382. *The Infrared Spectra and General Properties of Inorganic Thiocyanates.**

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The infrared spectra of a number of inorganic thiocyanates and thiocyanate complexes have been measured. The absorption band at between 2000 and 2200 cm.$^{-1}$ has been assigned to the C–N stretching frequency.[1] The position of the band depends upon the nature of the combination of the ligand with the central cation. By reference to compounds of known crystal structure we have found rough correlations between band frequency and the binding of the ligand when bound through (1) sulphur, (2) nitrogen, (3) or both sulphur and nitrogen in a bridge structure.[2] Other structural factors prevent the general use of the correlations in the diagnosis of the type of binding. Reasons are suggested for the observed orientation of the thiocyanate ion to the different cations. The conclusions are compared with the description of the compounds by ligand-field theory.

IN co-ordination compounds there are three ways in which the thiocyanate ion can be attached to a metal cation: (*a*) through nitrogen, M–NCS, (*b*) through sulphur, M–SCN, and (*c*) through both nitrogen and sulphur when the group SCN is a bridge, B–NCS–M, between two cations, B and M. In this paper we investigate the way in which the different bindings of the ligand affect the stretching frequency of the C–N bond. An analysis of the fundamental vibrations of the thiocyanate anion [1] assigned the infrared absorption band at 2053 cm.$^{-1}$ to this stretching vibration. Chatt *et al.*[2] have studied a number of thiocyanate complexes of palladium and platinum and also silver thiocyanate, and have shown that the CN stretching frequency is found at higher wave-numbers when the thiocyanate is bridging than when it acts as a monodentate co-ordinating ligand. In their compounds there is good reason to suppose that the latter thiocyanates afford instances of co-ordination through sulphur (Table 1). Vallarino [3] has also drawn attention to the differences in infrared absorption spectra between bridging and terminal thiocyanate ligands in rhodium(I) complexes. The infrared spectra of organic thiocyanates and isothiocyanates show [4] that the CN stretching frequency is at lower frequencies, 2060—2105 cm.$^{-1}$, in the isothiocyanates R–NCS than in the thiocyanates R–SCN, 2140 cm.$^{-1}$. This suggested to us that the infrared spectrum of inorganic thiocyanates might be used to diagnose the type

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* The material in this paper was discussed at the Conference on Co-ordination Chemistry, London, 1959, following Schäffer's paper (ref. 9). Inevitably some of the views expressed here owe something to the participants in the discussion who remain unknown to the authors.

[1] Penney and Sutherland, *Proc. Roy. Soc.*, 1936, *A*, **156**, 654.

[2] Chatt, Duncanson, Hart, and Owston, *Nature*, 1956, **178**, 997; 1958, **181**, 43.

[3] Vallarino, *J.*, 1957, 2473.

[4] Lieber, Rao, and Ramachandran, *Spectrochim. Acta*, 1959, **13**, 296.

of binding in *terminal* thiocyanate complexes. However, in inorganic complex salts, as opposed to organic molecules, there are a large number of additional factors which may or may not affect the vibration frequency of the CN group. Amongst these are (1) the co-ordination number and stereochemistry of the complex; (2) the cation B used to

TABLE 1.* *The* C–N *stretching frequency* (*cm.*$^{-1}$) *in some thiocyanates.*

Compound	Frequency	Structure	Ref.
$BaZn(NCS)_4,2H_2O$	2101	Zn–NCS	5
$(NH_4)_2Cd(NCS)_4,2H_2O$	2092 s 2041—2062 w	Cd–NCS–Cd and Cd–NCS	6
$K_2Hg(SCN)_4$	2105	Hg–SCN	6
$Zn(py)_2(NCS)_2$	2075 s 2096 w		
$Cd(py)_2(SCN)_2$	2096		
KNCS	2020		1
$K_2Mn(NCS)_4,6H_2O$	2058—2083		
$Fe(py)_2(NCS)_2$	2062		
$Co(py)_2(NCS)_2$	2088	Co–NCS–Co	7
$K_2Co(NCS)_4$	2058—2079	Co–NCS	8
$Ni(NH_3)_4(NCS)_2$	2096	Ni–NCS	9
$Ni(py)_4(NCS)_2$	2079	Ni–NCS	9
$(NH_4)_4Ni(NCS)_6,4H_2O$	2088—2101		
$Ni(en)_2(NCS)_2$	?	Ni–NCS	10
$Cu(py)_2(NCS)_2$	2096	Cu–NCS–Cu	7
$Cu(NH_3)_4(NCS)_2$	2119 s 2096 w		
$(NH_4)_3Mo(NCS)_6$	2066		
$(pyH)_3Mo(NCS)_6$	2037—2049		
$(pyH)_4Mo_2O_4(NCS)_6$	2066		
$K_3Rh(SCN)_6$	2075	Rh–SCN	11
$Rh(PR_3)_3SCN$	2092		
$Rh(PR_3)_2(SCN)_2$	2150	(Bridge suggested)	2
$Pd(PR_3)_2SCN$	2110		
$(dipy)Pd(SCN)_2$	2100		4
$(pyH)_3Cr(NCS)_6$	2062—2083		
$(NH_4)Cr(NH_3)_2(NCS)_4$	2114 s 2096 w	Cr–NCS	12
$(Choline)Cr(NH_3)_2(NCS)_4$	2083		6
$HgCr(NH_3)_2(NCS)_4$	2160	(Bridge suggested)	3, 13
$Cr(en)_2(NCS)_2Cl,H_2O$	2088		3
$Cr(NH_3)_5(NCS)(NO_3)_2$	2084		3
$Co(NH_3)_5(NCS)(NO_3)_2$	2114		3
$Co(NH_3)_4NO_2(NCS)HgCl_3$	2179	(Bridge suggested)	3, 13
$Co(en)_2(NCS)_2Cl,H_2O$	2122		3
$Ba(NCS)_2,2H_2O$	2060		2
$(py)_2W(OH)_3(NCS)_3$	2058		
$K_2Pt(SCN)_4$	2088 s 2119 w	Pt–SCN	14
$K_2Pt(SCN)_6$	2110	Pt–SCN	15
$(PR_3)_2Pt(SCN)_2$	2120		4
$(PR_3)_2Pt(SCN)Cl$	2162	(Bridge suggested)	4
$HgCo(NCS)_4$	2137	Hg–SCN–Co	16
$Ni(SCN)_2$	2151		
$Ag(SCN)$	2149	Ag–SCN–Ag	17
$Hg(SCN)_2$	2090		

* In the Table the formulæ have been written in the form indicated either by structure or by the rough correlations mentioned in the text. py is pyridine, pyH the pyridinium ion, PR_3 a phosphine derivative, dipy dipyridyl, and en ethylenediamine. s and w refer to strong and weak bands.

Refs.: (*a*) *CN stretching frequencies.* 1, Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253. 2, Vallarino, *J.*, 1957, 2473. 3, Fujito, Nakamoto, and Kobayashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3295. 4, Chatt, Duncanson, Hart, and Owston, *Nature*, 1956, **178**, 997; 1958, **181**, 43.

(*b*) *Structure determinations.* 5, Lindquist, *Acta Cryst.*, 1957, **10**, 176. 6, Zhdanov, *Zhur. Fiz. Khim.*, 1952, **26**, 1798. 7, Porai-Koshits, *Kristallografiya*, 1959, **4**, 239. 8, Zhdanov, Tishchenko, and Zvanhova, *Zhur. Fiz. Khim.*, 1950, **24**, 1950. 9, Porai-Koshits, *Kristollografiya*, 1958, **3**, 686. 10, Lingafelter, *Nature*, 1958, **182**, 1730. 11, Zhdanov and Antsypkina, *Zhur. Fiz. Khim.*, 1953, **27**, 100. 12, Saito, Tachenki, and Pepinsky, *Z. Krist.*, 1955, **106**, 476. 13, Waggener, Matlern, and Cartledge, *J. Amer. Chem. Soc.*, 1959, **81**, 2958. 14, Zhdanov, *Zhur. Fiz. Khim.*, 1952, **26**, 1806. 15, Hendricks and Merwin, *Amer. J. Sci.*, 1928, **15**, 487. 16, Jeffery, *Nature*, 1947, **159**, 610. 17, Lindquist, *Acta Cryst.*, 1957, **10**, 29.

neutralise the charge on anionic thiocyanate complexes of formula $B_nM(CN)^{n-}$. For example potassium, sodium, or pyridinium salts of formula $B_3M(CNS)_6^{3-}$ can be prepared (Where B as well as M can form co-ordination compounds with thiocyanate we must also expect all types of intermediate behaviour between terminal and strongly "bridged" thiocyanate complexes); (3) the valency of the cation, M; (4) the ionic or covalent character of the metal–thiocyanate bonds; (5) the angle M-S-C subtended at the metal atom by the thiocyanate group. Several of these factors will also be discussed by Dr. P. W. Smith, University College (London), in an independent publication which we have been allowed to examine. As the effects of these factors are difficult to resolve we have had to be content with a broad survey of the correlation between infrared band frequency and structure rather than to set up any definite diagnostic rules. Our main conclusions are: (1) The frequency is at higher wave-numbers in the order M-NCS $\leqslant$ M-SCN < B-SCN-M, when all other factors are constant. (2) For a given disposition of the thiocyanate ion, the more polarising the cation (the greater its charge or its electronegativity, or the smaller the cation) the greater the frequency of the CN vibration. (3) Bridged thiocyanates are formed with a variety of strengths. These conclusions will be illustrated by the information in Table 1, which includes references to the structures of many of the compounds. The CN stretching frequencies in complex cyanides (Table 2) are included, as this information helps in the understanding of the thiocyanate frequencies. Some of the cyanide frequencies have been discussed previously (see references in Table 2). In what follows we write the thiocyanate ion as CNS unless we wish to indicate the binding, in which case the co-ordinating atom will be written first, NCS or SCN.

TABLE 2. *Stretching frequency* (*cm.*$^{-1}$) *of the* C-N *group in some cyanides.**

Compound	Frequency	Ref.	Compound	Frequency	Ref.
$Zn(CN)_4^{--}$	2151	1	$Cu(CN)_4^{3-}$	2083	1
$Cd(CN)_4^{--}$	2146	1	$Ag(CN)_4^{3-}$	2092	1
$Hg(CN)_4^{--}$	2145	1	$Au(CN)_4^{3-}$	2184	1
$Ni(CN)_4^{--}$	2127	1	$Cu(CN)_2^{-}$	2125	3
$Pd(CN)_4^{--}$	2139	1	$Ag(CN)_2^{-}$	2164	3
$Pt(CN)_4^{--}$	2137	1	$Au(CN)_2^{-}$	2147	3
$Cr(CN)_6^{3-}$	2127	1	$Co(CN)_6^{3-}$	2130	1
$Mn(CN)_6^{3-}$	2125	1	$Rh(CN)_6^{3-}$	2136	1
$Fe(CN)_6^{3-}$	2119	1	$Ir(CN)_6^{3-}$	2132	1
$Cr(CN)_6^{4-}$	2028	2	$Fe(CN)_6^{4-}$	2041	1
$Mn(CN)_6^{4-}$	2060	2	$Ru(CN)_6^{4-}$	2048	1
$Mn(CN)_6^{5-}$	2048	2	$Os(CN)_6^{4-}$	2036	1

* Simple cyanides, *e.g.*, KCN, have frequencies around 2075 cm.$^{-1}$, while bridged cyanides such as AgCN have frequencies much nearer 2200 cm.$^{-1}$.

Refs.: 1, Mathieu and Poulet, *Compt. rend.*, 1959, **248**, 2315. 2, Caglioti, Sartori, and Scrocco, "Chemistry of the Co-ordination Compounds," Pergamon Press, London, 1958, p. 87. 3, Jones, *J. Chem. Phys.*, 1954, **22**, 965, 1165; 1956, **24**, 293.

Change of Cation, B.—There is some evidence [5] that change of B from one Group IA cation to another, or change from IA cation to a univalent organic base such as the pyridinium ion, affects the CN stretching frequency in thiocyanates. The only additional comparison we have made is that between $(NH_4)_3Mo(CNS)_6$ and $(pyH)_3Mo(CNS)_6$. The frequency is somewhat higher in the ammonium compound. If the group (cation) B is sufficiently electropositive it co-ordinates with the thiocyanate, forming an unsymmetrical bridge B-NCS-M or B-SCN-M, and the frequency moves to much higher values. The series of compounds $K_2Co(NCS)_4$, $K_2Hg(SCN)_4$, and $Hg(SCN)_4Co$ (Table 1) illustrate this. Between the formation of strong bridges, first recognised by Chatt [2] in silver(I), palladium(II), and platinum(II), and by Vallarino [3] in rhodium(I) complexes, and the absence of bridging in such compounds as $K_2Co(CNS)_4$, there is the possibility of weak bridging (one end firmly attached, the other weakly) such as is found in

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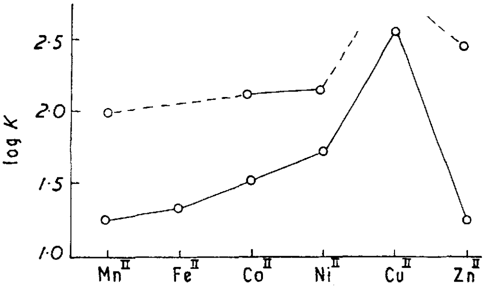
[5] Fujito, Nakamoto, and Kobayashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3295.

$(NH_4)_2Cd(NCS)_4,2H_2O$ and in $Ni(CNS)_2(NH_3)_3$. From Table 1 it is clear that a bridging thiocyanate can only be recognised by its infrared spectrum if it is strongly attached at both ends. The infrared spectrum of the cadmium compound $(NH_4)_2Cd(NCS)_4,2H_2O$ is particularly interesting as it shows two peaks which presumably correspond with the two types of thiocyanate ion known to occur from crystallographic studies. $Co(CNS)_2(py)_2$, which is also bridged, shows only one peak and there is only one type of thiocyanate ligand. A further case of interest is $(pyH)_4[MoO_2(CNS)_3]_2$. We find one low-frequency band in the spectrum of this compound, and we conclude that there are no thiocyanate bridges. It is obvious that if a bridged thiocyanate is to be formed one of the cations must be able to co-ordinate the thiocyanate through sulphur. The only cations known to co-ordinate to sulphur in bridged thiocyanates are Cd(II), Ni(II) [see also $Ni(CNS)_2$ in the Table], Co(II), Cu(II), having weak bridges with CN frequency around 2100 cm.$^{-1}$, and Ag(I), Pd(II), Pt(II), Hg(II), and Rh(I), having strong bridges with CN frequency around 2150 cm.$^{-1}$. There is no reason to suppose that strong bridges can be formed by any element in the first transition series or before technecium and rhenium in the second and the third transition series.

Change of Number of Thiocyanate Ions bound to M.—There is some evidence that increase in the number of cyanide or thiocyanate ions in a complex of fixed valency lowers the CN frequency. This is certainly observed in the cyanides $M(CN)_2^-$, $M(CN)_3^{2-}$, $M(CN)_4^{3-}$ of Cu^I, Ag^I, and Au^I, but these ions also have different co-ordination numbers. At fixed co-ordination number as in Ni(II) or Cr(III) complexes (Table 1) there are small unsystematic changes in frequency with change in the number of thiocyanate radicals bound.

The stability constants of some metal thiocyanates, M–CNS, *and* (*upper plot*) *of some thiosulphates,* $M\text{–}S_2O_3{}^{--}$.



Change of Valency of the Cation, M.—Increase in valency of the central cation appears to increase the frequency of the CN stretching. In cyanides this is very clear, *e.g.*, in Fe and Mn complexes. In thiocyanates the situation is not so clear, for in all three series of compounds for which there is information there are other changes concomitant with change of valency. In the molybdenum compounds there is a change in the number of the thiocyanate radicals, in the cobalt compounds a change from a high-spin Co(II) to low-spin Co(III) complexes, and in the palladium and platinum complexes there are changes in co-ordination number.

Change of Cation, M, *along a Row of the Periodic Table.*—Amongst the thiocyanates of the three transition series the frequency increases from the extreme ionic salts, *e.g.*, $Ba(CNS)_2$ and KCNS (2020—2050), to values around 2080—2130 {Cu(II), Ni(II), Pd(II), Pt(II)} for the most electropositive metals. In the middle of the series the values are intermediate, *e.g.*, Mn, Mo, and W. There is the suggestion of a gradual increase in frequency from manganese(II) to copper(II) with a possible decrease to zinc(II) following the Irving–Williams stability sequence. The sequence of stabilities of the thiocyanates is known [6] and is shown in the Figure. We do not regard the correlation between electronegativity and CN stretching frequency as more than probable, because the size of the differences and the widths of some of the bands make detailed interpretation dangerous.

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[6] Yatsimirski and Korableva, *Zhur. Neorg. Khim.*, 1958, **3**, 339.

Change of Cation, M, *down a Group of the Periodic Table.*—Amongst cyanides there is no marked change in frequency down a group of the Periodic Table. There is a change in the thiocyanates, *e.g.*, from Ni (2080—2100) to Pt (2110—2120) or from Zn (2075—2095) to Hg (2105). The situation in the thiocyanates is confused by the dispositions of the ligand.

Disposition of Thiocyanate Group: M–SCN *and* M–NCS *Binding.*—Table 1 shows that the CN frequencies are in general higher, though not without exception, in M–SCN than in M–NCS bound complexes. On the basis of this observation and the recorded frequencies and structures for other compounds we suggest that: (1) The following elements can bind terminal thiocyanate through sulphur, Co(III) (known to bind SCN through sulphur in vitamin B_{12} complexes [7]), Rh(I) and Rh(III), Pd(II) and Pd(IV), Pt(II) and Pt(IV), Au(III), Ag(I), and Hg(II). (2) Thiocyanate cannot be bound through sulphur by elements earlier than those of Group VII. (3) Weak binding to sulphur is also possible for the cations Co(II), Ni(II), Cu(II), Cd(II) but it is largely restricted to bridged structures. These observations are of importance in the discussion of the relative co-ordinating power of different ligands.

On ligand-field theory it is usual to associate the order of the strengths of the field due to the different ligands with the order of the frequency of a *d–d* band, the spectrochemical series. On several occasions we have stated that we believe this to be incorrect.[8] Thiocyanates provide an ideal opportunity for a further examination of this point, for we can obtain the supposed " field strengths " of both $\leftarrow$SCN and $\leftarrow$NCS from visible absorption spectra of complexes. This has been done,[9] and $\leftarrow$SCN has been shown to provide the weaker " field." The spectrochemical series is

$$\mathrm{Cl}^- \leqslant \leftarrow\mathrm{SCN}^- < \mathrm{H_2O} \leqslant \leftarrow\mathrm{NCS}^-$$

Now the equilibrium M$\leftarrow$NCS $\rightleftharpoons$ M$\leftarrow$SCN could be used to determine the real relative affinities of cations for the differently disposed anion. This free energy would be related directly to the relative fields of the ions as the entropy term in the reaction may be presumed to be very small. Unfortunately, no free-energy data for such equilibria are available, but we can observe the product of the reaction of thiocyanate with different cations. First transition series cations in bivalent states probably give only metal–nitrogen bonding in complexes in solution. The thiocyanate complexes of Cu(II) are possibly sulphur-bound.[10] However, the fact that there are bridged structures in solid Co(II), Ni(II), and Cu(II) complexes shows that binding sulphur is becoming of importance towards the end of the transition series. In higher valency states cobalt is known to bind thiocyanate through sulphur in vitamin B_{12}.[7] There is the distinct possibility that low-spin as opposed to high-spin states will prefer $\leftarrow$SCN to SCN$\rightarrow$. In the second and the third transition series, most complexes are now of low spin; the change from M–NCS to M–SCN bonding occurs at or immediately after Group VII, *i.e.*, where the cations become very strongly polarising, strong electron acceptors. Clearly for such cations the equilibrium M$\leftarrow$SCN $\rightleftharpoons$ M$\leftarrow$NCS is balanced far to the left. In such cases the thermodynamic and structural information is directly contrary to the suggestion made from the spectrochemical series that the $\leftarrow$SCN group gives the weaker field. It seems that the spectrochemical series is not a series of field strengths. A theoretical discussion of this point leads to the same conclusion.[8] It applies to all ligands, and we believe that calculations of the stabilisation energies of complex ions by reference to spectroscopic splitting energies are incorrect.[8] Further examples of the failure of the spectrochemical series to give a correct impression of the relative binding strengths of different ligands are provided by the stabilities of the hydroxide,[8] oxalate,[8] and the thiosulphate and nitrite complexes. For thiosulphate, the spectrochemical series suggests that the field due to $S_2O_3^{--}$ is weaker than that due to water.[10] The stability

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[7] D. L. Hodgkin, personal communication.

[8] Williams, *Discuss. Faraday Soc.*, 1958, **26**, 123; *J.*, 1956, 8.

[9] Schäffer, Conference on Co-ordination Chemistry, London, 1959.

[10] Jørgensen and Schäffer, " Absorption Spectra of Complexes of Heavy Metals," Technical Report, European Research Office, U.S. Dept., Army Contract No. DA*91-508-EUC-247.

sequence [11] for some bivalent transition-metal ions is given in the Figure and is the same as that given by ligands which lie higher than water in the spectrochemical series. The nitrite ion, like the thiocyanate ion, can form two series of complexes—the nitrites and the nitro. In nitro-complexes bonding is through nitrogen, and this disposition of the ligand is preferred by Co(III), Pd(II), and Pt(II), highly polarising cations. Of the less polarising cations at least one, Cr(III), forms nitrite complexes binding through oxygen. Thus in several cases the structural and thermodynamic data indicate that there is no universally applicable series of ligand-field strengths, while the spectrochemical series suggests that the relative field strengths of ligands are independent of cation. In what follows we indicate why the spectrochemical series fails to provide a guide to field strengths of ligands.

The change from M-NCS to M-SCN bonding coincides approximately in the Periodic Table with the change in relative binding of halide ions from $F^- > Cl^- > Br^- > I^-$ to $I^- > Br^- > Cl^- > F^-$. It has long been recognised that this change is due to a change in the relative importance of polarity (electrostatic binding) and polarisability (covalent binding). The discussion has been made at different levels of sophistication.[12,13] Most recent theories stress the importance of the overlap between particular sets of atomic orbitals. For example, Chatt and his colleagues [12] consider that the pecularities of the stability constants of the complexes of the highly polarising cations can be referred to the strength of $d_\epsilon\pi_L$ bonding. The cation acts as a strong acceptor of electrons from the anion through σ-bonding but also acts as a strong donor of electrons through π-bonding, much as in cyanide complexes. This treatment leads one to expect a large stabilisation of d_ϵ- as opposed to d_γ-electrons and the highly polarisable ligands should produce a large spectroscopic splitting. This is not observed; the heavier halides and $\leftarrow$SCN$^-$ appear low in the spectrochemical series, and are very different from cyanide in this respect. An alternative explanation [10,13] of the stabilities of compounds of highly polarising cations with highly polarisable ligands is that in such combinations there is considerable charge-transfer. The particular symmetry of the orbitals involved in this covalency need not concern us immediately, as there will be large energy changes independently of symmetry considerations. The first part of this change is an electronegativity effect [13] which we take to be obvious. The second part is a core effect.[10] The transfer of charge to the cation will reduce the effective nuclear charge of the cation as felt by the *d*-electrons and their mutual repulsion will be reduced. This term has been estimated recently by Jørgensen and Schäffer [10] who place ligands in the order of their ability to cause the core electrons to spread, *i.e.*, the nephelauxetic series. (In fact, the series is determined from spectroscopic observations and is unlikely to represent the character of the ground state of a complex except to a first approximation.) The nephelauxetic series is the reverse of the spectrochemical series in so far as the halide ions are concerned. Neither of these series can be expected to reflect all the changes in field of a given series of anions or ligands, and neither should be treated as a series from which thermodynamic stability data can be calculated. The further question arises as to the nature of the spectrochemical series. It appears to the authors that no treatment of this series which does not refer to differences between the covalent binding in the ground and the excited states can be successful,[8] for, if we are correct, the series remains the same when the relative field strengths of a series of ligands, as measured by stability constants, changes.

Experimental.—The infrared spectra were measured with a Perkin-Elmer Recording Spectrophotometer. All compounds were held in a Nujol suspension, and the Nujol absorption bands were used to check the calibration. We thank Dr. G. B. Meakins for all these measurements.

Preparations were standard in all cases. The following list of references gives the procedures we followed.

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[11] Irving and Williams, *J.*, 1953, 3192.
[12] Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.
[13] Williams, *J. Phys. Chem.*, 1954, **58**, 121.

$(NH_4)_2Cd(NCS)_4,2H_2O$, $K_2Co(NCS)_4$, $HgCo(NCS)_4$, $K_2Mn(NCS)_4,6H_2O$, $Ni(SCN)_2$, $Ni(py)_4(NCS)_2$, $BaZn(NCS)_4,2H_2O$, $K_2Pt(SCN)_4$, $K_2Pt(SCN)_6$, and $(py)_2W(OH)_3(NCS)_3$, see Williams, "Cyanogen Compounds," Arnold, London (1948), Chap. XI and XII and refs. therein. $(NH_4)_3Mo(NCS)_6$ and $(pyH)_3Cr(NCS)_6$, see Palmer, "Experimental Inorganic Chemistry," Cambridge U.P., Cambridge, 1954, pp. 415, 392. $Zn(py)_2(NCS)_2$, $Cd(py)_2(NCS)_2$, and $Cu(py)_2(NCS)_2$, see Vogel, "Quantitative Inorganic Analysis," Longmans, London, 1953, pp. 466, 429, 432. $(pyH)_3Mo(NCS)_6$, see Barbieri, *Atti R. Accad. Lincei*, 1930, **12**, 55. $K_3Rh(SCN)_6$, see *idem, ibid*, 1931, **13**, 433. $K_2Hg(SCN)_4$, see Brauer, "Handbuch der präparativen anorganischen Chemie," Stuttgart, 1951, p. 830. $(pyH)_4Mo_2O_4(NCS)_6$, see Furman, "Inorganic Syntheses," 1953, **4**, 97. $(NH_4)_4Ni(NCS)_6,4H_2O$, see Rosenheim and Cohn, *Z. anorg. Chem.*, 1901, **27**, 280. $Fe(py)_4(NCS)_2$, see Gmelin, "Handbuch der anorganischen Chemie," Eisen, Teil B, Berlin, 1932, p. 746. $Co(py)_2(NCS)_2$, see *op. cit.*, Kobalt, Teil B, p. 39. $Ni(NH_3)_4(NCS)_2$, see Grossman, *Ber.*, 1904, **37**, 559. $Cu(NH_3)_2(NCS)_2$, see Grossman, *Z. anorg. Chem.*, 1908, **58**, 265. A sample of Reinecke's salt was given to us by Dr. H. Irving.

Note added in proof.—Kinell and Strandberg (*Acta Chem. Scand.*, 1959, **13**, 1607) have shown that change of co-ordination number has a marked effect on the infrared frequency of CNS in silver thiocyanate solutions. Chamberlain and Bailar (*J. Amer. Chem. Soc.*, 1959, **81**, 6412) have examined a series of thiocyanates and their observations add weight to the correlations we have described.

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