_{\text{CS}}(\text{cm}^{-1})$	$\delta_{\text{NCS}}(\text{cm}^{-1})$	Ref
(NH <sub>4</sub> )[Ag(SCN) <sub>2</sub> ]	2101(s) 2086(s)	910(w)	718(w)	453(m)	A <sup>h</sup>
K[Au(SCN) <sub>4</sub> ]	2130(s) 2076(w)	915(w) 830(w)	700(w)	458(w) 413(s)	A
Rb <sub>2</sub> [Be(NCS) <sub>4</sub> ] · 4CH <sub>3</sub> CN <sup>b</sup>	2120		877	480	B
K <sub>3</sub> [Bi(SCN) <sub>6</sub> ]	2088		727 721		C
K <sub>2</sub> [Cd(SCN) <sub>4</sub> ] · 2H <sub>2</sub> O	2100 2090	941 932 918 913	758 727	470 460 456	D
(Et <sub>4</sub> N) <sub>3</sub> [Ce(NCS) <sub>6</sub> ]	2084(sh) 2059(s) 2050(s)			477(m)	A
(Et <sub>4</sub> N) <sub>2</sub> [Co(NCS) <sub>4</sub> ]	2062(s)		837(w)	481(m)	A
K <sub>3</sub> [Cr(NCS) <sub>6</sub> ] · H <sub>2</sub> O · CH <sub>3</sub> COOH	2078(s)	946(w)		475(m)	A
K <sub>3</sub> [Cr(NCS) <sub>6</sub> ]	2098(vs) 2058(vs)		820(vw)	474(s)	E
(Cat) <sup>2+</sup> [Cu(NCS) <sub>4</sub> ] <sup>c</sup>	2074(s)		835(w)		F
(Bu <sub>4</sub> N) <sub>3</sub> [Dy(NCS) <sub>6</sub> ] <sup>b</sup>	2052 <sup>d</sup>			484(m) 480(m)	G
(Bu <sub>4</sub> N) <sub>3</sub> [Er(NCS) <sub>6</sub> ] <sup>b</sup>	2055 <sup>d</sup>			486(m) 483(m)	G
(Bu <sub>4</sub> N) <sub>3</sub> [Eu(NCS) <sub>6</sub> ] <sup>b</sup>	2040(br)			485(m) 475(m)	G
(Et <sub>4</sub> N) <sub>3</sub> [Fe(NCS) <sub>6</sub> ]	2098(sh) 2052(s)		822(w)	479(m)	A
(Me <sub>4</sub> N) <sub>2</sub> [Fe(NCS) <sub>4</sub> ] <sup>b</sup>	2053(s)		830(w)		H
Ga(NCS) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub>	2076(s)		895(w)	475(m)	I
(Bu <sub>4</sub> N) <sub>3</sub> [Gd(NCS) <sub>6</sub> ] <sup>d</sup>	2045 <sup>d</sup>			483(m) 479(m)	G
(Et <sub>4</sub> N) <sub>2</sub> [Hf(NCS) <sub>6</sub> ]	1989(s)		876(w)	499(m)	J
K <sub>2</sub> [Hg(SCN) <sub>4</sub> ]	2134(m) 2122(sh) 2109(s)	919(w)	716(m) 709(sh) 703(sh)	461(m) 448(m) 432(sh) 419(m)	A
(Bu <sub>4</sub> N) <sub>3</sub> [Ho(NCS) <sub>6</sub> ] <sup>b</sup>	2053 <sup>d</sup>			486(m) 483(m)	G

TABLE 2 (continued)

Complex	$\nu_{\text{CN}}(\text{cm}^{-1})$	$2\delta_{\text{NCS}}(\text{cm}^{-1})$	$\nu_{\text{CS}}(\text{cm}^{-1})$	$\delta_{\text{NCS}}(\text{cm}^{-1})$	Ref
$(\text{Et}_4\text{N})_3[\text{In}(\text{NCS})_6]$	2085(s) 2030(w)		815(w)	475(m) 451(m)	K
$(\text{Bu}_4\text{N})_3[\text{Ir}(\text{SCN})_6]$	2127(m) 2098(s)		822(m) 693(w)	430(w)	L
$(\text{Et}_4\text{N})_3[\text{La}(\text{NCS})_6]$	2080(sh) 2051(s)			477(m)	A
$(\text{BuPh}_3\text{P})_2[\text{Mn}(\text{NCS})_4]$	2050(s) <sup>b</sup>		825(w) <sup>d</sup>		H
$\text{Cs}_3[\text{Mo}(\text{NCS})_6]$	2090(s)	947(w) 935(w)	815(w)	471(w)	A
$(\text{Et}_4\text{N})_2[\text{MoO}(\text{NCS})_5]$	2090(m) 2020(s)		884(m)	481(w)	A
$(\text{Et}_4\text{N})_3[\text{Nd}(\text{NCS})_6]$	2063(s) 2088(sh)			475(m)	A
$\text{Na}[\text{Nb}(\text{NCS})_6]$	1978(s, br)	958(w) 948(w)	818(m) 780(m) 746(w)	486(m) 475(w) 453(m) 446(w) 423(m)	M
$\text{K}[\text{Nb}(\text{NCS})_6]^b$	2080(m) 2025(sh) 2005(s) 1980(s) 1949(s) 1910(m)		930(sh) 927(m) 888(w)	499(m) 490(sh) 399	N
$\text{K}_2[\text{Nb}(\text{NCS})_6]^b$	2077(m) 2020(sh) 2005(s) 1980(s) 1948(s) 1908(m)		935(sh) 928(m) 888(w)	504(m)	N
$(\text{Et}_4\text{N})_4[\text{Ni}(\text{NCS})_6]$	2109(sh) 2102(s)		818(w)	469(m)	A
$(\text{Bu}_4\text{N})_3[\text{Os}(\text{NCS})_6]$	2103(s) 2070(sh)		818(w) 693(w)	420(w) Split bands	A
$(\text{Bu}_4\text{N})_3[\text{Os}(\text{NCS})_6]$	2090(s)		822(m) 689(w)	478(w) 463(w) 427(m) 430(w)	L
$\text{K}_2[\text{Pd}(\text{SCN})_4]$	2125(s) 2095(s)	942(w) 936(w) 929(w) 885(w) 876(w) 867(w)	703(w) 697(sh)	474(w) 467(w) 442(m) 432(m)	A



TABLE 2 (continued)

Complex	$\nu_{\text{CN}}(\text{cm}^{-1})$	$2\delta_{\text{NCS}}(\text{cm}^{-1})$	$\nu_{\text{CS}}(\text{cm}^{-1})$	$\delta_{\text{NCS}}(\text{cm}^{-1})$	Ref.
(Et <sub>4</sub> N) <sub>3</sub> [Pr(NCS) <sub>6</sub> ]	2087(s) 2050(s)			477(m)	A
K <sub>2</sub> [Pt(SCN) <sub>4</sub> ]	2128(s) 2099(s) 2077(sh)	940(w,b) 875(w)	696(w)	477(w) 469(w) 437(m) 426(m)	A
K <sub>2</sub> [Pt(SCN) <sub>6</sub> ]	2126(s) 2118(m) 2076(w)	924(w)	694(w)	427(m) 419(s)	A
Cs <sub>2</sub> [Re(CNS) <sub>6</sub> ]	2039(s) 2021(s)			484(m) 415(m)	A
Cs[Re(CNS) <sub>6</sub> ]	2068(s)			477(w) 469(w)	A
(Et <sub>4</sub> N) <sub>2</sub> [Re(CO) <sub>3</sub> (NCS) <sub>3</sub> ]	2115(sh) 2100(sh) 2090(s)		815(w)		O
(Bu <sub>4</sub> N) <sub>2</sub> [Re <sub>2</sub> (NCS) <sub>8</sub> ] <sup>b</sup>	2050(s)			475(m)	P
(Ph <sub>4</sub> As) <sub>2</sub> [Re <sub>2</sub> (NCS) <sub>8</sub> ] <sup>b</sup>	2025(s)		875(w) <sup>?</sup>		P
ReO(OH)(Ph <sub>3</sub> P) <sub>2</sub> (NCS) <sub>2</sub>	2090 2060		851(w)		Q
(Bu <sub>4</sub> N) <sub>3</sub> [Rh(SCN) <sub>6</sub> ]	2120(sh) 2098(s)		693(w)	424(w)	A
(Bu <sub>4</sub> N) <sub>3</sub> [Ru(NCS) <sub>6</sub> ]	2098(s)		695(w) 815(w)	460(w) 453(sh) 424(w) 420(sh)	A
(Bu <sub>4</sub> N) <sub>3</sub> [Ru(NCS) <sub>6</sub> ]	2095(s)		692(w) 812(m)	472(w) 453(w) 428(w)	L
K <sub>3</sub> [Sc(NCS) <sub>6</sub> ] <sup>b</sup>	2070		825		R
(Bu <sub>4</sub> N) <sub>3</sub> [Sm(NCS) <sub>6</sub> ] <sup>b</sup>	2059 <sup>d</sup>			487(m) 483(m)	G
(Et <sub>4</sub> N)[Sn(NCS) <sub>3</sub> ]	1950		821		S
K[Ta(NCS) <sub>6</sub> ] <sup>b</sup>	2039(s) 2012(s,br)	936(m) 954(sh)	825(m)	501(m) 492(m) 483(sh)	T
Ph <sub>4</sub> As[Ta(NCS) <sub>6</sub> ] <sup>b</sup>	2065(sh) 1937(vs) 1920(m)		928(m) 848(w)	505(m) 401(m)	N

TABLE 2 (continued)

Complex	$\nu_{\text{CN}}(\text{cm}^{-1})$	$2\delta_{\text{NCS}}(\text{cm}^{-1})$	$\nu_{\text{CS}}(\text{cm}^{-1})$	$\delta_{\text{NCS}}(\text{cm}^{-1})$	Ref.
$\text{K}[\text{Ta}(\text{NCS})_6]^b$	2095(m) 2035(sh) 2015(s) 1992(s) 1965(sh) 1922(sh)		940(sh) 932(m) 897(m)	501(m) 400(m)	N
$(\text{Me}_4\text{N})[\text{Ta}(\text{NCS})_6]$	2028		869	484	U
$\text{TiCp}_2(\text{NCS})_2^e$	2058(s) 2017(s)	*		496 491(w)	V
$(\text{Bu}_4\text{N})_3[\text{Tb}(\text{NCS})_6]^b$	2050 <sup>g</sup>			485(m) 480(m)	G
$\text{Cs}_4[\text{U}(\text{NCS})_8]$	2057(s) 2015(sh)	955(w)	826(w) 790(w)	478(m)	A
$\text{Cs}_3[\text{UO}_2(\text{NCS})_5]$	2091(s) 2056(s) 2005(sh)		844(w) 799(w)	484(m)	A
$(\text{Et}_4\text{N})_3[\text{V}(\text{NCS})_6]$	2055(s) 2093(s)			482(m)	A
$(\text{Et}_4\text{N})_2[\text{VO}(\text{NCS})_4]$	2061(s)			482(m)	A
$(\text{Et}_4\text{N})_3[\text{VO}(\text{NCS})_5]$	2080(s)		820(w)	482(m)	K
$(\text{Et}_4\text{N})_3[\text{Yb}(\text{NCS})_6]$	2057(s) 2015(sh)		821(w)	487(m)	A
$(\text{Et}_4\text{N})_2[\text{Zn}(\text{NCS})_4]$	2074(s)		832(w)	480(m)	A
$\text{Cs}[\text{Zn}(\text{NCS})_3] \cdot \text{H}_2\text{O}^{b,f}$	2173 2158 2090	982 960 898	827 789	482 475 445	W
$(\text{Et}_4\text{N})_2[\text{Zr}(\text{NCS})_6]$	1985(s)		879(w)	499(m)	J
$\text{ZrCp}_2(\text{NCS})_2^e$	2041(m) 2003(s)			497(w)	V

<sup>a</sup> In KBr pellet except as noted<sup>b</sup> Nujol mull<sup>c</sup>  $(\text{Cat})^{2+} = p\text{-xylylenebis}(\text{triphenylphosphonium})$ <sup>d</sup> Solution value, acetonitrile.<sup>e</sup> Cp = (cyclopentadienyl)<sup>-</sup>.<sup>f</sup> Believed to contain both bridging and terminal thiocyanate groups<sup>g</sup> Solution value, methanol<sup>h</sup> See also P.O. Kinell and B. Strandberg, *Acta Chem. Scand.*, 13 (1959) 1607.

## REFERENCES TO TABLE 2

A This work

B T.I. Pochkarev, L.M. Mikheeva, A.I. Gngor'ev and A. Ganem, *Russ. J. Inorg. Chem.*, 15 (1970) 45C A. Cyganski and Z. Galdecki, *Roczniki Chem.*, 42 (1968) 747.D A. Tramer, *J. Chim. Phys.*, 59 (1962) 232

TABLE 2 (continued)

E	M A. Bennett, R.J.H. Clark and A.D.J. Goodwin, <i>Inorg. Chem.</i> , 6 (1967) 1625.
F	D. Forster and D.M.L. Goodgame, <i>Inorg. Chem.</i> , 4 (1965) 823.
G	J.L. Burmeister, S.D. Patterson and A.E. Deardorff, <i>Inorg. Chim. Acta</i> , 3(1969) 105.
H	D. Forster and D.M.L. Goodgame, <i>J. Chem. Soc.</i> , (1965) 268.
I	S.J. Patel and D.G. Tuck, <i>Can. J. Chem.</i> , 47 (1969) 229.
J	R.A. Bailey, T.W. Michelsen and A.A. Nobile, <i>J. Inorg. Nucl. Chem.</i> , 32 (1970) 2427.
K	H.H. Schmidtke and D. Garthoff, <i>Z. Naturforsch., A</i> , 24 (1969) 126.
L	H.H. Schmidtke and D. Garthoff, <i>Helv. Chim. Acta</i> , 50 (1967) 1631.
M	H. Bohland, E. Tiede and E. Zenker, <i>J. Less-Common Metals</i> , 15 (1968) 89.
N	G.F. Knox and T.M. Brown, <i>Inorg. Chem.</i> , 8 (1969) 1401.
O	M.J. Hawkes and A.P. Ginsberg, <i>Inorg. Chem.</i> , 8 (1969) 2189.
P	F.A. Cotton, W.R. Robinson, R.A. Walton and R. Whyman, <i>Inorg. Chem.</i> , 6 (1967) 929.
Q	M. Freni, D. Guisto and P. Romiti, <i>Gazz. Chim. Ital.</i> , 99 (1969) 641.
R	T.M. Sas, L.N. Komissarova, V.G. Gulia and A.I. Grigor'ev, <i>Russ. J. Inorg. Chem.</i> , 12(1967) 1090.
S	B.R. Chamberlain and W. Moser, <i>J. Chem. Soc. A</i> , (1969) 354.
T	H. Bohland and E. Tiede, <i>J. Less-Common Metals</i> , 13 (1967) 224.
U	K. Schwochau and H.H. Pieper, <i>Inorg. Nucl. Chem. Letters</i> , 4 (1968) 711.
V	J.L. Burmeister, E.A. Deardorff, A. Jensen and V.H. Christiansen, <i>Inorg. Chem.</i> , 9 (1970) 58.
W	Yu Ya. Kharitonov, G.V. Tsintsadze and A.Ya. Tsvadze, <i>Russ. J. Inorg. Chem.</i> , 15 (1970) 204.

## D. DISCUSSION

## (1) Thiocyanate and isothiocyanate complexes

Table 2 presents a listing of the  $\nu_{\text{CN}}$ ,  $\nu_{\text{CS}}$ , and  $\delta_{\text{NCS}}$  (and  $2\delta_{\text{NCS}}$  when observed) bands for thiocyanate complexes of most of the transition metals and some others. Data labelled "this work" are our own measurements, but unless indicated these show no substantial disagreements with previous reports. Near infrared spectra were recorded on a Perkin-Elmer Model 621 grating spectrophotometer in the 300–4000  $\text{cm}^{-1}$  range. Normally, spectra were taken on both 1% and 5% KBr pellets and checked as nujol or hexachlorobutadiene mulls in order to guard against errors caused by replacement of thiocyanate by bromide ions.

A survey of these data shows that the  $\nu_{\text{CN}}$  band position is generally a good indication of bonding mode, but that exceptions do occur. In particular, N-bonded examples may be high (e.g.  $^{40}\text{Cr}^{\text{III}}$  and  $\text{Mo}^{\text{III}}$  which are near 2090  $\text{cm}^{-1}$ ) and therefore use of the position of this band alone as a criterion of bonding must be considered risky. Frequently, this band is complex, exhibiting two or more components; criteria are usually based on the position of the main peak and we have not attempted to tabulate all shoulders. Causes of these splittings may be distortions from regular  $O_h$  or  $T_d$  symmetry brought about by non-linearity, Jahn-Teller, or other effects which destroy the degeneracy of the band, but as most spectra are those of the solid, lattice interactions may be the predominant factor. Indeed, solution spectra show much less structure. When these splittings are of interest, low-temperature measurements may permit more effective resolution. For example, Lever et al.<sup>41</sup> have observed the isotopic satellite bands from  $^{13}\text{C}$  and  $^{15}\text{N}$  in some  $\text{M}(\text{L})_2(\text{NCS})_2$  complexes at liquid-nitrogen temperature.

Changes in medium (KBr pellets or nujol) may bring about small shifts in band position

for the  $\nu_{\text{CN}}$  and also for the other bands to be discussed. These are rarely significant in this context, however. The influence of the counter-ion on the  $\nu_{\text{CN}}$  frequency has been commented on by Mitchell and Williams<sup>10</sup>. The more polarizing the cation in anionic thiocyanates, the greater is the frequency of the CN vibration. This becomes a large effect when the cation can bond to the free end of the  $\text{NCS}^-$  group to give a bridged structure as discussed below. Mixed ligand species may be of quite different symmetry from the homogeneously substituted examples, resulting in additional peaks. This is illustrated by the *cis* and *trans* isomers of dithiocyanato compounds where only one of the C—N vibrations is active in the latter geometry<sup>42</sup>. This has been used by Chamberlain and Bailar<sup>33</sup> to establish the configuration of a number of species of this sort. Lack of splitting does not prove the *trans* isomer, as the bands may be insufficiently resolved. Lever et al.<sup>41</sup> find this to be the case in some  $\text{ML}_2(\text{NCS})_2$  compounds where stereochemical problems lead to unusually long M—N bonds in the *cis* isomers. The band could be resolved at low temperatures, however. It is clear that isomeric forms can be distinguished on the basis of infrared spectral data, but it is also clear that the proper interpretations require some care.

Changes in electron density about the metal ion with these other ligands attached may be expected to have a considerable effect on the bonding strength and consequently on the position of the C—N stretching frequency, but shifts due to this are usually surprisingly small. In extreme cases, effects of other ligands can result in a change in bonding mode through electronic or steric effects<sup>13,43-46</sup>. Ligands which accept  $\pi$ -bonding electrons from the metal favor N-bonding with typical class b ions such as  $\text{Pd}^{\text{II}}$ , but the same type of ligand may cause  $\text{Co}^{\text{II}}$  to become S-bonded. These effects and the problems associated with their explanation are discussed in detail by Norbury and Sinha<sup>45</sup>. Steric effects are also significant with S-bonded, non-linear systems, and in these cases other bulky ligands can cause a change to the nearly linear N-bonded form<sup>43,45</sup>. Different counter-ions (anions and cations) can also affect the bonding mode, presumably through more favorable crystal packing energies<sup>47,48</sup>. In a number of cases, effects of other ligands, ions, etc. are of such a magnitude that the two linkage modes have comparable stability, a number of linkage isomers have been isolated as listed in Table 3.

Clark and Williams<sup>9</sup> and Mitchell and Williams<sup>10</sup> have considered possible relations of the  $\nu_{\text{CN}}$  band position to coordination geometry, finding that there does not generally seem to be one. Octahedral nitrogen-bonded compounds show a general correlation with oxidation state of the metal ion in that the main band position seems to be at lower energy with higher oxidation state. This is particularly noticeable with IV and V states, such as  $\text{Zr}^{\text{IV}}$ ,  $\text{Hf}^{\text{IV}}$ , and the  $\text{Nb}^{\text{V}}$  and  $\text{Ta}^{\text{V}}$  complexes (Table 1), and has been related to the high oxidation state and lack of *d* electrons on the metal<sup>49,50</sup>.

It also will be noted from Table 1 that there is a discrepancy between the  $\nu_{\text{CN}}$  position reported for  $\text{Ta}^{\text{V}}$  compounds by Brown and Knox<sup>50,51</sup> and by Bohland et al.<sup>52-54</sup>. In the former, the main  $\nu_{\text{CN}}$  peak lies below  $2000\text{ cm}^{-1}$  in most cases, the latter report it above this value (Table 1). Knox and Brown<sup>50</sup> suggest that splitting of the band in this case may be due to different bond strengths in the coordinated thiocyanate ions (that is, not all of the thiocyanate ligands may be equivalent). This is not confirmed.

There is a similar discrepancy for the compounds of  $\text{Zr}^{\text{IV}}$  and  $\text{Hf}^{\text{IV}}$  as reported by Kharitonov et al.<sup>55,56</sup> and those reported in Table 1. The former find the  $\nu_{\text{CN}}$  band at

TABLE 3

Infrared spectra of thiocyanate linkage isomers<sup>d</sup>

Compound	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{CS}}(\text{cm}^{-1})$	$\delta_{\text{NCS}}(\text{cm}^{-1})$	Other	Ref.
$\text{K}_3[\text{Co}(\text{CN})_5\text{SCN}]$	2110(s)	719(w)			A
$\text{K}_3[\text{Co}(\text{CN})_5\text{NCS}]$	2065(br)	810(w)			B,C
$[\text{Co}(\text{DH})_2\text{Py}(\text{SCN})]^b$	2118(s, sp)			$1.2 \times 10^4 M^{-1} \text{cm}^{-2} c$	D
$[\text{Co}(\text{DH})_2\text{Py}(\text{NCS})]^b$	2128(s, sp)	837(w)		$10.24 \times 10^4 M^{-1} \text{cm}^{-2} c$	D
$[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+ d}$	2100(sp)	710(vw)	480(w) 459(w) 426(m)		E
$[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+ d}$	2125(b)	806(ms)	490(mw) 460(mw)		E
$[\text{Cu}(\text{tripyam})(\text{SCN})_2]^e$	2123(s, sp) 2100(s, sp)				F
$[\text{Cu}(\text{tripyam})(\text{SCN})(\text{NCS})]^e$	2128(s, sp) 2080(s, b)				F
$[\text{Cu}(\text{tripyam})(\text{NCS})_2]^e$	2100(s, b) 2070(sh, b)				F
$[\text{Cu}(\text{dppa})(\text{SCN})_2]^f$	2122(s, sp) 2100(s, sp)				F
$[\text{Cu}(\text{dppa})(\text{SCN})(\text{NCS})]^f$	2128(s, sp) 2081(s, b)				F
$[\text{Cu}(\text{dppa})(\text{NCS})_2]^f$	2100(s, b) 2072(sh, b)				F
$[\text{FeCp}(\text{CO})_2(\text{SCN})]^g$	2118(m) (in $\text{CHCl}_3$ )	698(w) (null)		$1.64 \times 10^4 M^{-1} \text{cm}^{-2} c$	G
$[\text{FeCp}(\text{CO})_2(\text{NCS})]^g$	2123(s) (in $\text{CHCl}_3$ )	830(m) (null)		$6.7 \times 10^4 M^{-1} \text{cm}^{-2} c$	G
$[\text{Ir}(\text{NH}_3)_5\text{SCN}]^{2+ h}$	2110(s, sp)	700(m)			H
$[\text{Ir}(\text{NH}_3)_5\text{NCS}]^{2+ h}$	2140(s, br)	825(s)			H
$[\text{Mn}(\text{CO})_5\text{SCN}]^i$	2160(sh) 2138(m) 2084(w) 2043(s, br) 1958(ms)	676(w)			I
$[\text{Mn}(\text{CO})_5\text{NCS}]^i$	2141(w) 2113(m) 2053(s) 1958(ms)	813(m)			I
$[\text{MoCp}(\text{CO})_3(\text{SCN})]^g$	2114(m-s) (in $\text{CHCl}_3$ )	699(w) (null)		$2.19 \times 10^4 M^{-1} \text{cm}^{-2} c$	G
$[\text{MoCp}(\text{CO})_3(\text{NCS})]^g$	2099(s) (in $\text{CHCl}_3$ )	Masked		$9.80 \times 10^4 M^{-1} \text{cm}^{-2} c$	G

TABLE 3 (continued)

Compound	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{CS}}(\text{cm}^{-1})$	$\delta_{\text{NCS}}(\text{cm}^{-1})$	Other	Ref
$[\text{Rh}(\text{NH}_3)_5\text{SCN}]^{2+}h$	2115(s,sp)	730(w,br)			H
$[\text{Rh}(\text{NH}_3)_5\text{NCS}]^{2+}h$	2145(s,br)	815(s)			H
$[\text{Rh}(\text{SCN})\text{Cl}_2(\text{PMe}_2\text{Ph})_3]$	2108(vs)			$\nu_{\text{M-SCN}}234$	J,K
$[\text{Rh}(\text{NCS})\text{Cl}_2(\text{PMe}_2\text{Ph})_3]$	2112(vs) 2122(sh)	809(w)		$\nu_{\text{M-NCS}}264$	J,K
$[\text{Pd}(\text{As}(\text{Ph})_3)_2(\text{SCN})_2]$	2119(s,br)	Masked	418(vw)	$\nu_{\text{M-SCN}}306(\text{m, sh})$	K,L,M
$[\text{Pd}(\text{As}(\text{Ph})_3)_2(\text{NCS})_2]$	2089(s,br)	854(m)	Masked	Masked	K,L,M
$[\text{Pd}(\text{bipy})(\text{SCN})_2]$	2117(m) 2108(s)	700(w)		$\nu_{\text{M-SCN}}316(\text{m})$ 304(m)	K,L,M
$[\text{Pd}(\text{bipy})(\text{NCS})_2]$	2100(s,br)	845(m)	458(w)	$\nu_{\text{M-NCS}}345(\text{s})$ 332(sh)	K,L,M
$[\text{Pd}(\text{dpp})(\text{SCN})_2]^f$	2120(sh) 2113(s,sp)	Masked	419(mw)		N
$[\text{Pd}(\text{dpp})(\text{NCS})_2]^f$	2110(s,br)	Masked	Masked		N
$[(\text{Et}_4\text{dien})\text{Pd}(\text{SCN})](\text{CNS})^k$	2125	710			O
$[(\text{Et}_4\text{dien})\text{Pd}(\text{NCS})](\text{CNS})^k$	2060	830			O

<sup>a</sup> Spectra in mulls except as noted.<sup>b</sup> DH = (dimethylglyoximate)<sup>-</sup><sup>c</sup> Integrated intensity of  $\nu_{\text{CN}}$  peak.<sup>d</sup> Prepared as perchlorate. Medium not specified.<sup>e</sup> tripyam = tri-2-pyridylamine<sup>f</sup> dppa = phenyl-di-2-pyridylamine<sup>g</sup> Cp = (cyclopentadienyl)<sup>-</sup>.<sup>h</sup> Anion and medium not specified.<sup>i</sup> S-bonded isomer as mull, N-bonded isomer stable only in solution (acetonitrile).  $\nu_{\text{CN}}$  listing also contains  $\nu_{\text{CO}}$  frequencies.<sup>j</sup> dpp = 4,7-diphenyl-*o*-phenanthroline.<sup>k</sup> Et<sub>4</sub>dien = tetraethyldiethylenetriamine, medium not given,  $\nu_{\text{CN}}$  from fluorophosphate.

## REFERENCES TO TABLE 3

- A J.L. Burmeister, *Inorg. Chem.*, **3** (1964) 919.  
 B I. Stotz, W.K. Wilmarth and A. Ham, *Inorg. Chem.*, **7** (1968) 1250.  
 C D.F. Gutterman and H.B. Gray, *J. Amer. Chem. Soc.*, **91** (1969) 3105.  
 D A.H. Norbury and A.I.P. Sinha, *Inorg. Nucl. Chem. Letters*, **4** (1968) 617.  
 E D.A. Buckingham, I.I. Creaser and A.M. Sargeson, *Inorg. Chem.*, **9** (1970) 655.  
 F G.C. Kulasingam and W.R. McWhinnie, *J. Chem. Soc. A*, (1968) 254.  
 G T.E. Sloan and A. Wojcicki, *Inorg. Chem.*, **7** (1968) 1268.  
 H H.H. Schmidtke, *J. Amer. Chem. Soc.*, **87** (1965) 2522.  
 I M.F. Farona and A. Wojcicki, *Inorg. Chem.*, **4** (1965) 857.  
 J P.R. Brookes and B.L. Shaw, *J. Chem. Soc. A*, (1967) 1079.  
 K D.M.L. Goodgame and B.W. Malerbi, *Spectrochim. Acta*, **24A** (1968) 1254.  
 L J.L. Burmeister and F. Basolo, *Inorg. Chem.*, **3** (1964) 1587.  
 M A. Sabatini and I. Bertini, *Inorg. Chem.*, **4** (1965) 1665.  
 N I. Bertini and A. Sabatini, *Inorg. Chem.*, **5** (1966) 1025.  
 O F. Basolo, W.H. Baddley and K.J. Weidenbaum, *J. Amer. Chem. Soc.*, **88** (1966) 1576.

TABLE 4  
Infrared spectra of bridged thiocyanate complexes

Compound	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{CS}}(\text{cm}^{-1})$	$\delta_{\text{NCS}}(\text{cm}^{-1})$	$\nu_{\text{M-L}}(\text{cm}^{-1})$	Ref
Cd(NCS) <sub>4</sub> Hg	2141 2127	772			A
Co(NCS) <sub>4</sub> Hg	2146(s) 2134(sh) 2093(w,sh)	786	465(m) 442(m)	303(s) 276(sh) 219(m)	B,C
[Cr(NCS) <sub>6</sub> ] <sub>2</sub> Hg <sub>3</sub>	2134	801	472 469 459	368	A
[Cr(NCS) <sub>6</sub> ] <sub>2</sub> Hg <sub>3</sub>	2148(vs) 2100(sh)	800(w)	462(s) 452(s)	369(s)	D
Cu(NCS) <sub>4</sub> Hg	2170 2154	795	459 437	318(s) 282(vs) 266(sh,w)	A,C
Fe(NCS) <sub>4</sub> Hg				296(s) 256(m) 216(m)	C
Mn(NCS) <sub>4</sub> Hg				278(br) 213(m,br)	C
Ni(NCS) <sub>4</sub> Hg	2145	752 747		303(m) 250(s,br)	A,C
Pb(NCS) <sub>4</sub> Hg	2132 2122	758			A
Pt(SCN) <sub>6</sub> Hg	2154 2142	712			A
Tl <sub>2</sub> (NCS) <sub>4</sub> Hg	2117 2081	738 723			A
Co(NCS) <sub>4</sub> Cd				303(vs) 276(sh) 230(m)	C
Pt(SCN) <sub>6</sub> Co	2166	732			A
Pt(SCN) <sub>6</sub> Pb	2124 2112 2109	702			A
Pt(SCN) <sub>6</sub> Zn	2169 2166	730			A
Cr(NH <sub>3</sub> ) <sub>2</sub> (NCS) <sub>4</sub> Co	2158 2095 2065	855 785	471 464 444		E
Cr(NH <sub>3</sub> ) <sub>2</sub> (NCS) <sub>4</sub> Cu	2110 2095 2075	825 810	475 460		E

TABLE 4 (continued)

Compound	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{CS}}(\text{cm}^{-1})$	$\delta_{\text{NCS}}(\text{cm}^{-1})$	$\nu_{\text{M-L}}(\text{cm}^{-1})$	Ref
$\text{Cr}(\text{NH}_3)_2(\text{NCS})_4\text{Hg}$	2160 2095 2065	845 798			E
$\text{Cr}(\text{NCS})_6\text{Ag}_3$	2165(sh) 2150(s) 2120(sh)	810(w)	464(s)	369(s)	D
$[\text{Cr}(\text{NCS})_6]_2\text{Cd}_3 \cdot 2\text{H}_2\text{O}$	2120(s,br)	812(w)	475(s) 456(m,sh)	368(s)	D
$\text{Cr}(\text{NCS})_6\text{Ti}_3$	2105(s)	820(w)	462(s)	365(s)	D
$[\text{Cr}(\text{NCS})_6]_2\text{Cu}_3$	2150(s)	800(w)	468(sh) 458(s) 444(sh)	370(s)	D
$[\text{Cr}(\text{NCS})_6]_2\text{Pb}_3$	2100(s)	805(w)	468(s) 450(s)	370(s)	D
$\text{Co}(\text{Py})_2(\text{NCS})_2^a$	2099(s)	787(w)	472(m) 468(m)	268(s)	F
$\text{Cu}(\text{Py})_2(\text{NCS})_2^a$	2085(s)	826(m)	477(w) 468(w)	319(s)	F
$\text{Co}(\text{NCS})\text{Hg}_2 \cdot \text{C}_6\text{H}_6^b$	2160(s)				G
$\text{Zn}(\text{NCS})_4\text{Hg}$	2157 2146	786		327(s) 250(sh) 217(m)	A,C

<sup>a</sup> X-ray structure shows bridging thiocyanate. Several other analogous examples are included in this reference.

<sup>b</sup> The structure is  $\text{Hg} \begin{array}{c} \diagup \text{SCN-Co} \\ \diagdown \end{array}$  (ref. 3)

## REFERENCES TO TABLE 4

- A A. Tramer, *J. Chim. Phys.*, 59 (1962) 232  
 B Our measurements  
 C D. Forster and D.M.L. Goodgame, *Inorg. Chem.*, 4 (1965) 715  
 D J.R. Wasson and C. Trapp, *J. Inorg. Nucl. Chem.*, 30 (1968) 2437  
 E H. Oki, E. Kyuno and R. Tsuchiya, *Bull. Chem. Soc. Japan*, 41 (1969) 2357  
 F R.J.H. Clark and C.S. Williams, *Spectrochim. Acta*, 22 (1966) 1081  
 G R. Baur, M. Schellenberg and G. Schwarzenbach, *Helv. Chim. Acta*, 45 (1962) 775

2025  $\text{cm}^{-1}$  for Hf, and 2024–2075  $\text{cm}^{-1}$  for Zr pyridinium salts. The true identity of the preparations of Kharitonov may be questioned since at least the Zr compounds admitted-ly contain material with Zr–O bonds.

Bridging thiocyanate groups,  $\text{M}-\text{N}-\text{C}-\text{S}-\text{M}'$  (Table 4), have been claimed to give a band in the 2140–2150  $\text{cm}^{-1}$  region<sup>11,12</sup>. However, many examples can be found where  $\nu_{\text{C-N}}$



lies between 2100 and 2130  $\text{cm}^{-1}$  and which involve second metal ions which are at least potentially capable of being coordinated to the "free" ends of the thiocyanate ligands<sup>15</sup>. A number of other examples of bridged thiocyanates is given by Clark and Williams<sup>9</sup> and Mitchell and Williams<sup>10</sup> with the  $\nu_{\text{CN}}$  frequency in the 2090  $\text{cm}^{-1}$  region. On the other hand, Chamberlain and Bailar<sup>33</sup>, and Baldwin<sup>34</sup> have reported the energy of the  $\nu_{\text{CN}}$  band for a number of N-bonded mixed ligand complexes of  $\text{Co}^{\text{III}}$  to be unusually high; e.g.  $[\text{Co}(\text{NH}_3)_5\text{NCS}]\text{Cl}_2$ , 2141  $\text{cm}^{-1}$ , *cis*- $[\text{Co}(\text{en})_2\text{Cl}(\text{NCS})]\text{ClO}_4$ , 2135  $\text{cm}^{-1}$ . (Most other  $\text{Co}^{\text{III}}$  examples are lower, but generally above 2100  $\text{cm}^{-1}$ , no homogeneous  $\text{Co}^{\text{III}}$  thiocyanate complex is known.) There seems no reason to expect thiocyanate bridging in these examples, so that it is evident that this criterion also must be applied with care. In case of bridging,  $\nu_{\text{CS}}$  is generally found lowered from its value in the analogous non-bridged N-bonded complex, but it is most often well above the normal S-bonded range (the  $\text{Pt}^{\text{IV}}$  compounds in Table 4 are among the exceptions to this). Data for the other known bridging type are too rare for comment.

The position of the  $\nu_{\text{C-S}}$  band seems to be a more reliable guide to N or S bonding<sup>10</sup>. No example appears which clearly contradicts the published criterion, i.e. near 700  $\text{cm}^{-1}$  for S-bonding and near or above 800  $\text{cm}^{-1}$  for N-bonding. Some weak, long Cu-SCN bonds give values only slightly below the free-ion value<sup>57</sup>. Occasional splitting is noted. Unfortunately, as mentioned, the weak band is frequently difficult to identify with certainty<sup>31</sup>. This is well illustrated by the tetraethylammonium salts of the rare earth isothiocyanate complexes, where a band at 821  $\text{cm}^{-1}$  in the ytterbium compound may be assigned to this bond, but is hidden by a stronger peak from the cation in the other members of this series which were examined.

Clark and Williams<sup>9</sup> have noted a correlation between the position of the  $\nu_{\text{C-S}}$  band and structure. For a series of Co, Ni, Fe, and Cu N-bonded systems involving pyridine ligands, monomeric octahedral compounds gave this band at 798–805  $\text{cm}^{-1}$ , for octahedral polymers (bridging  $\text{SCN}^-$ ) it was at 780–790  $\text{cm}^{-1}$ , while for tetrahedral monomers it fell at 840–851  $\text{cm}^{-1}$ . These ranges would undoubtedly expand and overlap if other systems were considered, but it does appear that some structural differentiation is possible. Results of Table 2 show  $\nu_{\text{CS}}$  of tetrahedral complexes to be generally higher than octahedral, although oxidation state is an important consideration. Higher frequencies are found with higher oxidation states, especially IV and V;  $\text{Zr}^{\text{IV}}$  and  $\text{Hf}^{\text{IV}}$ , in particular, are above 870  $\text{cm}^{-1}$ . The niobium and tantalum (V) systems are again interesting in this respect. Brown and Knox<sup>50,51</sup> assign this band to 880–940  $\text{cm}^{-1}$  for a number of salts of both metals, while Böhlund et al. reports it near 800–825  $\text{cm}^{-1}$  for Ta in other salts<sup>52–54</sup>. The former values seem very high, even considering the effect of oxidation state; confusion with peaks from the organic cation remains conceivable in some cases, since it must be kept in mind that some changes in cation spectra with anion can take place, probably as a result of crystal lattice effects. However, this does not explain similar values when no organic material is present. The bands in question may just possibly be overtones of the bending modes, but in any event, the disagreements in the spectra reported by these two groups remain unexplained. There seems little doubt of N-bonding, however. The generally low  $\nu_{\text{CN}}$  and high  $\nu_{\text{CS}}$  values found in the  $\text{Nb}^{\text{V}}$  and  $\text{Ta}^{\text{V}}$  compounds were justified by Knox and Brown<sup>50</sup> on the basis of a reciprocal relationship between the  $\nu_{\text{CN}}$  and  $\nu_{\text{CS}}$  frequencies which was noticed for organic isothiocyanates and silicon tetraisothiocyanate<sup>29,58</sup> and which is evident also in the  $\text{Zr}^{\text{IV}}$  and  $\text{Hf}^{\text{IV}}$  compounds.

The iridium, osmium, and ruthenium compounds also give rise to difficulties. The  $\nu_{CS}$  band was assigned by Schmidtke and Garthoff<sup>59</sup> to 822  $\text{cm}^{-1}$  and 812  $\text{cm}^{-1}$  for Os and Ru respectively, although a weaker band was observed in his and our work at 690  $\text{cm}^{-1}$ . Iridium, with similar bands, was considered to be S-bonded as is rhodium<sup>8</sup> with only a 693  $\text{cm}^{-1}$  peak. Interpretations of the other bands are somewhat ambiguous, but lean toward S-bonding. Again, confusion with a cation band becomes a possibility, and in this case the positional criteria are unreliable. These compounds are of particular interest, as the change from class a to class b behavior occurs in this region of the Periodic Table.

The  $\delta_{NCS}$  frequency also seems to be a fairly reliable, if empirical, indicator of bonding mode, although in some cases considerable splitting of the band may occur even for N-bonded systems (Table 1). All such examples, however, show a component near 480  $\text{cm}^{-1}$ , as anticipated. It is not possible with the presently available data to say if splitting correlates with non-linearity of the M—N—C—S group, but this could partially allow modes which are not infrared active in a linear case. Knox and Brown<sup>50</sup> attribute two medium-intensity bands in the 400–500  $\text{cm}^{-1}$  region of the Nb and Ta spectra to deformation modes, as did Carlson<sup>29</sup> in his treatment of  $\text{Si}(\text{NCS})_4$ . This is not found to be the case generally; most assignments propose the second bending mode to be below the  $\nu_{M-N}$  band and consequently<sup>24</sup> near or below 200  $\text{cm}^{-1}$  as in  $[\text{Zn}(\text{NCS})_4]^{2-}$ . The S-bonded systems only rarely show a band as high as 470  $\text{cm}^{-1}$  ( $\text{Pd}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$ ) but these are highly split with several low-energy components. Bridging (—N—C—S—) gives results similar to S-bonding.

#### (ii) Selenocyanate and isoselenocyanate complexes

Band positions for selenocyanate complexes are collected in Table 5. The  $\nu_{CSe}$  band clearly can be found in one of two definite areas; above the free-ion value and near 620–700  $\text{cm}^{-1}$ , or below the former and in the 500–550  $\text{cm}^{-1}$  region. These are assigned to the N- and Se-bonded forms respectively, and when other evidence for bonding mode is available the above criterion agrees with it. The position of the  $\nu_{CN}$  frequency for the apparently N-bonded cases is generally below about 2080  $\text{cm}^{-1}$ , but higher values in the range typical for Se bonding are found as well. Indeed,  $\nu_{CN}$  is often very close for analogous  $\text{CNS}^-$  and  $\text{CNSe}^-$  complexes. Several examples which are believed to be bridged via the —NCS— mode also are given in Table 5. As for many bridged thiocyanate compounds, the  $\nu_{CN}$  band lies well above 2100  $\text{cm}^{-1}$ .

The  $\delta_{NCS}$  band also appears to follow the  $\text{CNS}^-$  pattern. Se-bonded compounds show at least one component of this vibration below 400  $\text{cm}^{-1}$ , while the N-bonded systems, even when split, do not lie this low.

As with thiocyanate, the selenocyanate bonding mode is sensitive to other ligands. According to the work of Burmeister et al.<sup>47,60</sup>, however, electronic effects are of much less significance as the charge distribution would imply. Steric factors are important, and the examples of change of expected bonding mode with this ligand can be related to this. Examples of linkage isomers are given in Table 5.

TABLE 5

Infrared spectra of selenocyanate complexes<sup>a</sup>

Compound	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{CSe}}(\text{cm}^{-1})$	$\delta_{\text{NCSe}}(\text{cm}^{-1})$	$\nu_{\text{M-L}}(\text{cm}^{-1})$	Ref
$\text{K}[\text{Ag}(\text{SeCN})_2]$	2105(sh) 2097	540	398 419		A
$\text{Na}_3[\text{Bi}(\text{SeCN})_6]$	2110 2085 2073	548 535	405		B
$(\text{Bu}_4\text{N})_2[\text{Cd}_2(\text{CNSe})_6]^b$	2125(sh) 2109(s)	589(sh) 582(m)	417(w) 408(m)		C
$\text{cat}^{2+}[\text{Co}(\text{NCSe})_4]^c$	2073(vs) 2062(vs)	654(vw)	430(m)	261(s)	D
$(\text{Me}_4\text{N})_4[\text{Co}(\text{NCSe})_6]$	2087(s)	623(w) 606(w)	426(m)	214(s)	D
$(\text{Me}_4\text{N})_3[\text{Cr}(\text{NCSe})_6]$	2167(s) 2141(sh)	668(m) 663(m)			E
$\text{CuL}_2(\text{SeCN})_2^d$	2072(s)	530(m)			F
$(\text{Bu}_4\text{N})_3[\text{Dy}(\text{NCSe})_6]$	2047 <sup>e</sup>	644(s)	434(m)		G
$(\text{Bu}_4\text{N})_3[\text{Er}(\text{NCSe})_6]$	2050 <sup>e</sup>	646(s)	435(m)		G
$\text{cat}^{2+}[\text{Fe}(\text{NCSe})_4]^c$	2062(vs) 2049(vs)	662(vw) 646(vw)	428(w)	249(s)	D
$(\text{Me}_4\text{N})_4[\text{Fe}(\text{NCSe})_6]$	2083(s)	606(w)	422(m)	205(s)	D
$\text{K}_2[\text{Hg}(\text{SeCN})_4]$	2098(s)	543(w)	407(w) 389(w)		H
$(\text{Bu}_4\text{N})_3[\text{Hg}(\text{NCSe})_6]$	2048 <sup>e</sup>	642(s)	433(m)		G
$\text{cat}^{2+}[\text{Mn}(\text{NCSe})_4]^c$	2058(vs) 2049(vs)	649(vw) 636(vw)	429(w)	243(s)	D
$(\text{Me}_4\text{N})_4[\text{Mn}(\text{NCSe})_6]$	2072(s)	623(w)	420(m)	195(s)	D
$(\text{Bu}_4\text{N})_3[\text{Nd}(\text{NCSe})_6]$	2058 <sup>e</sup>	615(s)	428(m)		G
$\text{cat}^{2+}[\text{Ni}(\text{NCSe})_4]^c$	2145(m) 2092(vs) 2075(s)	653(vw)	429(w)	237(s)	D
$(\text{Me}_4\text{N})_4[\text{Ni}(\text{NCSe})_6]$	2096(s)	606(w)	423(m)	237(s)	D
$(\text{Me}_4\text{N})_2[\text{Pd}(\text{SeCN})_4]$	2114(s) 2105(s)	521(w)	410(w) 374(m)	240(m)	D
$(\text{Bu}_4\text{N})_3[\text{Pr}(\text{NCSe})_6]$	2055(br)	619(m)	428(m) 417(w)		G,I
$\text{Cs}_2[\text{Pt}(\text{SeCN})_6]$	2132(s)	522(m)	387(w) 376(w) 363(m)	219(mw) 203(mw)	J
$(\text{Bu}_4\text{N})_2[\text{Pt}(\text{SeCN})_4]$	2105(s) 2060(w)	516(w)			C

TABLE 5 (continued)

Compound	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{CSe}}(\text{cm}^{-1})$	$\delta_{\text{NCSe}}(\text{cm}^{-1})$	$\nu_{\text{M-L}}(\text{cm}^{-1})$	Ref
(Bu <sub>4</sub> N) <sub>3</sub> [Sm(NCSe) <sub>6</sub> ]	2063 <sup>e</sup>	614(s)	425(m)	-	G
TiCp <sub>2</sub> (NCSe) <sub>2</sub> <sup>f</sup>	2050	600 593	457 448	-	K
(Me <sub>4</sub> N) <sub>3</sub> [V(NCSe) <sub>6</sub> ]	2075 2060	663	443	-	L
(Bu <sub>4</sub> N) <sub>2</sub> {VO(NCSe) <sub>4</sub> }	2071(s) 2052(s)	680(m) 600(s)	495(m) 485(sh)	-	M
(Bu <sub>4</sub> N) <sub>3</sub> [Y(NCSe) <sub>6</sub> ]	2067(s) 2030(sh)	634(m)	429(m)	-	C,G
(Et <sub>4</sub> N) <sub>2</sub> [Zn(NCSe) <sub>4</sub> ]	2066(vs)	660(w)	432(m) 415(w)	233(s)	D
Cd(NCSe) <sub>4</sub> Hg <sup>g</sup>	2141 2126 2109	606	407	-	N
(Bu <sub>4</sub> N) <sub>3</sub> {V(NCSe) <sub>6</sub> } <sup>i</sup>	2073(s) 2059(s)	681(m) 664(m)	442(m)	308(s)	M
Co(NCSe) <sub>4</sub> Hg <sup>g</sup>	2135(s)	639(m)	417(w) 403(w)	-	N,H
Cu(NCSe) <sub>4</sub> Hg <sup>g</sup>	2148	597 563	405	-	N,O
Pb(NCSe) <sub>4</sub> Hg <sup>g</sup>	2122	582 564 545	<400	-	O
Zn(NCSe) <sub>4</sub> Hg · H <sub>2</sub> O <sup>g</sup>	2155 2100	627	417 407	-	N
[Hg(SeCN) <sub>3</sub> ] <sub>2</sub> Pb <sup>g</sup>	2140 2124	545 535	<400	-	O
[Hg(SeCN) <sub>3</sub> ] <sub>2</sub> Cu <sup>g</sup>	2160 2141	607 592 570	417 407 -	-	O
[Pd(Et <sub>4</sub> dien)SeCN]Ph <sub>4</sub> B <sup>h</sup>	2121(s)	533(w)	404(w)	282(w)	P
[Pd(Et <sub>4</sub> dien)NCSe]Ph <sub>4</sub> B <sup>h</sup>	2085(s)	618	-	-	P

<sup>a</sup> All spectra taken in nujol mulls except as indicated<sup>b</sup> Proposed structure has 2 bridging and 4 terminal (N-bonded) CNSe groups<sup>c</sup> cat<sup>2+</sup> = [*p*-xylylenebis(triphenylphosphonium)]<sup>2+</sup><sup>d</sup> L = *N,N*-diethyl-1,2-diaminoethane<sup>e</sup> In nitrobenzene solution<sup>f</sup> Cp = (cyclopentadienyl)<sup>-</sup><sup>g</sup> Known or believed to be bridged<sup>h</sup> Et<sub>4</sub>dien = 1,1,7,7-tetraethyldiethylenetriamine<sup>i</sup> KBr pellet

TABLE 5 (continued)

## REFERENCES TO TABLE 5

- A Yu.Ya. Khantonov and G.V. Tsintsadze, *Russ J Inorg Chem*, 10 (1965) 18  
 B V.V. Skopenko, A. Zhurnbau and G.V. Tsintsadze, *Ukr Khim Zh*, 36 (1970) 329  
 C J.L. Burmeister and L.E. Williams, *Inorg Chem*, 5 (1966) 1113  
 D D. Forster and D.M.L. Goodgame, *Inorg Chem*, 4 (1965) 1712  
 E K. Michelsen, *Acta Chem Scand*, 17 (1963) 1811  
 F M.E. Farago and J.M. James, *Inorg Chem*, 4 (1965) 1706.  
 G J.L. Burmeister and E.A. Deardorff, *Inorg Chim Acta*, 4 (1970) 97  
 H A. Turco, C. Pecile and M. Nicolini, *J Chem Soc*, (1962) 3008  
 I J.L. Burmeister, S.D. Patterson and E.A. Deardorff, *Inorg Chim Acta*, 3 (1969) 105  
 J A. Sabatini and I. Bertini, *Inorg Chem*, 4 (1965) 959  
 K J.L. Burmeister, E.A. Deardorff and C.E. Van Dyke, *Inorg Chem*, 8 (1969) 170  
 L V.V. Skopenko and E.I. Ivanova, *Russ J. Inorg Chem*, 14 (1969) 388  
 M H.H. Schmidtke and D. Garthoff, *Z Naturforsch*, 24A (1969) 126  
 N Yu.Ya. Khantonov and V.V. Skopenko, *Russ J Inorg Chem*, 10 (1965) 984  
 O R.M. Alasaniya, V.V. Skopenko and G.V. Tsintsadze, *Tr Gruzinsk Politekhn Inst*, (1967) 21.  
 P J.L. Burmeister, H.J. Gysling and J.C. Lim, *J Amer Chem Soc*, 91 (1969) 44

## (iii) Cyanate complexes

Infrared spectra of cyanate complexes are collected in Table 6. All examples show an increase in  $\nu_{CN}$  and a decrease in  $\delta_{NCO}$  on coordination, and in most of these,  $\nu_{CO}$  is increased, with the Fermi resonance present in the free ion being eliminated. Although mixing makes interpretation of shifts more uncertain for this ion, this is the behavior expected for N-bonding, and there seems little doubt that this is the bonding mode here. Oxygen bonding has been proposed for a few compounds on the basis of a different behavior of the  $\nu_{CO}$  band. In the  $Re^{IV}$  and  $Mo^{III}$  compounds bands near  $1300\text{ cm}^{-1}$  and  $1140\text{ cm}^{-1}$  are explained<sup>38</sup> by Fermi resonance from an overtone of  $\delta_{NCO}$  and the  $\nu_{CO}$  frequency near  $1220\text{ cm}^{-1}$ . This would represent a decrease of the expected magnitude. (The  $Re^V$  compound is tentatively grouped with these, although no  $\nu_{CO}$  bands were seen.) Burmeister et al.<sup>39</sup> have used the same argument with some  $Ti^{IV}$ ,  $Zr^{IV}$  and  $Hf^{IV}$  compounds. In all of these cases, no band assignable to  $\nu_{CO}$  was seen above the free-ion value. Unfortunately in the above compounds, rather complex organic spectra are present in these regions which raise some possibility of the appearance of new bands through symmetry effects, or the cyanate bands may be obscured by ligand absorption. While there is some other evidence for O-bonding in these cases, an absolute determination of bonding mode here would lead to a good deal more confidence in the existence of this linkage type and in the reliability of this infrared criterion.

Several compounds included in Table 6 require further comment. One,  $K_2[Hg(OCN)_4]$ , is listed as oxygen-bonded, and if confirmed would be very interesting in comparison with  $K[Hg(NCO)_3]$ . However, confidence in the assignments given for these and for the silver complex described by the same authors<sup>61</sup> is shaken by a certain arbitrariness and by the presence of as many as 20 other frequencies spread over the spectrum. Some of these may be accounted for as overtones or combination bands but most seem inexplicable if the complexes are pure compounds of the formulae given. No analytical data or preparation details are provided.

TABLE 6

Infrared spectra of cyanate complexes<sup>a</sup>

Compound	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{CO}}(\text{cm}^{-1})$	$\delta_{\text{NCO}}(\text{cm}^{-1})$	$\nu_{\text{ML}}(\text{cm}^{-1})$	Ref.
$\text{K}[\text{Ag}(\text{NCO})_2]$ <sup>b</sup>	2215 2165	1318 1303	665 638 629 608 598		A
$(\text{Ph}_4\text{As})[\text{Au}(\text{NCO})_2]$ <sup>e</sup>	2251(s) 2179(sh)	1355(m)			B
$(\text{Et}_4\text{N})_2[\text{Cd}(\text{NCO})_4]$	2262(sh) 2174(vs)	1328(w)	621(s)	298(s)	C
$\text{K}[\text{Cd}(\text{NCO})_3]$ <sup>b,c</sup>	2246 2203 2151 2140 2113 2088	1368 1350 1300 1291	658 646 620	290 280	D
$\text{K}[\text{Cd}(\text{NCO})_3]$ <sup>c</sup>	2250 2202	1328	680 647 625 620		E
$(\text{Et}_4\text{N})_2[\text{Co}(\text{NCO})_4]$	2217(sh) 2179(vs)	1335(w)	620(m) 617(sh)	345(s) 213(m)	C
$[\text{Co}(\text{NH}_3)_5(\text{NCO})](\text{ClO}_4)_2$	2265	1335			F
$\text{Et}_4\text{N}[\text{Cr}(\text{CO})_5(\text{NCO})]$	2224(m) <sup>d</sup>	1288(s-m)	595(s)	280	G
$(\text{Ph}_4\text{As})_3[\text{Cr}(\text{NCO})_6]$	2205(s)	1335(m)	619(m) 601(m)	345(s)	H
$(\text{Et}_4\text{N})_2[\text{Cu}(\text{NCO})_4]$	2247(sh) 2183(vs)	1328(w)	619(m) 617(m) 612(sh)	338(s)	C
$\text{K}[\text{Cu}(\text{NCO})_3]$ <sup>b,c</sup>	2270 2251 2220 2163 2150 2105	1348 1318	703 660 642 609	400 355 340 320	D
$(\text{Bu}_4\text{N})_3[\text{Er}(\text{NCO})_6]$	2155(s)	1322(m)	608(m)		I
$(\text{Et}_4\text{N})_2[\text{Fe}(\text{NCO})_4]$	2182(vs)	1337(w)	619(m)	325(s)	C
$(\text{Ph}_4\text{As})[\text{Fe}(\text{NCO})_4]$	2208(sh) 2171(vs)	1370(vw)	626(m) 619(m)	410(s) [239(w)]	C
$\text{HfCp}_2(\text{OCN})_2$ <sup>e,f</sup>	2246(s) 2211(s)	1257(w) <sup>g</sup> 1071(sh)	632(m) 606(m)		J

TABLE 6 (continued)

Compound	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{CO}}(\text{cm}^{-1})$	$\delta_{\text{NCO}}(\text{cm}^{-1})$	$\nu_{\text{ML}}(\text{cm}^{-1})$	Ref
$\text{K}[\text{Hg}(\text{NCO})_3]^b$	2295 2195 2132	1380 1305	665 638 628 618 610		A
$\text{K}_2[\text{Hg}(\text{OCN})_4]^b$	2150	1162	666 638 590		A
$\text{InPy}_3(\text{NCO})_3^h$	2210 2190(sh)			334(m) 309(m)	K
$\text{Ir}(\text{Ph}_3\text{P})_2(\text{CO})(\text{NCO})^e$	2240(s)	1353(s-m)			B
$(\text{Et}_4\text{N})_2[\text{Mn}(\text{NCO})_4]$	2222(sh) 2174(vs)	1335(m)	623(s)	325(s)	C
$(\text{Ph}_4\text{As})_3[\text{Mo}(\text{OCN})_6]^e$	2205(s)	1296(m) <sup>g</sup> 1140(m)	595(m)		L
$(\text{Et}_4\text{N})[\text{Mo}(\text{CO})_5(\text{NCO})]$	2220(s) <sup>d</sup>	1302(s) <sup>e</sup>			G
$(\text{Et}_4\text{N})_2[\text{Ni}(\text{NCO})_4]$	2237(sh) 2186(vs)	1330(w)	619(sh) 617(s)	341(s)	C
$(\text{Me}_4\text{N})_2[\text{Pd}(\text{NCO})_4]$	2190- 2200(s)	1319(m)	637(vw) 613(m) 604(m) 594(s)	408(sh) 384(s) 350(sh) 274(vw)	M
$(\text{Ph}_4\text{As})_2[\text{Pt}(\text{NCO})_4]$	2252(sh) 2235- 2245(s)	1322(m)	587(vw) 577(vw)		N
$(\text{Ph}_4\text{As})_2[\text{Re}(\text{OCN})_6]^e$	2224(s)	1306(w) <sup>g</sup> 1138(w)	595(m)		L
$(\text{Ph}_4\text{As})[\text{Re}(\text{OCN})_6]^e$	2220(s)				L
$\text{Rh}(\text{Ph}_3\text{P})_2(\text{CO})\text{NCO}^e$	2239(s)	1340(m)			B
$(\text{Me}_4\text{N})_2[\text{Sn}(\text{NCO})_6]$	2270(sh) 2188(vs)	1307(vw)	667(sh) 622(s,br)	383(vs) [235(s)] [216(s)]	M
$\text{TiCp}_2(\text{OCN})_2^{e,f}$	2235(s) 2196(s)	1132(m) <sup>g</sup>	626(m) 593(m)		J
$\text{TiCp}_2(\text{NCO})^{e,f}$	2216(s)	1302(m-s)	599(m) 590(m)		J
$(\text{Et}_4\text{N})_2[\text{UO}_2(\text{NCO})_4]$	2193(s)	1322(w)	656(m) 620(m)	276(s) 262(s)	H
$\text{VCp}_2(\text{NCO})_2^{e,f}$	2239(s) 2213(s)	1329(m-s)	603(m) 592(m)		J
$(\text{Et}_4\text{N})[\text{W}(\text{CO})_5\text{NCO}]$	2230(m) <sup>d</sup>	1320(m) <sup>e</sup>	592(m)	292(m)	G

TABLE 6 (continued)

Compound	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{CO}}(\text{cm}^{-1})$	$\delta_{\text{NCO}}(\text{cm}^{-1})$	$\nu_{\text{ML}}(\text{cm}^{-1})$	Ref.
(Et <sub>4</sub> N)[Zn(NCO) <sub>4</sub> ]	2174(vs)	1335(w)	623(s)	321(s)	C
ZrCp <sub>2</sub> (OCN) <sub>2</sub> <sup>e,f</sup>	2233(s)	1257(w) <sup>g</sup>	631(m)		J
	2200(s)	1070(sh)	607(m)		

<sup>a</sup> Mull spectra except as noted<sup>b</sup> See discussion in text<sup>c</sup> Possibly bridged<sup>d</sup> In acetone solution<sup>e</sup> KBr pellet<sup>f</sup> Cp = (cyclopentadienyl)<sup>-</sup><sup>g</sup> Fermi resonance between  $\nu_{\text{CO}}$  and  $2\delta_{\text{NCO}}$  is proposed<sup>h</sup> Py = pyridine

## REFERENCES TO TABLE 6

- A G V. Tsintsadze, A Yu Tsivadze and Ts L. Makhataidze, *Sobshch Akad Nauk Gruz, SSR*, 56 (1969) 301.  
 B W Beck, W P Fehlhammer, P. Pollmann and H. Schachl, *Chem Ber*, 102 (1969) 1976  
 C D Forster and D M L Goodgame, *J Chem Soc*, (1965) 262  
 D A Yu Tsivadze, G V Tsintsadze, Yu Ya Kharitonov, A M Golub and A M Mamulashvili, *Zh Neorg Khim*, 15 (1970) 1818  
 E J L. Burmeister and T P O'Sullivan, *Inorg Chim Acta*, 3 (1969) 479  
 F R J. Balahura and R B. Jordan, *Inorg Chem*, 9 (1970) 1567  
 G W Beck, H Werner, H. Engelmann and H.S. Smedal, *Chem. Ber.*, 101 (1968) 2143.  
 H R A. Bailey and T W Michelsen, unpublished results  
 I J L. Burmeister, S D Patterson and E A Deardorff, *Inorg Chim Acta*, 3 (1969) 105  
 J J L. Burmeister, E A. Deardorff, A. Jensen and V H Christiansen, *Inorg Chem*, 9 (1970) 58  
 K S J. Patel and D G Tuck, *J Chem Soc*, (1968) 1870.  
 L R A. Bailey and S L Kozak, *J Inorg Nucl Chem*, 31 (1969) 689  
 M D Forster and D M L Goodgame, *J Chem Soc*, (1965) 1286  
 N A H Norbury and A I P Sinha, *J Chem Soc*, (1968) 1598.

The spectrum of the [Cu(NCO)<sub>3</sub>]<sup>-</sup> compound in Table 6 is also questionable in view of the large number of peaks; this and the spectrum<sup>62</sup> of K[Cd(NCO)<sub>3</sub>] are to be compared with the data for the latter compound by Burmeister and O'Sullivan<sup>63</sup> also included. They are very likely bridged

The only established mode of bridging for cyanate is >NCO. This has been discussed by Nelson and Nelson<sup>64</sup>, some of whose data are summarized in Table 7. The  $\nu_{\text{CN}}$  band is not diagnostic for bridging; the frequency is less for bridged than for non-bridged complexes of the same metal, but this is a very small effect, well within the shift caused by changes of other ligands. The  $\nu_{\text{CO}}$  band is 30–60 cm<sup>-1</sup> lower in bridged than in non-bridged examples, and has a much reduced intensity. Still more diagnostic is the splitting of  $\delta_{\text{NCO}}$ . This is often split in terminally bonded NCO<sup>-</sup> groups, but only by a few wave numbers. In bridged compounds, splitting is 30–50 cm<sup>-1</sup> (correlating with the ionization potential of the metal) with the high-energy component near or above 600 cm<sup>-1</sup>. (The O-bonded cyclopentadienyl compounds in Table 5 show nearly 30 cm<sup>-1</sup> splitting, but the high component is much lower.) This has been explained<sup>64</sup> on the basis of the bent M–NCO group necessary for bridging of this sort, while terminal N-bonding gives a more nearly linear grouping.



TABLE 7

Infrared spectra of bridged and terminal cyanates<sup>a</sup>

Compound <sup>b</sup>	Structure <sup>c</sup>	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{CS}}(\text{cm}^{-1})$	$\delta_{\text{NCO}}(\text{cm}^{-1})$
MnL <sub>2</sub> (NCO) <sub>2</sub>	Bridged	2185s	1300w	658, 629m
MnL <sub>4</sub> (NCO) <sub>2</sub>	Terminal	2205s	1334m	628, 620m
FeL <sub>2</sub> (NCO) <sub>2</sub>	Bridged	2180s	1305w	661, 622m
FeL <sub>4</sub> (NCO) <sub>2</sub>	Terminal	2216s	1350m	620, 613m
CoL <sub>2</sub> (NCO) <sub>2</sub>	Bridged	2185s	1303w	667, 623m
CoL <sub>4</sub> (NCO) <sub>2</sub>	Terminal	2222s	1334m	620, 613m
NiL <sub>2</sub> (NCO) <sub>2</sub>	Bridged	2180s	1300w	671, 621m
NiL <sub>4</sub> (NCO) <sub>2</sub>	Terminal	2222s	1330m	620, 612m
AgNCO	Bridged	2170s	1350w	657, 598m

<sup>a</sup> Taken from J. Nelson and S. M. Nelson, *J. Chem. Soc.*, (1969) 1597.<sup>b</sup> L = 3-cyanopyridine<sup>c</sup> Bridged in the form  $\begin{array}{c} \text{M} \\ \diagup \quad \diagdown \\ \text{NCO} \end{array}$ 

Attempts to change the bonding mode of cyanate ligands as has been done with the thiocyanate and selenocyanate have been unsuccessful<sup>22,63</sup>, this ligand is much less sensitive to both electronic and steric effects. Discussion is given by Norbury and Sinha<sup>22</sup>.

TABLE 8

Infrared spectra of fulminate complexes<sup>a</sup>

Compound	$2\nu_{\text{NO}}(\text{cm}^{-1})$ ( $2\nu_s$ )	$\nu_{\text{CN}}(\text{cm}^{-1})$ ( $\nu_{\text{as}}$ )	$\nu_{\text{NO}}(\text{cm}^{-1})$ ( $\nu_s$ )	$\delta_{\text{NCO}}(\text{cm}^{-1})$	Ref
[Co(phen) <sub>3</sub> ] <sub>3</sub> [Co(CNO) <sub>6</sub> ] <sub>2</sub> ·10H <sub>2</sub> O <sup>b</sup>	2229(m)	2154(m-s)	1100(s)		A
[Cr(en) <sub>3</sub> ][Co(CNO) <sub>6</sub> ]·3H <sub>2</sub> O	2241(m-s)	2161(m)	1097(s)		B
Na <sub>4</sub> [Fe(CNO) <sub>6</sub> ]·18H <sub>2</sub> O		2195(m) 2147(w,sh) 2057(w)	1049(s)		B
[Fe(phen) <sub>2</sub> (CNO) <sub>2</sub> ]·H <sub>2</sub> O <sup>b</sup>	2200(m)	2119(m)	1101(s) 1085(s)		A
Na <sub>4</sub> [Fe(CN) <sub>5</sub> CNO]· $\frac{3}{2}$ H <sub>2</sub> O		2187(m)	1050(s)	465(w)	C
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeCNO	2540(m)	2164(s)	1276(m)		D
(Ph <sub>4</sub> As) <sub>2</sub> [Hg(CNO) <sub>4</sub> ]	2336(m) 2294(m)	2154(s) 2136(s)	1156(s) 1138(s)	485(w)	E
Hg(CNO) <sub>4</sub> <sup>c</sup>	2405(m)	2200(s)	1205(s)	488(m) 481(m)	F
K <sub>2</sub> [Hg(CNO) <sub>4</sub> ]	2270(m)	2130(s)	1143(s)		E

TABLE 8 (continued)

Compound	$2\nu_{\text{NO}}(\text{cm}^{-1})$ ( $2\nu_s$ )	$\nu_{\text{CN}}(\text{cm}^{-1})$ ( $\nu_{\text{as}}$ )	$\nu_{\text{NO}}(\text{cm}^{-1})$ ( $\nu_s$ )	$\delta_{\text{NCO}}(\text{cm}^{-1})$	Ref
$[\text{Mn}(\text{phen})_2(\text{CNO})_2] \cdot \frac{1}{3} \text{H}_2\text{O}^b$	2274(w) 2184(w)	2076(s) 2067(sh)	1140(s)	497(m) 492(m)	A
$\text{Na}_2[\text{Ni}(\text{CNO})_4] \cdot 5\text{H}_2\text{O}$	2263(s)	2184(m)	1122(s)	479(m) 470(m)	G
$[\text{Ni}(\text{phen})_3][\text{Ni}(\text{CNO})_4] \cdot \text{H}_2\text{O}^b$	2257(w-m)	2151(s)	1126(s)	502(m) 483(m-s)	A
$(\text{C}_6\text{H}_5)_3\text{PbCNO}$	2294(m)	2123(s)	1149(s)	492(m) <sup>d</sup> 483(m)	D
<i>trans</i> -( $\text{P}(\text{C}_2\text{H}_5)_3$ ) <sub>2</sub> PtHCNO	2268(m)	2110(s)	1136(s)	463(m)	H
$\text{Na}_2[\text{Pd}(\text{CNO})_4] \cdot 5\text{H}_2\text{O}^e$	2269(s)	2188(s)	1127(s)	465(m)	G
$\text{Na}_2[\text{Pt}(\text{CNO})_4] \cdot 5\text{H}_2\text{O}$	2276(s)	2193(s)	1122(s)	482(m) 464(m-s)	G
$(\text{C}_6\text{H}_5)_3\text{SnCNO}$	2315(w-m)	2156(s)	1165(s)	499(m) <sup>d</sup> 484(m)	D
$\text{K}[\text{Ag}(\text{CNO})_2]^f$		2070 2175	1145 1182	480 470 460	I

<sup>a</sup> In nujol except as indicated<sup>b</sup> phen = *o*-phenanthroline<sup>c</sup>  $\nu_{\text{Hg-CNO}}$ , 340(s).<sup>d</sup> Assigned as  $\nu_{\text{Me-CNO}}$ <sup>e</sup> KBr pellet<sup>f</sup> Spectrum of questionable validity

## REFERENCES TO TABLE 8

- A W. Beck and E. Schuierer, *Chem. Ber.*, 95 (1962) 3048  
 B W. Beck, *Z. Naturforsch.*, 17b (1962) 130.  
 C W. Beck, *Z. Anorg. Allgem. Chem.*, 333 (1964) 115.  
 D W. Beck and E. Schuierer, *Chem. Ber.*, 97 (1964) 3517  
 E W. Beck and E. Schuierer, *Z. Anorg. Allgem. Chem.*, 347 (1966) 304  
 F W. Beck and E. Schuierer, *J. Organometal. Chem.*, 3 (1965) 55.  
 G W. Beck and E. Schuierer, *Chem. Ber.*, 98 (1965) 298  
 H W. Beck and K. Feldt, *Z. Naturforsch.*, 21b (1966) 588.  
 I G.V. Tsintsadze, A.Y. Tsivadze and Ts. L. Makhatadze, *Soboch Akad. Nauk Gruz. SSR*, 56 (1969) 301.

## (iv) Fulminate complexes

Infrared spectra for most of the known fulminate complexes are given in Table 8. All of these are presumed to be bonded through carbon, and all bonds show increases in frequency, with the exception of  $\nu_{\text{NO}}$  in some of the  $\text{Fe}^{\text{II}}$  compounds. There does not seem to be any evidence to indicate that the small decrease here is due to a different bonding type. One bridged example ( $\text{Fe}^{\text{II}}\text{-CNO-BF}_3$ ) is suggested, but only the  $\nu_{\text{CN}}$  band is reported<sup>65</sup> at  $2200 \text{ cm}^{-1}$ . This is higher than usual. A band assignable to the first overtone of  $\nu_{\text{NO}}$  is seen in most examples between  $2290 \text{ cm}^{-1}$  and  $2300 \text{ cm}^{-1}$ . Considerable sensitivity of band positions to counter ions and to other ligands is evident.

TABLE 9

Integrated intensity data for thiocyanate complexes

Complex	Solvent	$\Delta\nu_{\frac{1}{2}}(\text{cm}^{-1})$	$\nu_{\text{max}}(\text{cm}^{-1})$	$A(\times 10^{-4} \text{ M}^{-1} \text{ cm}^{-2})$	Ref
$\text{K}[\text{Au}(\text{SCN})_4]$	Acetonitrile	13	2132	0.5	A
$(\text{Et}_4\text{N})_3[\text{Ce}(\text{NCS})_6]^a$	Nitromethane	44	2057	5.6	A
$(\text{Et}_4\text{N})_2[\text{Co}(\text{NCS})_4]$	Acetone	22	2074	8.8	A
$\text{K}_3[\text{Cr}(\text{NCS})_6]$	Acetone	20	2096	8.5	A
$(\text{Bu}_4\text{N})_3[\text{Dy}(\text{NCS})_6]$	Acetonitrile		2052	18	C
$(\text{Bu}_4\text{N})_3[\text{Er}(\text{NCS})_6]$	Methanol		2050	32	C
$(\text{Et}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$	Acetone	38	2062	15.2	A
$(\text{Bu}_4\text{N})_3[\text{Gd}(\text{NCS})_6]$	Methanol		2045	24	C
$(\text{Et}_4\text{N})_2[\text{Hf}(\text{NCS})_6]$	Acetonitrile	20	2030	9.9	A
$\text{K}_2[\text{Hg}(\text{SCN})_4]$	Acetone	17	2113	2.12	B
$(\text{Bu}_4\text{N})_3[\text{Ho}(\text{NCS})_6]$	Methanol		2045	32	C
$\text{Cs}_3[\text{Mo}(\text{NCS})_6]$	Acetone	18	2069	10.5	A
$(\text{Et}_4\text{N})_3[\text{Nd}(\text{NCS})_6]^a$	Acetone	23.4	2057	5.6	A
$(\text{Bu}_4\text{N})_3[\text{Nd}(\text{NCS})_6]$	Methanol		2046	17	C
$(\text{Et}_4\text{N})_4[\text{Ni}(\text{NCS})_6]$	Acetone	31	2089	6.2 <sup>b</sup>	A
		14	2059		
$(\text{Bu}_4\text{N})_3[\text{Os}(\text{NCS})_6]$	Acetone	41.6	2066	8.9 <sup>b</sup>	A
		36.4	2106		
$\text{K}_2[\text{Pd}(\text{SCN})_4]$	Acetone	12	2110	1.5	A
$\text{Pd}(\text{ASP})(\text{SCN})(\text{NCS})^c$	Dichloromethane	17.2	2118	4.2	D
		53.6	2085	8.2	
$\text{Pd}(\text{PP})(\text{SCN})(\text{NCS})^d$	Dichloromethane	14	2121	2.5	D
		41	2086	10.7	
$\text{Pd}(\text{PC}_2\text{N})(\text{SCN})(\text{NCS})^e$	Nitromethane	14	2125	1.76	D
		24	2089	9.68	
$(\text{Bu}_4\text{N})_3[\text{Pr}(\text{NCS})_6]$	Acetonitrile		2059	13	C
$\text{K}_2[\text{Pt}(\text{SCN})_4]$	Acetone	12	2115	2.3	A
$\text{K}_2[\text{Pt}(\text{SCN})_6]$	Acetone	11	2123	0.7	A
$\text{Cs}_2[\text{Re}(\text{CNS})_6]$	Acetone	20	2047	15.8	A
$\text{Cs}[\text{Re}(\text{CNS})_6]$	Acetone	31	2086	10.7	A
$(\text{Bu}_4\text{N})_3[\text{Rh}(\text{SCN})_6]$	Acetone	17	2126	2.4 <sup>b</sup>	A
		22	2106		
$(\text{Bu}_4\text{N})_3[\text{Ru}(\text{NCS})_6]$	Acetone	32.2	2090	7.1 <sup>b</sup>	A
		28.6	2190		
$(\text{Et}_4\text{N})_3[\text{Ce}(\text{NCS})_6]^a$	Nitromethane	44	2057	5.6	A
$(\text{Bu}_4\text{N})_3[\text{Sm}(\text{NCS})_6]$	Acetonitrile		2059	13	C

TABLE 9 (continued)

Complex	Solvent	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$\nu_{\text{max}}(\text{cm}^{-1})$	$A(\times 10^{-4} M^{-1} \text{ cm})$	Ref
$(\text{Bu}_4\text{N})_3[\text{Tb}(\text{NCS})_6]$	Methanol		2050	21	C
$\text{Cs}_4[\text{U}(\text{NCS})_8]$	Acetonitrile	36	2052	13.0	A
$\text{Cs}_3[\text{UO}_2(\text{NCS})_5]$	Acetone	24	2057	11.6	A
$(\text{Et}_4\text{N})_3[\text{V}(\text{NCS})_6]$	Acetone	24	2074	12.3	A
$(\text{Et}_4\text{N})_2[\text{VO}(\text{NCS})_4]$	Acetonitrile	14 31	2086 2073	13.3 <sup>b</sup>	A
$(\text{Et}_4\text{N})_2[\text{Zn}(\text{NCS})_4]$	Acetonitrile	20	2071	9.2	A
$(\text{Et}_4\text{N})_2[\text{Zr}(\text{NCS})_6]$	Acetone	20	2000	13.5	A
$(\text{Et}_4\text{N})_3[\text{Yb}(\text{NCS})_6]$	Nitromethane	19	2053	10.5	A
$(\text{Bu}_4\text{N})_3[\text{Yb}(\text{NCS})_6]$	Methanol		2048	30	C

<sup>a</sup> Dissociated in solution<sup>b</sup> Sum for both peaks<sup>c</sup> ASP = diphenyl(*o*-diphenylarsinophenyl)phosphine<sup>d</sup> PP = 1,2-bis(diphenylphosphino)ethane<sup>e</sup> PC<sub>2</sub>N = diphenyl(2-dimethylaminoethyl)phosphine

## REFERENCES TO TABLE 9

A R. A. Bailey, T. W. Michelsen and W. N. Mills, *J. Inorg. Nucl. Chem.*, in pressB C. Pecile, *Inorg. Chem.*, 5 (1966) 210C J. L. Burmeister, S. D. Patterson and E. A. Deardorff, *Inorg. Chim. Acta*, 3 (1969) 105D D. W. Meek, P. E. Nicpon and V. I. Meek, *J. Amer. Chem. Soc.*, 92 (1970) 5351*(v) Intensity considerations*

The values found for the integrated intensities of thiocyanate complexes are given in Table 9. The integrated intensities, generally, are determined using Ramsay's method of direct integration<sup>66</sup>. This uses the equation

$$\text{Area} = \frac{K}{cl} \ln \left( \frac{T_0}{T} \right)_{\nu_{\text{max}}} \Delta\nu_{1/2}^a$$

where  $K$  is a correction factor which relates the actual absorbance and half band width to the measured values,  $\Delta\nu_{1/2}^a$  is the apparent band width at half the absorption maximum,  $c$  is the molar concentration,  $l$  is the cell thickness,  $T$  is the transmittance of the sample solution, and  $T_0$  that of the solvent, at the absorption maximum.  $K$  can be taken as  $\pi/2$  for most cases where slit width/apparent band width at half intensity is less than 0.40.

There is little question that this is a legitimate criterion for distinguishing bonding mode, but considerable care must be taken in interpreting the results. Many peaks are not simple in solution, and this clearly is evident when scale expansion is used to minimize measurement errors. In order to arrive at a reasonable estimate of integrated intensity by Ramsay's method of direct integration<sup>66</sup>, these must be resolved into their components

The origin of the several peaks must also be considered. In many cases this may be due to a lack of the regular octahedral or other symmetry which predicts degeneracy of the stretching modes of each C—N group; many complexes are inherently irregular as mentioned. However, in solution measurements, partial dissociation or reaction with solvent to give a mixture of species may take place, and a component falling in the position of "free" thiocyanate is suggestive of this. As a consequence, values are increased for S-bonded, and decreased for N-bonded cases if total area is used. Knowing the intensity of free  $\text{CNS}^-$ , this effect can be corrected for. However, distinguishing free  $\text{CNS}^-$  remains a major uncertainty. The  $\text{Ni}^{\text{II}}$  compound which gives an intermediate value of intensity (Table 9) may be an example of such dissociation. If the component at  $2058\text{ cm}^{-1}$  in this example is considered to be free thiocyanate, it would imply a loss of 2 ligands and the second component gives a good value ( $8.1 \times 10^4$ ) for N-bonding. The same type of observation was made for the rare earth complexes, most of which are known to be at least partially dissociated in solution<sup>67</sup> and indeed most are completely dissociated here. The most stable, Yb, gave an integrated intensity as expected for an N-bonded case with little free  $\text{CNS}^-$  apparent. Burmeister et al.<sup>68</sup>, on the other hand, report no dissociation in acetonitrile and methanol solutions, and find exceptionally large values for the integrated intensities of some of them.

The choice of solvent is of some importance in making these measurements, as it will affect the shape and intensity of the peak (as well as possible dissociation reactions). In general, hydrogen bonded solvents such as alcohols produce considerable broadening, but the integrated intensity values seem to vary by only a small amount from solvent to solvent. Little comparative work in different solvents is available, however. A few values of  $\text{KCNS}$  which illustrate the magnitude of the effect are<sup>16</sup>:  $(\text{CH}_3)_2\text{CO}$ , 4.4,  $\text{HCON}(\text{CH}_3)_2$ , 4.4,  $\text{H}_2\text{O}$ , 5.7,  $\text{C}_2\text{H}_5\text{OH}$ ,  $7.2 \times 10^4\text{ M}^{-1}\text{cm}^{-2}$ . It has also been reported that the nature of the solvent can determine the bonding mode of thiocyanate in solution<sup>69</sup> (solvation energy may stabilize one form preferentially) and awareness of this possibility is essential.

The integrated intensity values of the Os and Ru compounds (Table 9) show that these are indeed N-bonded, while the Rh compound is S-bonded<sup>6</sup> and illustrate the advantage of intensity data over the purely positional criteria.

Application of the intensity criterion to selenocyanate complexes gives similar results as for thiocyanates. Intensities as shown in Table 10 are above the free ion value (over  $5 \times 10^4\text{ M}^{-1}\text{cm}^{-1}$ ) for systems for which positional and other indications imply N-bonding, while below this (less than  $2 \times 10^5\text{ M}^{-1}\text{cm}^{-1}$ ) for Se-bonding. The same limitations apply. The analogous behavior of the  $\text{Ni}^{\text{II}}\text{NCSe}^-$  and  $\text{NCS}^-$  compounds is notable.

The integrated intensity of the  $\nu_{\text{CN}}$  band of cyanates has been measured<sup>22,39,49</sup> with results which are summarized in Table 11. All values lie above that for the free ion, including the  $\text{Ti}^{\text{IV}}$ ,  $\text{Zr}^{\text{IV}}$  and  $\text{Hf}^{\text{IV}}$  compounds believed to be O-bonded. Indeed, two peaks are reported for these, both of a high intensity. A simple argument as to the intensity change to be expected in this case does not take account of the effects of mixing of the vibrational modes, and it is not clear if these observations can be justified for an O-bonded cyanate. In any event, it provides no support for the oxygen-bonded interpretation.

An attempt to extend the intensity criterion to insoluble materials has been made using an internal standard technique<sup>70</sup>. The C—O (carbonyl stretching) band of salicylic

TABLE 10

Integrated intensities of  $\nu_{\text{CN}}$  for complexes of the selenocyanate ion<sup>a</sup>

Compound	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$\epsilon_{\text{max}}$	$A(\times 10^{-4} M^{-1} \text{cm}^{-2})$	Ref
KCNSe	2068	16	307	1.8	A
KCNSe <sup>b</sup>	2069	18	470	3.1	B
(Bu <sub>4</sub> N) <sub>2</sub> [Cd <sub>2</sub> (NCSe) <sub>6</sub> ] <sup>c</sup>	2120	16	557	3.2	A
	2076	24	300	2.6	
(Et <sub>4</sub> N) <sub>2</sub> [Co(NCSe) <sub>4</sub> ]	2070	20	1400	9.5	B
CrCp(NO) <sub>2</sub> (NCSe) <sup>d,e</sup>	2104			5.71	C
(Bu <sub>4</sub> N) <sub>3</sub> [Dy(NCSe) <sub>6</sub> ] <sup>f</sup>	2047			16	D
(Bu <sub>4</sub> N) <sub>3</sub> [Er(NCSe) <sub>6</sub> ] <sup>f</sup>	2050			17	D
(Bu <sub>4</sub> N) <sub>2</sub> [Fe(NCSe) <sub>4</sub> ]	2064	27	1080	11	A
(Bu <sub>4</sub> N) <sub>4</sub> [Fe(NCSe) <sub>6</sub> ]	2064	27	1050	10	A
FeCp(CO) <sub>2</sub> (SeCN) <sup>d,e</sup>	2126			0.81	C
(Bu <sub>4</sub> N) <sub>3</sub> [Ho(NCSe) <sub>6</sub> ] <sup>f</sup>	2048			17	D
K <sub>2</sub> [Hg(SeCN) <sub>4</sub> ]	2116	16	245	1.45	B
MoCp(CO) <sub>3</sub> (SeCN) <sup>d,e</sup>	2130			1.07	C
(Bu <sub>4</sub> N) <sub>4</sub> [Mn(NCSe) <sub>6</sub> ]	2064	26	920	8.7	A
(Bu <sub>4</sub> N) <sub>3</sub> [Nd(NCSe) <sub>6</sub> ] <sup>f</sup>	2058			12	D
(Bu <sub>4</sub> N) <sub>4</sub> [Ni(NCSe) <sub>6</sub> ]	2100	30	364	4.0	A
	2070	20	210	1.5	
(Bu <sub>4</sub> N) <sub>2</sub> [Pd(SeCN) <sub>4</sub> ]	2113	10	170	0.62	A
[Pd(Et <sub>4</sub> dien)SeCN]Ph <sub>4</sub> B <sup>g</sup>	2125			0.63	E
[Pd(Et <sub>4</sub> dien)NCSe]Ph <sub>4</sub> B <sup>g</sup>	2089			6.6	E
[Pd(dien)SeCN]Ph <sub>4</sub> B	2127			0.85	E
(Bu <sub>4</sub> N) <sub>3</sub> [Pr(NCSe) <sub>6</sub> ] <sup>f</sup>	2058			10	D
(Bu <sub>4</sub> N) <sub>2</sub> [Pt(SeCN) <sub>4</sub> ]	2117	13	124	0.59	A
K <sub>2</sub> [Pt(SeCN) <sub>6</sub> ]	2122	14	127	0.55	B
(Bu <sub>4</sub> N) <sub>3</sub> [Rh(SeCN) <sub>6</sub> ]	2107	15	176	0.96	A
(Bu <sub>4</sub> N) <sub>3</sub> [Sm(NCSe) <sub>6</sub> ] <sup>f</sup>	2063			11	D
TiCp(NCSe) <sub>2</sub> <sup>d,e</sup>	2050			12	F
	2015			10	
WCp(CO) <sub>3</sub> (SeCN) <sup>d,e</sup>	2132			0.81	C
(Bu <sub>4</sub> N) <sub>3</sub> [Y(NCSe) <sub>6</sub> ]	2068	27	514	5.0	A
(Bu <sub>4</sub> N) <sub>2</sub> [Zn(NCSe) <sub>4</sub> ]	2087	25	1050	9.5	A

<sup>a</sup> In acetone except as noted.<sup>b</sup> In CH<sub>3</sub>COC<sub>2</sub>H<sub>5</sub>.<sup>c</sup> Proposed structure. 4 terminal NCSe (1st entry), 2 bridged -NCSe- (2nd entry).

TABLE 10 (continued)

<sup>d</sup> Cp = (cyclopentadienyl)<sup>-</sup>.<sup>e</sup> In chloroform.<sup>f</sup> In nitrobenzene<sup>g</sup> Et<sub>4</sub>dien = 1,1,7,7-tetraethyldiethylenetriamine.

## REFERENCES TO TABLE 10

A J.L. Burmeister and I. E. Williams, *Inorg. Chem.*, 5 (1966) 1113B C. Pecile, *Inorg. Chem.*, 5 (1966) 210C M.A. Jennings and A. Wojcicki, *J. Organometal. Chem.*, 14 (1968) 231D J.L. Burmeister and E. A. Deardorff, *Inorg. Chim. Acta*, 4 (1970) 97.E J.L. Burmeister, H. J. Gysling and J. C. Lim, *J. Amer. Chem. Soc.*, 91 (1969) 44F J.L. Burmeister, E. A. Deardorff and C. E. Van Dyke, *Inorg. Chem.*, 8 (1969) 170

TABLE 11

Integrated intensities of the  $\nu_{\text{CN}}$  band of complexes of the cyanate ion

Compound	$\nu_{\text{CN}}(\text{cm}^{-1})$	$\Delta\nu_{1/2}(\text{cm}^{-1})$	$\epsilon$	$A(\times 10^{-4} \text{ M}^{-1} \text{ cm}^{-2})$	Ref.
Ph <sub>4</sub> AsNCO <sup>a</sup>	2158	25	925	8.4	A
(Et <sub>4</sub> N) <sub>2</sub> [Co(NCO) <sub>4</sub> ] <sup>b</sup>	2208			16	B
(Et <sub>4</sub> N) <sub>2</sub> [Cd(NCO) <sub>4</sub> ] <sup>b</sup>	2193			14	B
(Et <sub>4</sub> N) <sub>2</sub> [Cu(NCO) <sub>4</sub> ] <sup>b</sup>	2225			12	B
HfCp <sub>2</sub> (OCN) <sub>2</sub> <sup>c</sup>	2246			12	C
	2211			18	
(Et <sub>4</sub> N) <sub>2</sub> [Mn(NCO) <sub>4</sub> ] <sup>b</sup>	2198			15	B
(Et <sub>4</sub> N) <sub>2</sub> [Ni(NCO) <sub>4</sub> ] <sup>b</sup>	2205			13	B
(Me <sub>4</sub> N) <sub>2</sub> [Pd(NCO) <sub>4</sub> ] <sup>a</sup>	2202	58	809	17.0	A
(Et <sub>4</sub> N) <sub>2</sub> [Pt(NCO) <sub>4</sub> ] <sup>a</sup>	2252	42	968	14.8	A
TiCp <sub>2</sub> (OCN) <sub>2</sub> <sup>c</sup>	2235			13	C
	2196			18	
VCp <sub>2</sub> (NCO) <sub>2</sub> <sup>c</sup>	2239			14	C
	2213			15	
(Et <sub>4</sub> N) <sub>2</sub> [Zn(NCO) <sub>4</sub> ] <sup>b</sup>	2212			13	B
ZrCp <sub>2</sub> (OCN) <sub>2</sub> <sup>c</sup>	2233			12	C
	2200			16	

<sup>a</sup> In acetone.<sup>b</sup> In nitromethane.<sup>c</sup> Cp = (cyclopentadienyl)<sup>-</sup>. Spectrum taken in dichloromethane,  $A$  calculated per mole of NCO<sup>-</sup> for each band in the doublet.

## REFERENCES TO TABLE 11

A A. H. Norbury and A. P. Sinha, *J. Chem. Soc. A*, (1968) 1598.B J. L. Burmeister, E. A. Deardorff and C. E. Van Dyke, *Inorg. Chem.*, 8 (1969) 170.C J. L. Burmeister, E. A. Deardorff, A. Jensen and V. H. Christiansen, *Inorg. Chem.*, 9 (1970) 58

TABLE 12

Internal standard ratios for thiocyanate complexes<sup>a</sup>

Compound	$\nu_{\text{CN}}(\text{cm}^{-1})$	Internal standard ratio <sup>b</sup>
NH <sub>4</sub> [Ag(SCN) <sub>2</sub> ]	2121 2091	0.7
K[Au(SCN) <sub>4</sub> ]	2128	0.3
K <sub>2</sub> [Hg(SCN) <sub>4</sub> ]	2134 2124	0.4
K <sub>2</sub> [Pd(SCN) <sub>4</sub> ]	2124 2093	0.4
K <sub>2</sub> [Pt(SCN) <sub>6</sub> ]	2123 2117	0.3
(Bu <sub>4</sub> N) <sub>3</sub> [Rh(SCN) <sub>6</sub> ]	2097	1.0
(Et <sub>4</sub> N) <sub>2</sub> [Co(NCS) <sub>4</sub> ]	2063	1.7
K <sub>3</sub> [Cr(NCS) <sub>6</sub> ]	2078	2.7
(Et <sub>4</sub> N) <sub>3</sub> [Fe(NCS) <sub>6</sub> ]	2058	2.5
(Et <sub>4</sub> N) <sub>2</sub> [Hf(NCS) <sub>6</sub> ]	1996	3.9
Cs <sub>3</sub> [Mo(NCS) <sub>6</sub> ]	2088	2.9
(Et <sub>4</sub> N) <sub>2</sub> [MoO(NCS) <sub>5</sub> ]	2088 2023	4.8
(Et <sub>4</sub> N) <sub>3</sub> [Nd(NCS) <sub>6</sub> ]	2058	1.6
(Et <sub>4</sub> N) <sub>4</sub> [Ni(NCS) <sub>6</sub> ]	2098	1.6
(Et <sub>4</sub> N) <sub>3</sub> [Pr(NCS) <sub>6</sub> ]	2050	1.9
Cs[Re(CNS) <sub>6</sub> ]	2046	4.2
Tl <sub>2</sub> [Re(CNS) <sub>6</sub> ]	2039	3.6
(Et <sub>4</sub> N) <sub>4</sub> [U(NCS) <sub>8</sub> ]	2049	2.4
(Et <sub>4</sub> N) <sub>3</sub> [V(NCS) <sub>6</sub> ]	2059	3.0
(Et <sub>4</sub> N) <sub>3</sub> [VO(NCS) <sub>4</sub> ]	2062	2.8
(Et <sub>4</sub> N) <sub>3</sub> [Yb(NCS) <sub>6</sub> ]	2059	2.0
(Et <sub>4</sub> N) <sub>2</sub> [Zn(NCS) <sub>4</sub> ]	2069	2.5
(Et <sub>4</sub> N) <sub>2</sub> [Zr(NCS) <sub>6</sub> ]	1988	5.4
Hg[Co(NCS) <sub>4</sub> ] <sup>c</sup>	2143	1.3
Co[Pt(SCN) <sub>6</sub> ] <sup>c</sup>	2165 2116	0.4
Cu[Pt(SCN) <sub>6</sub> ] <sup>c</sup>	2183 2144	0.5
Fe[Pt(SCN) <sub>6</sub> ] <sup>c</sup>	2156 2152	0.6

<sup>a</sup> Taken from R.A. Bailey, T.W. Michelsen and W.N. Mills, *J. Inorg. Nucl. Chem.*, in press<sup>b</sup> See text for explanation of ratio.<sup>c</sup> Bridged.



acid ( $1654\text{ cm}^{-1}$ ) was chosen as reference, as it is intense and rarely overlaps with bands of the complex. A nujol mull or KBr pellet was prepared containing known weights of salicylic acid and complex. The areas under the  $\nu_{\text{CN}}$  and carbonyl peak of the salicylic acid were measured approximately (as peak height times half-width) and expressed as a ratio calculated to unit concentration. There is usually an obvious difference in the magnitude of this ratio between N- and S-bonded examples, and this approach can permit the intensity criterion to be used with samples which cannot be run in solution, provided that thiocyanates of known structure are used to calibrate the technique. Representative values are given in Table 12, and it may be seen that the lanthanide compounds which were dissociated in solution now all agree with the N-bonded range.

#### (vi) Far infrared data

The far infrared spectra of a number of thiocyanate complexes have been considered by Forster and Goodgame<sup>19</sup>, Clark and Williams<sup>9</sup> and others<sup>5,17,71-74</sup>. Bands which can be assigned to the metal-ligand stretch are seen in the  $200\text{--}400\text{ cm}^{-1}$  range. This will be referred to as  $\nu_{\text{M-N}}$  or  $\nu_{\text{M-S}}$ , although in all probability the frequency is determined by the entire thiocyanate ion<sup>9</sup> (Like the near infrared assignments, it is not implied that these are absolutely pure modes.) Some values are given in Table 13. Bending modes are expected below  $200\text{ cm}^{-1}$ . For S-bonded compounds,  $\nu_{\text{M-S}}$  is found as a medium intensity band lying between the values found for the  $\nu_{\text{M-Cl}}$  and  $\nu_{\text{MBr}}$  frequencies in the analogous halide complexes, while N-bonded compounds have a more intense  $\nu_{\text{M-N}}$  band slightly above the corresponding  $\nu_{\text{M-Cl}}$  band<sup>19</sup> ( $\nu_{\text{MN}} > \nu_{\text{MS}}$ ). In attempting to apply this criterion, however, care must be taken as geometry is of considerable importance. As shown by Clark and Williams<sup>9</sup>,  $\nu_{\text{M-N}}$  (tetrahedral)  $>$   $\nu_{\text{M-N}}$  (octahedral),  $\nu_{\text{M-Cl}} >$   $\nu_{\text{M-N}}$  for tetrahedral  $\text{MX}_2\text{L}_2$  compounds, but  $\nu_{\text{M-Cl}} <$   $\nu_{\text{M-N}}$  for octahedral complexes. The latter is not always true, as the apparently octahedral zirconium(IV) and hafnium(IV) hexaisothiocyanates<sup>75</sup> have  $\nu_{\text{MN}} <$   $\nu_{\text{MCl}}$ , although by a very small amount. In addition, Clark and Williams<sup>9</sup> have found that the M-N frequency is at a higher value in tetrahedral than in octahedral polymeric (—N—C—S—bridged) compounds, and this is suggested as a criterion for distinguish between these two situations. While shown only for a limited number of mixed ligand compounds, it follows the same pattern as the M-Cl frequency. Lowering of symmetry from regular tetrahedral or octahedral (for example in mixed ligand compounds) may give rise to more than one M-L frequency. These may be separated by upwards of  $50\text{ cm}^{-1}$  in some tetrahedral  $\text{ML}_2(\text{NCS})_2$  complexes<sup>9</sup>, although in others they may not be resolved.

Bridging has a very small effect on the M-N frequency in comparing bridged polymeric and monomeric octahedral compounds, this is in contrast to the case of bridging halogens. It rarely seems possible to detect both the M-N and M-S bands of bridged compounds. There does not seem to be any correlation between M-N frequency and strength of the other ligands in mixed complexes, although one may anticipate some relation between this and the stability of the complex as has been noted for some cyanates<sup>17</sup>.

The assignments of Keller et al.<sup>72</sup> contradict the conclusions above that  $\nu_{\text{MN}} >$   $\nu_{\text{MS}}$ ; several linkage isomers of palladium were reported with  $\nu_{\text{PdS}}$  at  $290\text{--}320\text{ cm}^{-1}$ ,  $\nu_{\text{PdN}}$  at  $260\text{--}270\text{ cm}^{-1}$ . Thus, they suggest  $\nu_{\text{M-N}} <$   $\nu_{\text{MS}}$ , and point to the paper by Kharitonov

TABLE 13

Far infrared spectral data for thiocyanate complexes

Complex	$\nu_{ML}(\text{cm}^{-1})$	Other bands ( $\text{cm}^{-1}$ )	Ref
$(\text{Me}_4\text{N})[\text{Au}(\text{SCN})_4]$	301(m) 227(w) 224(w)		A
$(\text{Me}_4\text{N})_2[\text{Co}(\text{NCS})_4]$	304(s)		A
$(\text{Me}_4\text{N})_3[\text{Cr}(\text{NCS})_6]$	364(s)		A
$\text{K}_3[\text{Cr}(\text{NCS})_6]$	358(s)		B
$(\text{Et}_4\text{N})_2[\text{Cu}(\text{NCS})_4]^a$	327(s)	249(w)	A
$(\text{Et}_4\text{N})_2[\text{Fe}(\text{NCS})_4]$	293(s)		A
$(\text{Me}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$	298(sh) 272(s) 233(sh)		A
$(\text{Et}_4\text{N})_2[\text{Hf}(\text{NCS})_6]$	262(s) 235(s)	180(s) 80(m,br)	C
$\text{K}_2[\text{Hg}(\text{SCN})_4]$	285(m) 255(w)	166(s) 124(vs)	D
$\text{K}_2[\text{Hg}(\text{SCN})_4]$	Not seen	210(w,br)	A
$(\text{Me}_4\text{N})_3[\text{Mo}(\text{NCS})_6]$	303(s)		A
$(\text{Ph}_3\text{BuP})_2[\text{Mn}(\text{NCS})_4]$	287(s,br)		A
$(\text{Quin})_4[\text{Mn}(\text{NCS})_6]^b$	$\sim 222$ (s,br)		A
$(\text{Ph}_4\text{As})_2[\text{Ni}(\text{NCS})_4]^c$	309(assym)		A
$(\text{Ph}_4\text{As})_2[\text{Ni}(\text{NCS})_4]^a$	294(s)	266(m) 230(m,br)	A
$(\text{Et}_4\text{N})_4[\text{Ni}(\text{NCS})_6]$	239(s)		A,D
$\text{K}[\text{Nb}(\text{NCS})_6]$	340(m)		E
$\text{K}_2[\text{Nb}(\text{NCS})_6]$	342(s)		E
$\text{K}_2[\text{Pd}(\text{SCN})_4]$	300(w) 286(m)	194(m) 172(m) 146(m) 127(m)	D
$(\text{Me}_4\text{N})_2[\text{Pd}(\text{SCN})_4]$	298(sh) 289(m) 207(w,br)		A
$\text{K}_2[\text{Pt}(\text{SCN})_4]$	293(w) 283(m)	196(m) 179(m) 150(m) 139(m) 123(m) 109(m)	D

TABLE 13 (continued)

Complex	$\nu_{ML}(\text{cm}^{-1})$	Other bands ( $\text{cm}^{-1}$ )	Ref.
$(\text{Me}_4\text{N})_2[\text{Pt}(\text{SCN})_4]$	280(m) 226(w)		A
$\text{K}_2[\text{Pt}(\text{SCN})_6]$	291(mw) 281(m)	191(ms) 154(m) 131(mw)	D
$\text{K}[\text{Ta}(\text{NCS})_6]$	313(s)		E
$(\text{Bu}_4\text{N})_3[\text{V}(\text{NCS})_6]$	330(s)		F
$(\text{Et}_4\text{N})_3[\text{VO}(\text{NCS})_5]$	340(s)		F
$(\text{Et}_4\text{N})_2[\text{Zn}(\text{NCS})_4]$	287(s)	169(m,s)	D
$(\text{Et}_4\text{N})_2[\text{Zr}(\text{NCS})_6]$	291(s)	174(m) 76(m,br)	C

<sup>a</sup> Octahedral form (2 bridging ligands).<sup>b</sup> Quin = (quinolinium)<sup>+</sup>.<sup>c</sup> Distorted tetrahedral form.

## REFERENCES TO TABLE 13

- A D. Forster and D.M.L. Goodgame, *Inorg. Chem.*, 4 (1965) 715  
 B M.A. Bennett, R.J.H. Clark and A.D.J. Goodwin, *Inorg. Chem.*, 6 (1967) 1625  
 C R.A. Bailey, T.M. Michelsen and A.A. Noble, *J. Inorg. Nucl. Chem.*, 32 (1970) 2427  
 D A. Sabatini and I. Bertini, *Inorg. Chem.*, 4 (1965) 959  
 E G.F. Knox and T.M. Brown, *Inorg. Chem.*, 8 (1969) 1401  
 F H.H. Schmidtke and D. Garthoff, *Z. Naturforsch.*, 24A (1969) 126.

et al.<sup>26</sup> for theoretical justification. In view of the limitations of the latter, other observations on metal-ligand frequencies above, and the values given by Goodgame and Malerbei<sup>74</sup> for some of the same compounds which are in the order  $\nu_{\text{PdN}} > \nu_{\text{PdS}}$  ( $\nu_{\text{PdS}}$  near  $300 \text{ cm}^{-1}$ ,  $\nu_{\text{PdN}}$  near  $340 \text{ cm}^{-1}$ ), the conclusions of Keller et al. seem doubtful.

The only thiocyanate systems considered here for which real ambiguity of bonding mode exists are the hexathiocyanates of  $\text{Re}^{\text{IV}}$  and  $\text{Re}^{\text{V}}$ . These were originally considered<sup>76,77</sup> to be S-bonded on the basis of a band at  $699 \text{ cm}^{-1}$  in  $[\text{Re}(\text{NCS})_6]^{2-}$  and  $702 \text{ cm}^{-1}$  in  $[\text{Re}(\text{CNS})_6]^-$ , which were assigned to the C-S frequency. The  $\nu_{\text{CN}}$  band is low for this mode, but approximate intensity measurements seemed consistent. A band reported at  $865 \text{ cm}^{-1}$  in the tetraphenylarsonium salt of the  $\text{Re}^{\text{IV}}$  compound suggested N-bonding<sup>78</sup> but this could also be assigned to a cation band. Repeated measurements on different preparations were unable to verify the  $700 \text{ cm}^{-1}$  band, which may have been an unknown impurity, and were, moreover, unable to locate any band in the  $\nu_{\text{CS}}$  region which could be assigned to  $\nu_{\text{CS}}$ ; this includes values as high as  $900 \text{ cm}^{-1}$ . A very weak band near  $746 \text{ cm}^{-1}$  could be detected in some preparations of both compounds, but this is most likely assigned to  $\text{CsCNS}$  impurity. The integrated intensity for both compounds is in the range of metal-nitrogen bonding, but the peak was split into two components in the  $\text{Re}^{\text{IV}}$  case. The  $\delta_{\text{NCS}}$  band is split, but at energies more characteristic of

metal-N-bonding. Broad bands were found at  $288\text{ cm}^{-1}$  for  $\text{Cs}_2[\text{Re}(\text{NCS})_6]$  and at  $267\text{ cm}^{-1}$  for  $\text{Cs}[\text{Re}(\text{CNS})_6]$ , while the Re-Cl and Re-Br frequencies are  $302\text{ cm}^{-1}$  and  $260\text{ cm}^{-1}$ , respectively.<sup>79</sup> Thus, the far infrared spectra are also somewhat ambiguous. Of these various conflicting indications, the integrated intensity which indicated N-bonding would seem to be most reliable, but the case is not proved. Other rhenium compounds listed in Table 2 (and other examples in these same papers) evidently are N-bonded from the spectral data which have been given for them.

Far infrared spectra of the selenocyanate systems, in so far as values are available, are included in Table 5. In general, the M-L stretching frequencies are  $40\text{--}80\text{ cm}^{-1}$  lower in these than in the analogous thiocyanates. Although it has not been shown, one may anticipate similar structural correlations.

The M-L stretching frequencies for N-bonded cyanate complexes are given in Table 6; these fall between  $260\text{ cm}^{-1}$  and  $350\text{ cm}^{-1}$ , slightly higher than for the analogous chlorides.<sup>79a</sup> (The very high value in the  $\text{Fe}^{\text{III}}$  compound is notable.) There are limited data on which to build significant correlations, but Sabatini and Bertini<sup>17</sup> have pointed out the relationship between  $\nu_{\text{M-L}}$  and the order of complex stability. Measurement of these frequencies for the oxygen-bonded cyclopentadienyl cyanates of  $\text{Ti}^{\text{IV}}$  and  $\text{Zr}^{\text{IV}}$  gave tentative values of  $269\text{ cm}^{-1}$  and  $365\text{ cm}^{-1}$ , respectively. These may be compared with  $\nu_{\text{M-Cl}}$ ,  $297\text{ cm}^{-1}$  and  $303\text{ cm}^{-1}$ , and  $\nu_{\text{M-NCS}}$ ,  $264\text{ cm}^{-1}$  and  $329\text{ cm}^{-1}$ , in the analogous chloride and thiocyanate compounds<sup>80</sup>. Assignments are difficult because of a number of bands in this region, and other than showing that both pseudohalides of Ti are unusually low (possibly implying a weak bond through steric effects) these values suggest no significant conclusions. Indeed, there is little reason to expect this frequency to offer a simple bonding mode criterion.

#### (vii) Mixed thiocyanate complexes

In all of the examples considered to this point a single bonding mode is found for all of the coordinated groups. A few examples exist for which there are suggestions of mixed bonding modes with some N-bonded and some S-bonded  $\text{CNS}^-$  ions (Numerous cases can be found for coordinated and "free" thiocyanate.) Examples of possible mixed linkage systems are  $[\text{CuL}(\text{SCN})(\text{NCS})]$  where  $\text{L} = \text{tri-2-pyridylamine}$  and phenyldi-2-pyridylamine<sup>81</sup>;  $[\text{PdL}(\text{SCN})(\text{NCS})]$  where  $\text{L} = 4,4'$ -dimethylbipyridyl<sup>82</sup> or diphenyl(*o*-diphenylarsinophenyl) phosphine<sup>83</sup>,  $[\text{Pd}_2(\text{CNS})_4(\text{bis}(\text{diphenylphosphino})\text{acetylene})_2]$  and its Pt analogue<sup>84</sup>, and several palladium compounds of phosphine and arsine chelates<sup>46</sup>. Only  $\nu_{\text{CN}}$  bands are available for these, although intensities are given in the last case. The values for the two bands observed are in the ranges for N- and S-bonding. Vibrational spectra of the  $\text{Cd}^{\text{II}}-\text{CNS}$  system in solution and in solid  $\text{K}_2[\text{Cd}(\text{SCN})_4 \cdot 2\text{H}_2\text{O}]$  have been interpreted by Taylor et al.<sup>85</sup> in terms of mixed-linkage species, and indeed the crystal structure<sup>86</sup> shows each Cd to be surrounded by 4 S and 2 N atoms (hence bridged). Few X-ray studies are available to confirm the existence of other mixed-linkage compounds. Such a study of one possibility<sup>87</sup>,  $[\text{Cu}(\beta, \beta', \beta''\text{-tri-aminotriethylamine})(\text{CNS})_2]$  showed one ionic thiocyanate group<sup>88</sup>, but  $[\text{Pd}(\text{diphenyl}(3\text{-dimethylaminopropyl})\text{phosphine})(\text{NCS})(\text{SCN})]$ <sup>89</sup> and  $[\text{Pd}((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)(\text{NCS})(\text{SCN})]$ <sup>90</sup> have been confirmed.

Infrared evidence for mixed-linkage behavior should be looked for in the form of  $\nu_{CS}$  bands near  $800\text{ cm}^{-1}$  and  $700\text{ cm}^{-1}$ , while such a band near  $740\text{ cm}^{-1}$  implies ionic thiocyanate. The intensity criterion would seem to be the best test when the bands are resolved adequately<sup>46</sup>.

In summary, when carefully applied, infrared criteria for bonding mode are reliable for thiocyanate complexes, although occasionally ambiguous Selenocyanate complexes seem to follow equally well, but cyanates must be regarded with more caution. In all cases it must be kept in mind that use of these empirical indications forms an indirect method and cannot be regarded as absolute proof of structure.

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#### REFERENCES

- 1 H.E. Williams, *Cyanogen Compounds*, 2nd edn., Arnold, London, 1948.
- 2 R.G. Pearson, *J. Chem. Educ.*, **45** (1968) 581, 643.
- 3 R. Gronbaek and J.D. Dunitz, *Helv. Chim. Acta*, **47** (1964) 1889.
- 4 C. Panattoni and E. Frasson, *Acta Crystallogr.*, **16** (1963) 1258.
- 5 H.Oki, E. Kyuno and R. Tsuchiya, *Bull. Chem. Soc. Japan*, **41** (1968) 2357.
- 6 M.A. Porai-Koshits and G.V. Tsintsadze, *Itogi Nauki i Kristallokhim.*, (1965) 168.
- 7 D. Britton and J.D. Dunitz, *Acta Crystallogr.*, **18** (1965) 424.
- 8 J. Lewis, R.S. Nyholm and P.W. Smith, *J. Chem. Soc.*, (1961) 4590.
- 9 R.J.H. Clark and C.S. Williams, *Spectrochim. Acta*, **22** (1966) 1081.
- 10 P.C.H. Mitchell and R.J.P. Williams, *J. Chem. Soc.*, (1960) 1912.
- 11 J. Chatt and L.A. Duncanson, *Nature*, **178** (1956) 997.
- 12 J. Chatt, L.A. Duncanson, F.A. Hart and P.G. Owston, *Nature*, **181** (1958) 43.
- 13 A. Turco and C. Pecile, *Nature*, **191** (1961) 66.
- 14 S. Fronaeus and R. Larsson, *Acta Chem. Scand.*, **16** (1962) 1447.
- 15 A. Tramer, *J. Chim. Phys.*, **59** (1962) 232.
- 16 C. Pecile, *Inorg. Chem.*, **5** (1966) 210.
- 17 A. Sabatini and I. Bertini, *Inorg. Chem.*, **4** (1965) 959.
- 18 D. Forster and D.M.L. Goodgame, *J. Chem. Soc.*, (1965) 262.
- 19 D. Forster and D.M.L. Goodgame, *Inorg. Chem.*, **4** (1965) 715.
- 20 J.S. Thayer and R. West, *Advan. Organometal. Chem.*, **5** (1967) 169.
- 21 L.H. Jones, *J. Chem. Phys.*, **25** (1956) 1069.
- 22 A.H. Norbury and A.I.P. Sinha, *J. Chem. Soc. A*, (1968) 1598.
- 23 S. Fronaeus and R. Larsson, *Acta Chem. Scand.*, **16** (1962) 1447.
- 24 D. Forster and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **6** (1967) 339.
- 25 E.L. Wagner, *J. Chem. Phys.*, **43** (1965) 2728.
- 26 Yu. Ya. Kharitonov, G.V. Tsintsadze and M.A. Porai-Koshits, *Russ. J. Inorg. Chem.*, **10** (1965) 427.
- 27 Yu. Ya. Kharitonov and G.V. Tsintsadze, *Russ. J. Inorg. Chem.*, **10** (1965) 645.
- 28 Yu. Ya. Kharitonov, G.V. Tsintsadze and M.A. Porai-Koshits, *Dokl. Akad. Nauk SSSR*, **160** (1965) 1351.
- 29 G.L. Carlson, *Spectrochim. Acta*, **18** (1962) 1529.

- 30 F.A. Müller and G.L. Carlson, *Spectrochim Acta*, 17 (1961) 977.
- 30a D. Forster and D M L Goodgame, *J. Chem Soc.*, (1965) 1286
- 31 A. Sabatini and I. Bertini, *Inorg Chem*, 4 (1965) 1665, 5 (1966) 1025
- 32 H F. Schmidtke, *J. Amer Chem Soc*, 87 (1965) 2522.
- 33 M.M. Chamberlain and J.C. Bailar, Jr, *J Amer Chem Soc*, 81 (1959) 6412
- 34 M E. Baldwin, *J. Chem Soc.*, (1961) 471.
- 35 F A. Cotton, D.M.L. Goodgame, M. Goodgame and T.E. Haas, *Inorg. Chem.*, 1 (1962) 565.
- 36 A. Turco, C. Pecile and M. Nicolini, *J. Chem. Soc.*, (1962) 3008
- 37 C. Pecile, A. Turco and G. Pizzolotto, *Ric Sci Parte 2 Ser. A*, 31 (1961) 247.
- 38 R A. Bailey and S L. Kozak, *J Inorg Nucl Chem*, 31 (1969) 689
- 39 J L. Burmeister, E A. Deardorff, A. Jensen and V H. Christiansen, *Inorg Chem*, 9 (1970) 58
- 40 J R. Knox and K. Eriks, *Inorg Chem*, 7 (1968) 84.
- 41 A B P. Lever, B S. Ramaswamy, S H. Simonsen and L K. Thompson, *Can J Chem*, 48 (1970) 3076
- 42 I. Stoltz, W K. Wilmarth and A. Haim, *Inorg Chem*, 7 (1968) 1250
- 43 J L. Burmeister, *Coord Chem Rev*, 1 (1966) 205.
- 44 J.L. Burmeister, *Coord Chem Rev*, 3 (1968) 225
- 45 A H. Norbury and A I P. Sinha, *Quart Rev*, 24 (1970) 69
- 46 D W. Meek, P E. Nicpon and V I. Meek, *J Amer Chem Soc*, 92 (1970) 5351
- 47 J L. Burmeister, H J. Gysling and J C. Lim, *J Amer. Chem Soc*, 91 (1969) 44
- 48 D F. Gutterman and H B. Gray, *J Amer. Chem Soc*, 91 (1969) 3105
- 49 J L. Burmeister, E A. Deardorff and C E. Van Dyke, *Inorg Chem*, 8 (1969) 170
- 50 G F. Knox and T M. Brown, *Inorg Chem*, 8 (1969) 1401
- 51 T M. Brown and G F. Knox, *J Amer Chem Soc*, 89 (1967) 5296
- 52 H. Bohland and E. Tiede, *J Less-Common Metals*, 13 (1967) 224
- 53 H. Bohland and E. Zenker, *J Less-Common Metals*, 14 (1968) 397
- 54 H. Bohland, E. Tiede and E. Zenker, *J Less-Common Metals*, 15 (1968) 89
- 55 Yu Ya. Kharitonov and I A. Rozanov, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, (1962) 402
- 56 Yu Ya. Kharitonov, I A. Rozanov and I V. Tintzadze, *Izv Akad. Nauk SSSR Otd. Khim. Nauk*, (1963) 596
- 57 M.E. Farago and J M. James, *Inorg Chem*, 4 (1965) 1706
- 58 N S. Ham and J B. Willis, *Spectrochim Acta*, 16 (1960) 279
- 59 H H. Schmidtke and D. Garthoff, *Helv Chim Acta* 50 (1967) 1631
- 60 J L. Burmeister and H J. Gysling, *Inorg Chim Acta*, 1 (1967) 100
- 61 G.V. Tsintsadze, A.Yu. Tsvadze and Ts L. Makhataidze, *Soobshch. Akad. Nauk Gruz. SSR* 56 (1969) 301.
- 62 A.Yu. Tsvadze, G.V. Tsintsadze, Yu.Ya. Kharitonov, A M. Golub and A.M. Mamulashvili, *Zh Neorg. Khim.*, 15 (1970) 1818
- 63 J L. Burmeister and T P. O'Sullivan, *Inorg. Chim. Acta*, 3 (1969) 479
- 64 I. Nelson and S M. Nelson, *J. Chem Soc A*, (1969) 1597.
- 65 W. Beck and K. Feldt, *Z. Naturforsch.*, 20b (1965) 272
- 66 D A. Ramsay, *J. Amer. Chem. Soc.* 74 (1952) 72
- 67 J.L. Martin, L.C. Thompson, L J. Radonovich and M D. Gluck, *J Amer Chem Soc*, 90 (1968) 4493
- 68 J L. Burmeister, S D. Paterson and E.A. Deardorff, *Inorg Chim. Acta* 3 (1969) 105
- 69 J L. Burmeister, R L. Hassel and R J. Phelan, *Chem Commun*, (1970) 679.
- 70 R A. Bailey, T.W. Michelsen and W N. Mills, *J Inorg Nucl Chem*, in press
- 71 R J. Mureinik and W. Robb, *Spectrochim Acta*, 24A (1968) 837.
- 72 R N. Keller, N B. Johnson and L L. Westmoreland, *J Amer. Chem. Soc.*, 90 (1968) 2729
- 73 H. Oki, E. Kyuno and R. Tsuchiya, *Bull Chem Soc Japan*, 41 (1968) 2362
- 74 D M L. Goodgame and B W. Malerbi, *Spectrochim Acta*, 24A (1968) 1254
- 75 R A. Bailey, T.W. Michelsen and A A. Nobile, *J Inorg Nucl Chem*, 32 (1970) 2427
- 76 R A. Bailey and S L. Kozak, *Inorg Chem*, 6 (1967) 2155.
- 77 R A. Bailey and S L. Kozak, *Inorg Chem*, 6 (1967) 419

- 78 F.A. Cotton, W R. Robinson, R A Walton and R. Whyman, *Inorg Chem* , 6 (1967) 929  
79 K. Schwochau and W Krasser, *Z Naturforsch* , 24A (1969) 403.  
79a1 D M Adams, *Metal-Ligand and Related Vibrations* St. Martin's Press, New York, 1968  
80 R.A. Bailey and T W. Michelsen, unpublished results.  
81 G.L. Kulasingam and W R Mc Whinnie, *J. Chem. Soc. A*, (1968) 254  
82 I Bertini and A Sabatini, *Inorg Chem* , 5 (1966) 1025  
83 P Nicpon and D W Meek, *Inorg Chem* , 6 (1967) 145  
84 A J Carty and A Efraty, *Can J Chem* , 47 (1969) 2573  
85 K A Taylor, T V. Long and R.A. Plane, *J Chem. Phys* , 47 (1967) 138.  
86 G.S. Zhdanov and Z.V. Zvonkova, *Tr. Inst. Kristallogr. Akad Nauk SSSR*, 9 (1954) 221; *Chem Abstr.*, 48 (1955) 13331h.  
87 K N Raymond and F. Basolo, *Inorg. Chem* , 5 (1966) 1632.  
88 P C. Jam and E C Lingafelter, *J Amer Chem Soc* 89 (1967) 6131  
89 G R Clark, G J Palenik and D W. Meek, *J Amer Chem Soc* , 92 (1970) 1077.  
90 G R. Clark and G J Palenik, *Inorg Chem* , 9 (1970) 2754

*Coord. Chem. Rev.*, 6 (1971) 407-445