899. *The Structure of Complex Molybdenum*(III) *Thiocyanates.*

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The nature of the metal–ligand bond in molybdenum(III) thiocyanate complexes has been investigated. The infrared spectra of a number of transition-metal thiocyanates and isothiocyanates of the types $[M(CNS)_6]^{n-}$ and $[M(CNS)_4]^{n-}$ have been studied: the feature most characteristic of metal–sulphur bonding is a lower C–S stretching frequency, ~ 700 cm.$^{-1}$, to be compared with ~ 800 cm.$^{-1}$ when the bonding is to the nitrogen atom. This leads to the conclusion that the $[Mo(CNS)_6]^{3-}$ complexes are isothiocyanates. Additional evidence in favour of this formulation is provided by X-ray isomorphism and visible and ultraviolet spectra. The role of the water molecules in the hydrated $[Mo(NCS)_6]^{3-}$ complexes is discussed and it is concluded that they are not co-ordinated to the metal atom. Magnetic data on a number of tervalent molybdenum complexes are reported. In all cases except $K_4Mo(CN)_7,2H_2O$ the magnetic moments correspond to the presence of three unpaired electrons and hence to six-co-ordination. For the complex cyanide the moment is 1·75 B.M. and the molybdenum atom is considered to be seven-co-ordinate. Finally, factors which are important in deciding whether a metal atom will bond to sulphur or nitrogen in $[NCS]^-$ are discussed briefly and an explanation is proposed.

THE hexathiocyanatomolybdenum(III) * complexes have been of interest, partly because of the doubt expressed in some quarters as to whether the Mo(III) atom is really six-co-ordinate therein and partly because of the uncertainty as to the way in which the (CNS) group is attached to the metal atom.

As discussed by Lindqvist and Strandberg,[1] the transition metals may be classified into two groups according to whether they are bonded to the thiocyanate group through the nitrogen or sulphur atom. Thus, metals in the first transition series appear to form isothiocyanate complexes (N-bonded), whereas elements in the second half of the second and third transition series tend to form thiocyanates (S-bonded). It is significant that this behaviour closely parallels the division into class (*a*) and class (*b*) acceptors proposed recently by Ahrland, Chatt, and Davies [2] for the co-ordination of metal ions with an extensive series of ligands. This (*a*)–(*b*) division is based upon the stability constants of ions in solution, *i.e.*, the free energies of replacement of one ligand by another. For class (*a*) metals the order of strength of attachment in water is $F^- > Cl^- > Br^- > I^-$ and for class (*b*) metals the order is reversed. The behaviour of molybdenum is of particular interest since it has been assigned a border-line position. In the case of the thiocyanate complexes no X-ray data are available to establish whether it is nitrogen or sulphur which is bound to molybdenum, but we have been able to obtain information by other physical methods. The fact that the bonding extremes are M–N=C=S and M–S–C≡N on conventional formulation suggested that it should be possible to distinguish between the two forms by studying the CN and CS frequencies in the infrared spectrum. In addition we have investigated the visible spectra of these complexes with a view to correlating the different ways in which bonding can occur with the difference in position of –SCN and –NCS in the spectrochemical series. The positions of the latter have been demonstrated by Yamada and Tsuchida [3] and more recently by Schäffer.[4]

The second aspect of interest arises from recent evidence that the well-known tendency

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* " Thiocyanate " and (CNS) are used without prejudice as to whether the group is sulphur- or nitrogen-bonded to a metal atom.

[1] Lindqvist and Strandberg, *Acta Cryst.*, 1957, **10**, 176.
[2] Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.
[3] Yamada and Tsuchida, *Bull. Chem. Soc. Japan*, 1953, **26**, 492.
[4] Schäffer, Internat. Conf. Co-ordination Chemistry, *Chem. Soc. Special Publ.*, 1959, No. 13, p. 153.

of molybdenum to exhibit co-ordination numbers greater than 6 when quadri-, quinque-, and sexi-valent extends also to the lower oxidation states. Recently seven-co-ordinate molybdenum(II) has been shown to occur in compounds of the type $[Mo(Diarsine)(CO)_3X_2]^0$ where X = I or Br; these complexes are monomeric and non-electrolytes in suitable organic solvents such as nitrobenzene.[5] The well-known heptacyanomolybdate(III) ion [6] has also been considered for some time to be an example of seven-co-ordinate molybdenum(III). Unlike the complex molybdenum(III) thiocyanates, however, in both of these classes of compound spin pairing occurs, as will be discussed below.

These facts revive interest in the question whether a co-ordination number of seven should be assigned to the hydrated hexathiocyanate complexes of molybdenum(III). The ammonium and potassium salts, for example, crystallise as yellow tetrahydrates but there has been some controversy as to whether the complex ions should be formulated as $[Mo(CNS)_6]^{3-}$ (ref. 7) or $[Mo(CNS)_6(H_2O)]^{3-}$ (ref. 8); the difference in viewpoint is based upon conflicting evidence on the retention of one molecule of water in the potassium and ammonium salts when dehydration occurs. We have observed that, although it is possible to prepare the anhydrous potassium salt, in the case of the ammonium salt the final product of " dehydration " under a vacuum is the monohydrate, as previously reported. Further apparent evidence for the assignment of a co-ordination number exceeding six is the formation of a series of addition compounds involving one molecule of water and an organic molecule to give compounds of the formula $M^I_3Mo(CNS)_6,H_2O,HA$, where HA = hydrochloric acid, acetic acid, potassium hydrogen oxalate, or ethyl or propyl alcohol. Most of these compounds appear to be more stable in air and less soluble in water than the parent hydrates. For the hydrogen chloride and ethyl alcohol adducts of the ammonium salt, we have found that the alcohol and hydrogen chloride are lost readily in a vacuum, leaving the monohydrate. However, we have been unable to detect the presence of a hydrogen–chlorine stretching frequency in the infrared spectrum of the hydrogen chloride adduct and this suggests that this complex is not simply an addition compound of hydrogen chloride and the metal complex.

Although a co-ordination number of seven is certainly possible for molybdenum(III) complexes, evidence for this based solely on the facility with which a molecule of water is retained in the complex is by no means conclusive. In an attempt to determine the co-ordination number of molybdenum in these complexes we have investigated the magnetic properties of a series of compounds. This follows recent work which has led to a better understanding of the magnetic properties of the second- and third-row transition elements. If the hexathiocyanates are formulated as six-co-ordinate complexes, the molybdenum ion would have a configuration d_ϵ^3; in a perfect cubic crystal field this would split, to give an orbital singlet at the lowest level, and hence to a first-order approximation the magnetic moment would be expected to correspond to the spin-only value for three unpaired electrons (3·88 B.M.). However, spin–orbit coupling will mix in to this lowest singlet level some higher levels with orbital angular momentum, and as shown by Penny and Schlapp, the observed magnetic moment will then be given by

$$\mu_{obs} = \mu_{spin-only}\left(1 - \frac{4\lambda}{10Dq}\right)$$

where λ is the spin–orbit coupling constant for the set of d-electrons, and Dq is the crystal-field splitting parameter. For molybdenum(III), λ is 267 cm.$^{-1}$ for the free ion and $10Dq$ will be of the order 20,000 cm.$^{-1}$; the former will be reduced a little by complex formation, but the expected moment is of the order of 3·7 B.M. and, as the magnetic moment will be independent of temperature, the susceptibility should obey a Curie law.

[5] Nigam, Nyholm, and Stiddard, *J.*, 1960, 806.
[6] Young, *J. Amer. Chem. Soc.*, 1932, **54**, 1402.
[7] Rosenheim, *Ber.*, 1909, **42**, 2295.
[8] Maas and Sand, *Ber.*, 1909, **42**, 2642.

In the case of a seven-co-ordinate complex such as $[Mo(CNS)_6(H_2O)]^{3-}$ the magnetic behaviour is not so clearly defined, but since the compounds $Mo(CO)_3(Diars)X_2$ are diamagnetic, the d-orbitals of the molybdenum must be split by the crystal field to give two low-lying d-orbitals separated from the next d-orbitals by energy greater than the electron-pairing energy. In the case of a seven-co-ordinate molybdenum(III) complex, this could involve one electron less and we should expect a moment corresponding to one unpaired electron. However, without a detailed analysis of the problem, it is not possible to say how the susceptibility would vary with temperature.

In agreement with this, the magnetic moment of the heptacyanomolybdate(III) complex indicates one unpaired electron (Table 1), but the susceptibility deviates from the Curie law near room temperature, whereas at low temperatures Curie law behaviour is observed (Fig. 1). For the other compounds cited in the Table, the magnetic properties
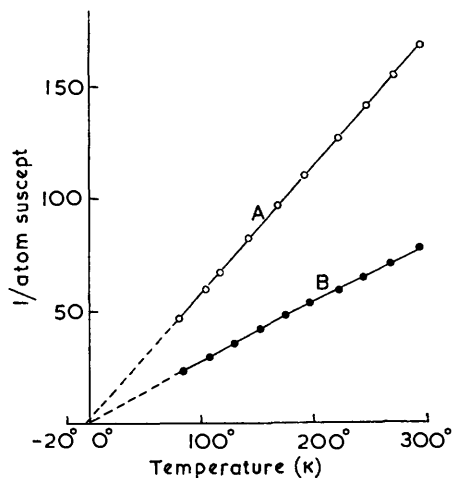

FIG. 1. Plot of the inverse of atomic susceptibility against temperature for (A) potassium hexathiocyanatomolybdate(III) and (B) heptacyanomolybdate(III).

are those expected for a six-co-ordinate complex. In the case of the potassium hexathiocyanatomolybdate(III) hydrate, the susceptibility differs little from that expected from the Curie law; θ is $3°$ in the Curie–Weiss equation, $\chi_A(T + \theta) = $ Constant. Thus, the magnetic properties appear to favour a co-ordination number of six for these complexes.

TABLE 1.

Compound	μ_{eff} at 295° K	Compound	μ_{eff} at 295° K
K_3MoCl_6	3·79	$(NH_4)_3Mo(CNS)_6,HCl,H_2O$	3·70
$(NH_4)_3Mo(CNS)_6,4H_2O$	3·70	$K_3Mo(CNS)_6,4H_2O$	3·79
$(NH_4)_3Mo(CNS)_6,EtOH,H_2O$ ...	3·80	$K_4Mo(CN)_7,2H_2O$	1·75

We now come to the question of how the (CNS) group is attached to the metal atom. Since the shape and bond order within the group are expected to be affected by the mode of attachment, it is useful to summarise, at this stage, the X-ray structural data which are available on complexes in which (CNS) has a terminal position. These are given in Table 2.

It will be noted that only first-row transition elements form isothiocyanates and only the later second- and third-row transition metals form thiocyanates. In all cases the NCS group is linear. However, preliminary X-ray results [9] have been taken to indicate sulphur bonding in $K_4Ni(CNS)_6,4H_2O$ and $K_3Cr(CNS)_6,4H_2O$. This result for nickel(II) seems most unlikely in view of the more recent findings for the series of isothiocyanato-ammines included in Table 2. Furthermore, sulphur bonding for chromium(III) is against chemical evidence. Seel,[10] for example, concluded that nitrogen bonding existed in

[9] Zvonkova, *Zhur. fiz. Khim.*, 1957, **31**, 2074.
[10] Seel, Co-ordination Chem. Conference, Copenhagen, 1953, p. 46; *Z. anorg. Chem.*, 1956, **283**, 351.

$K_3Cr(CNS)_6$, $K_2Co(CNS)_4$, and $NH_4[Cr(NH_3)_2(CNS)_4]$. Other structures have been reported in which the thiocyanate group serves to bridge two metal atoms, so increasing the co-ordination number of the metal. Examples of these compounds are: $Co py_2(NCS)_2$, $Ni(NH_3)_3(NCS)_2$, $Cu py_2(NCS)_2$, AgSCN, $[Pt_2\{P(C_3H_7)_3\}_2Cl_2(SCN)_2]$, $Hg(SCN)_4Co$,

TABLE 2.

X-Ray structures of thiocyanate complexes.

Compound	Stereochemistry of central atom	Arrangement of (CNS) groups in complex ion	Ref.
Isothiocyanates			
$[Cr(NH_3)_2(NCS)_4]^-$	Octahedral	Co-planar, M–NC co-linear	*a*
$[Co(NCS)_4]^{2-}$	Tetrahedral	Angular, $\angle$M–NC approx. 120°	*b*
$[Ni(NH_3)_2(NCS)_4]^{2-}$	Octahedral	Co-planar, M–NC co-linear	*c*
$[Ni(NH_3)_3(NCS)_3]^-$	Octahedral	M–NC co-linear	*c, d*
$[Ni(NH_3)_4(NCS)_2]$	Octahedral	*trans-*, M–NC co-linear	*c*
$[Ni py_4(NCS)_2]$	Octahedral	*trans-*, $\angle$M–NC 165°	*c*
$[Ni en_2(NCS)_2]$	Octahedral	*trans-*	*e, f*
$[Ni tren (NCS)_2]$	Octahedral	*cis-*, $\angle$M–NC 163°, 156°	*f*
Thiocyanates			
$[Rh(SCN)_6]^{3-}$	Distorted octahedral	–SCN groups parallel (in two sets) $\angle$M–SC 120°	*g*
$[Pt(SCN)_4]^{2-}$	Square planar	–SCN groups approx. parallel (in two sets)	*h*
$[Hg(SCN)_4]^{2-}$	Distorted tetrahedral	–SCN groups angular $\angle$M–SC 120° ?	*i*
$[Ag(SCN)_2]^-$	Distorted tetrahedral	AgSCN and SCN$^-$, $\angle$Ag–SC 110°	*j*
$Pt(NH_3)_2(SCN)_2$ (cis- and trans-) } Square planar		–SCN angular	*k*

a, Saito, Takeuchi, and Pepinsky, *Z. Krist.*, 1955, **106**, 476; Takeuchi and Pepinsky, *ibid.*, 1957, **109**, 29; 1958, **110**, 474; Takeuchi and Saito, *Bull. Chem. Soc. Japan*, 1957, **30**, 319. *b*, Zhdanov and Zvonkova, *Zhur. fiz. Khim.*, 1950, **24**, 1339. *c*, Porai-Koshits, Iukhno, Antsishkina, and Dikareva, *Soviet Phys. Cryst.*, 1957, **2**, 366. *d*, Porai-Koshits, *Trudy Inst. Krist., Akad. Nauk S.S.S.R.*, 1954, **10**, 117. *e*, Lingafelter, *Nature*, 1958, **182**, 1730. *f*, Rasmussen, *Acta Chem. Scand.*, 1959, **13**, 2009. *g*, Zvonkova, *Zhur. fiz. Khim.*, 1953, **27**, 100. *h*, Zvonkova, *Zhur. fiz. Khim.*, 1952, **26**, 1804. *i*, Zvonkova, *Zhur. fiz. Khim.*, 1952, **26**, 1798. *j*, Lindqvist and Strandberg, *Acta Cryst.*, 1957, **10**, 173. *k*, Bleidelis, *Soviet Phys. Cryst.*, 1957, **2**, 270; Bleidelis and Bokii, *ibid.*, p. 274.

$Hg(SCN)_4Ni,2H_2O$. The infrared results reported below are, however, for compounds containing no bridging group.

The infrared frequencies attributed to the vibrations of the thiocyanate group are listed in Table 3, the groupings being on the basis of the detailed assignments for KNCS,[11,12a] NH$_4$NCS,[12b] and HNCS.[13] No complete investigation of a thiocyanate complex of the type we have considered has been reported, except by Kinell and Strandberg [14] for AgSCN and Ag(SCN)$_2^-$. The band we ascribe to the C–S (symmetrical N–C–S) stretching vibration is often of low intensity and difficult to find when normal mull thicknesses are used but that it is clearly not an overtone is shown by examination of spectra at longer wavelengths. A similar difficulty has been reported in identifying C–S linkages in organic compounds.[15] Chamberlain and Bailar [16] have adopted the same assignment for a series of cobalt complexes. In connection with the assignment of the lowest frequencies to the bending modes, the possibility of a metal–nitrogen stretching frequency in the same region (500—400 cm.$^{-1}$) has to be considered. However, in the hexaisothiocyanates we have been able to detect one band system only; the general similarity of this to the band in the alkali-metal thiocyanates, along with other results, suggests that this stretching frequency must lie below 400 cm.$^{-1}$. Jones [11] has drawn attention to a remarkable feature of the KNCS spectrum, namely, that the first overtones of the bending frequencies are of about the same intensity as the fundamentals themselves. In general, we find that this

[11] Jones, *J. Chem. Phys.*, 1956, **25**, 1069; 1958, **28**, 1234.
[12] Tramer, *Compt. rend.*, 1959, **249**, (*a*) 2531, (*b*) 2755.
[13] Reid, *J. Chem. Phys.*, 1950, **18**, 1512.
[14] Kinell and Strandberg, *Acta Chem. Scand.*, 1959, **13**, 1607.
[15] Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1958, p. 350.
[16] Chamberlain and Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 6412.

TABLE 3.

Infrared frequencies (cm.⁻¹) of the thiocyanate group.

Compound	Mull (M) or soln. (S)	C–N stretch (NCS antisymmetric)	C–S stretch (NCS symmetric)	NCS bending Fundamental *	Overtone
Isothiocyanates					
$(NH_4)_3V(NCS)_6,4H_2O$	M	2076—2078 s	830 vw	478 m	966—950 m, br
$K_3Cr(NCS)_6,4H_2O$ [a]	M	2105 s	820 vw	476 m	961 wm
	S	2092 s			
$Tl_3Cr(NCS)_6$	M	2106 s	820 w	---	—
$NH_4[Cr(NH_3)_2(NCS)_4]$	M	2120 s, 2055 sh	823 w	466 m	955 w
	S	2071 s			
py $H[Cr(NH_3)_2(NCS)_4]$	M	2085 s	836 w	---	---
Choline$[Cr(NH_3)_2(NCS)_4]$	M	2081 s	(879 w)	---	---
$K_2Co(NCS)_4,4H_2O$ [a]	M	2093—2097 s, 2065 sh	820 vw	475 m	950 wm
	S	2076 s			
$K_4Ni(NCS)_6,4H_2O$	M	2123 sh, 2101 s	766 w	469 m	940 w
	S	2072 s			
$K_2Zn(NCS)_4,4H_2O$	M	2101 sh, 2076 s	822 sh, 815 vw, 802 sh	479 w, 470 w, (412 w)	974—955 w, br
	S	2079 s			
Thiocyanates					
$K_3Rh(SCN)_6$ [a]	M	2110 sh, 2098 s, 2084 s	705 w, 695 sh	471 vw, 452 vw, 438 wm	939 vw, 893 vw, 884 w
	S	2106 s			
$Tl_3Rh(SCN)_6$	M	2088 s, 2066 s	706 w	465 w, 428 w	939 vw, 859 w, 851 sh
$K_2Pd(SCN)_4$	M	2122 s, 2116 sh, 2098 sh, 2092 sh, 2088 s, 2047 w	708 sh, 703 w, 694 sh	473 w, 465 w, 439 w, 430 w	940 vw, 927 vw, 883 vw, 873 vw, 865 vw
	S	2108 s			
$K_2Cd(SCN)_4,2H_2O$ [b]	M	2112 sh, 2093 s	754 wm, 726 wm	466 w, 458 m, 453 m, 417 w	940 vw, 929 vw, 909 vw
	S	2125 s, 2073 sh			
$K_2Pt(SCN)_6$	M	2128 sh, 2122 s, 2115 s, 2075 w	699 sh, 694 w, 686 sh	464 w, 426 w, 415 w	918 vw, 858 vw, 840 vw
	S	2120 s			
$K_2Pt(SCN)_4$	M	2127 s, 2098 s	(705 sh), 700 w, 692 sh	479 w, 472 w, 437 wm, 427 wm, 417 w	952 vw, 939 vw, 881 vw, 871 vw, 865 vw
	S	2114 s			
$K_2Hg(SCN)_4$ [a]	M	2132 s, 2119 s	716 w, 710 w, 705 w	461 m, 457 sh, 436 sh, 431 m, 416 w, br	920 w, 883 w
Molybdenum complexes					
$K_3Mo(CNS)_6,4H_2O$ [a]	M	2093 sh, 2077 s	820 w	476 wm	953 wm, br
	S	2071 s			
$K_3Mo(CNS)_6,CH_3 \cdot CO_2H,H_2O$	M	2105 sh, 2084 s, 2048 sh	811 w	—	955 w, 943 w
	S	2062 s			
$(NH_4)_3Mo(CNS)_6,4H_2O$	M	2070 s	815 w	—	953 w, br
	S	2070 s			
$(NH_4)_3Mo(CNS)_6,HCl,H_2O$	M	2070—2075 s	813 w	474 wm, br	950 w, br
$(NH_4)_3Mo(CNS)_6,C_2H_5 \cdot OH,H_2O$	M	2100 s	814 w	—	950 w, br
$(pyH)_3Mo(CNS)_6,3H_2O$	M	2078 sh, 2051 s	826 w, br	—	960 m, br
	S	2061 s			
$Tl_3Mo(CNS)_6$	M	2066 s	812 w	—	940 wm, br

M mull (normally in paraffin), S solution (in acetophenone).
* Normal limit 410 cm.⁻¹; compounds marked (a) examined down to 375 cm.⁻¹ by Dr. J. Bertie.
(b) $[Cd(SCN)_4]^{2-}$ contains two terminal —SCN and two bridging —SCN— groups.

applies to the isothiocyanates, but not to the thiocyanates (where the overtones appear weaker).

Table 3 shows that the C–S frequencies fall into two groups, all those for the thiocyanates lying near 700 (694—723) cm.$^{-1}$ and all those for isothiocyanate complexes higher, around 820 (760—880) cm.$^{-1}$. The " bending " frequencies also show a clear difference in trend between the two types of complex. The isothiocyanates have a band or bands of medium intensity lying near 470 cm.$^{-1}$, while the thiocyanates show, first, a shift to lower values and intensities and, secondly, a wider separation and greater number of frequencies. With the C–N frequencies, values lie higher, in general, for the thiocyanates than for the isothiocyanates but overlap occurs, as between $[Cr(NH_3)_2(NCS)_4]^-$ and $[Hg(SCN)_4]^{2-}$. To check for crystal effects we have compared C–N frequencies in acetophenone solution and these results are included in Table 3. The isothiocyanates exhibit varying behaviour: some show no change between solid and solution but others a pronounced drop in frequency, e.g., $[Cr(NH_3)_2(NCS)_4]^-$ from 2120 to 2070 cm.$^{-1}$; $[Co(NCS)_4]^{2-}$ from 2095 to 2076 cm.$^{-1}$. We do not consider that dissociation affects these results. For the thiocyanates in solution the average of the two C–N frequencies shows either no change or a small increase in frequency. However, Johnson and Basolo [17] have reported for $[Pt\ en_2(SCN)_2](NO_3)_2$ a marked drop in frequency. A further feature from our results is that all thiocyanates exhibit in the solid state two main C–N bands. If the metal–thiocyanate attachment is not linear we should expect at least two bands for all complexes: for the isothiocyanates there is no clear indication of this, even with high resolution. However, in solution spectra the C–N band broadens and becomes Gaussian in shape, but no splitting is observed.

Previous investigations have been concentrated on the measurement of C–N frequencies to decide between thiocyanato- and isothiocyanato-bonding, for both organic [18] and inorganic compounds.[19] Mitchell and Williams [20] have recently examined this criterion in extensive detail for inorganic complexes and have made some broad correlations. Difficulty arises in that the C–N frequency is affected by a number of variables apart from the donor atom, and particularly in that overlap between the two classes occurs.

With C–S frequencies, however, the position does appear to be more clear-cut. There is evidence in several respects that this frequency follows structural changes more closely than does the C–N frequency. Thus where thiocyanate groups serve two functions in the structure, as in $Cd(SCN)_4^{2-}$ or $Ni(NH_3)_2(NCS)_2$,* two separate bands have been observed. Splitting effects have been noted in $[Zn(NCS)_4]^{2-}$ and $[Hg(SCN)_4]^{2-}$, as would be expected from symmetry considerations. Only one band has been noted for $[Co(NCS)_4]^{2-}$, but the difficulty here may have been connected with the low intensity of the band. The C–S frequencies also reflect the C–S bond lengths in the set of Reinecke salts {C–S = 1·80 Å in $NH_4[Cr(NH_3)_2(NCS)_4]$, 1·76 in $C_5H_6N[Cr(NH_3)_2(NCS)_4]$, 1·64 in $Me_3N·CH_2·CH_2·OH[Cr(NH_3)_2(NCS)_4]$; cf. C–N bond lengths of 1·14, 1·15, and 1·37 Å respectively}. In comparing C–S frequencies it is of interest that the two groups lie on either side of the value for NCS$^-$ in KNCS, viz., 749 cm.$^{-1}$. Jones has considered three possible forms for this ion, (a), (b), and (c), and has calculated that form (a) predominates (71%). With this basis the change in C–S frequency between KNCS and the complexes we have considered can be understood. X-Ray results imply that, for sulphur bonding, form (g) is important, whilst for nitrogen bonding form (f) or (d) occurs.

This would agree with the fact that where there is co-ordination to nitrogen electron drift will occur towards the nitrogen, that is, a structure of the type (f) should be stabilised,

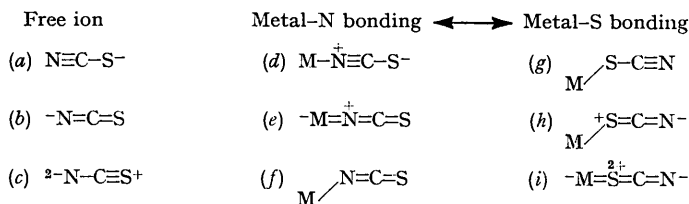* Personal communication from Dr. N. Gill, Imperial College of Science and Technology, London.
[17] Johnson and Basolo, *J. Inorg. Nuclear Chem.*, 1960, **13**, 36.
[18] Lieber, Rao, and Ramachandran, *Spectrochim. Acta*, 1959, **13**, 296; Hoyer, *Chem. Ber.*, 1956, **89**, 2677.
[19] Fujita, Nakamoto, and Kobayashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3296; Rao, Ramachandran, Shankar, *J. Sci. Ind. Res., India*, 1959, **18**, B, 169.
[20] Mitchell and Williams, *J.*, 1960, 1912.

whilst for sulphur-co-ordination electron drift will occur towards the sulphur, which would favour structure (g). For the sulphur-bonded ligand we should therefore always expect a bent M–S–C bond, whilst for the nitrogen either a linear (d) or a bent (f) bond is possible for the M–N–C linkage.

Free ion	Metal–N bonding $\longleftrightarrow$ Metal–S bonding	
(a) N≡C–S⁻	(d) M–N̈≡C–S⁻	(g) M S–C≡N
(b) ⁻N=C=S	(e) ⁻M=N̈=C=S	(h) M ⁺S=C=N⁻
(c) ²⁻N–C≡S⁺	(f) M N=C=S	(i) ⁻M=S̈=C=N⁻

On the basis of the similarity of the spectra of $[Mo(CNS)_6]^{3-}$ and other isothiocyanates, particularly in regard to the C–S frequency, we suggest that bonding in these molybdenum complexes occurs to the nitrogen atom. Indirect evidence in favour of this is also given by the difference in X-ray powder patterns of the hexathiocyanates of rhodium on the one hand and chromium and molybdenum on the other. From optical measurements, isomorphism between $K_3Cr(CNS)_6,4H_2O$ and $K_3Mo(CNS)_6,4H_2O$ has been reported.[21] We have confirmed this by using X-ray methods and have determined also that isomorphism persists in the dehydrated salts. In neither case do the patterns show any correspondence with those of $K_3Rh(SCN)_6$. The same result is found when the thallium(I) salts of the three complexes are compared. Introduction of the large thallium(I) ions into the crystal lattice might be expected to minimise minor effects due to the presence of water molecules. Zhdanov *et al.*[22] have reported the cell constants for the potassium salts of the hexathiocyanates of Cr(III), Ni(II), Rh(III), and Pt(IV). It is of interest that the chromium and nickel, and hence from our result molybdenum(III) also, are closely related in spite of differences in stoicheiometry.

Additional evidence is also afforded by the ultraviolet and visible spectra of the compounds. Recently, Schäffer[4] has suggested that it is possible to differentiate between an isothiocyanate and a thiocyanate structure on the basis of the position of the ligand in the spectrochemical series. The thiocyanate group is considered to be approximately in the same position as chloride in the series, whilst the isothiocyanate falls between water and ammonia, *i.e.*, Cl ≈ ⁻SCN < F < H_2O < ⁻NCS < NH_3 < CN. In agreement with Schäffer, we find that for $K_3Rh(SCN)_6$ a ligand-field band is observed at 20,000 cm.⁻¹ as compared with 19,300 cm.⁻¹ for the complex K_3RhCl_6. Since the first ligand-field band for $[MoCl_6]^{3-}$ has been assigned[23] at 19,000 cm.⁻¹, the corresponding band for the thiocyanate complex would be expected at 19,000—20,000 cm.⁻¹, or for an isothiocyanate at 23,000—24,000 cm.⁻¹. In the spectrum of $K_3[Mo(CNS)_6]$ no band was observed in the thiocyanate region (Fig. 2). However, the isothiocyanate region is masked by the presence of an electron-transfer band, which makes the determination of the presence of a ligand-field band virtually impossible. This evidence may therefore be taken as pointing indirectly to nitrogen bonding.

Molybdenum(III), thus, appears to be the first element in the second-row transition elements in which bonding occurs through the nitrogen rather than sulphur. The main study of thiocyanate bonding in this series has been restricted to elements further to the right-hand side of the transition block than molybdenum, *i.e.*, to Rh, Pd, Ag, Cd.

The question arises why some metals prefer to bond to the nitrogen and some to the

[21] Steinmetz, *Z. Krist.*, 1909, **46**, 377.
[22] Zhdanov, Zvonkova, and Glushkova, *Zhur. fiz. Khim.*, 1953, **27**, 106.
[23] Jørgensen, "Absorption Spectra of Complexes of Heavy Metals," Tech. Rept., European Res. Office U.S. Dept. Army, 1958.

sulphur of the (NCS) group. In proposing an explanation,* we make the following assumptions that: (*a*) in the (NCS)⁻ ion the lone pairs on the sulphur atom are more easily polarised than those on the nitrogen atom; (*b*) the permanent lone-pair dipole on the nitrogen atom is larger than that on the sulphur atom; (*c*) the way in which the (NCS) group is bound (*i.e.*, through S or N) will be decided by the relative bond energies of a covalent metal–S bond and of the more ionic metal–N bond. For a covalent bond, we further assume that the bond strength is roughly proportional both to the total ionisation potential and to the overlap integral, but as a simplification we shall use total ionisation potential alone as a guide to the relative strengths of covalent bonds between different metal atoms and the same ligand. To compare the relative strengths of ionic bonds

FIG. 2. Absorption spectra in aqueous solution of (1) $K_3Mo(CNS)_6,4H_2O$, (2) $K_3Rh(SCN)_6$, and (3) KNCS.
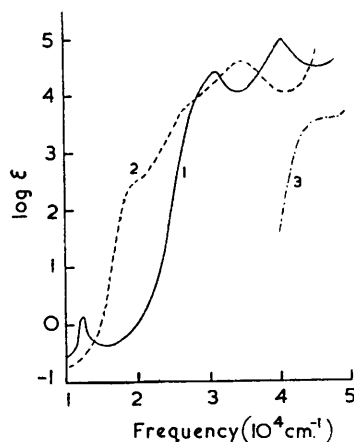
we use the expression ne/r, where r is the radius of the metal ion and ne is the formal charge on the ion. For reasons discussed elsewhere the expression $(ne)^2/r$ is sometimes more convenient. Here we shall compare only metal atoms having the same oxidation state and hence it is irrelevant whether ne or $(ne)^2$ is used. If we now compute the ratio $R =$ I.P. $\frac{ne}{r}$ (cf. Williams [24]), where I.P. is the ionisation potential in volts, and r is in Å, a number between 5 and 20 is obtained. This number is related to the ratio of the strength of a bond if covalent to its strength if ionic. We assume that the higher values of R indicate covalent binding and hence a metal–sulphur link. For univalent ions one obtains values of $R = 7$ if the metal falls into class (*b*) (*e.g.*, Cu^+, Ag^+, Au^+, Tl^+) whereas it is about 6·5 or less for those which fall into class (*a*) (*e.g.*, Li^+ or Na^+). Similarly, for bivalent ions, class (*b*) metals have R values of 10 or more, whereas those for class (*a*) metals are less than this figure (*e.g.*, Pb^{2+} 12·5, Hg^{2+} 16·0, whereas Mg^{2+} 7·4). For tervalent ions the distinction is not so obvious, the borderline between class (*a*) and class (*b*) lying about 12. Now there is considerable doubt as to the ionic radius of Mo^{3+}. Values between 0·70 and 0·78 Å have been put forward, but in either case one obtains R values *less* than the figure obtained for the undoubtedly S-bonded Rh^{3+} ion. It is not suggested that R proves that the binding is to nitrogen but rather that it provides an explanation for the borderline position of molybdenum(III) and establishes that it is more likely to form a metal–nitrogen link that is rhodium.

Finally, it is of interest that, in agreement with our conclusions, Jørgensen,[25] on the basis of the nephelauxetic series, places molybdenum(III) before chromium(III) and iron(III),

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* This proposal refers only to those complexes in which all ligands are [SCN]⁻.

[24] Williams, *Proc. Chem. Soc.*, 1960, 20.
[25] Jørgensen, *Acta Chem. Scand.*, 1958, **12**, 903.

i.e., he suggests that it has a greater tendency to form bonds with considerable ionic character and hence to favour N- over S-bonding in thiocyanate complexes.

<div align="center">EXPERIMENTAL</div>

Preparations.—Tripotassium hexathiocyanatomolybdate(III),4H$_2$O. This was prepared as described by Maas and Sand [26] [Found: K, 18·6; Mo, 15·0, 15·1; C, 11·5; N, 12·6; S, 30·0; H, 1·5. Calc. for K$_3$Mo(CNS)$_6$,4H$_2$O (for 5H$_2$O in parentheses): K, 18·5 (18·0); Mo, 15·1 (14·7); C, 11·4 (11·1); N, 13·3 (12·9); S, 30·35 (29·5); H, 1·3 (1·5)%].

Tripotassium hexathiocyanatomolybdate(III),AcOH,H$_2$O. Dilute acetic acid was added in excess to a moderately concentrated aqueous solution of the tetrahydrate.[26] Amber-coloured crystals were deposited on cooling and storage [Found: Mo, 15·6; C, 15·3; N, 14·0; H, 1·6. Calc. for K$_3$Mo(CNS)$_6$,CH$_3$·CO$_2$H,H$_2$O: Mo, 15·0; C, 15·0; N, 13·1; H, 1·0%].

Triammonium hexathiocyanatomolybdate(III),4H$_2$O was prepared as detailed by Palmer [27] [Found: C, 12·9; N, 22·5; H, 3·5. Calc. for (NH$_4$)$_3$Mo(CNS)$_6$,4H$_2$O: C, 12·6; N, 22·1; H, 3·5%].

Triammonium hexathiocyanatomolybdate(III),C$_2$H$_5$·OH,H$_2$O. The tetrahydrate was dissolved in ethanol and the solution filtered. Addition of benzene precipitated the compound as a fine yellow powder [27] (Found: Mo, 16·9; C, 15·9; N, 20·4; S, 34·8; H, 3·6. Calc. for (NH$_4$)$_3$Mo(CNS)$_6$,C$_2$H$_5$·OH,H$_2$O: Mo, 17·05; C, 17·1; N, 22·4; S, 34·2; H, 3·6%). In the infrared spectrum bands arising from ethanol were observed at 1250w, 1027m, 866w cm.$^{-1}$.

Triammonium hexathiocyanatomolybdate(III),HCl,H$_2$O was obtained on cooling a concentrated hydrochloric acid solution of the tetrahydrate.[27] The yellow crystals were not as stable on storage as the alcoholate.

Trithallium(I) *hexathiocyanatomolybdate*(III),xH$_2$O. Thallous acetate or nitrate solution, added to an aqueous solution of K$_3$Mo(CNS)$_6$,4H$_2$O, produced an immediate orange-yellow precipitate. This was washed with water and dried over P$_2$O$_5$. On storage in air the compound darkened.[28]

Tripyridinium hexathiocyanatomolybdate(III),3H$_2$O was prepared by the addition of pyridine to an aqueous solution of K$_3$Mo(CNS)$_6$ acidified with acetic acid [29] [Found: Mo, 13·3; N, 17·3. Calc. for (C$_5$H$_5$N)$_3$Mo(CNS)$_6$,3H$_2$O: Mo, 13·0; N, 17·1%].

Tetrapotassium heptacyanomolybdate(III),2H$_2$O was prepared from K$_3$MoCl$_6$ [6] and similarly from K$_2$MoCl$_5$,H$_2$O. The compound separated as fine dark crystals, with a green tinge and dull lustre [Found: K, 34·2; Mo, 20·5; C, 18·3; N, 20·4; H, 1·0. Calc. for K$_4$Mo(CN)$_7$,2H$_2$O: K, 33·2; Mo, 20·4; C, 17·9; N, 20·8; H, 0·9%].

Trithallium(I) hexathiocyanatochromate(III),xH$_2$O was precipitated as a greyish-pink powder on addition of a thallous salt to a solution of K$_3$Cr(NCS)$_6$.

Tripotassium hexathiocyanatorhodate(III) was prepared by Barbieri's method [30] except that K$_2$RhCl$_5$ was used as starting material {Found: K, 21·5 (by direct precipitation with [BPh$_4$]$^-$); C, 12·2; N, 15·9. Calc. for K$_3$Rh(SCN)$_6$: K, 20·5; C, 12·7; N, 14·8%}.

Trithallium(I) *hexathiocyanatorhodate*(III). Addition of a solution of thallous acetate to an aqueous solution of the above potassium salt produced immediately an orange-red precipitate. This was filtered off and washed with water. It was stable on storage.

Dipotassium hexathiocyanatoplatinate(IV),2H$_2$O was obtained by long digestion of potassium chloroplatinate(IV) with the stoicheiometric amount of potassium thiocyanate followed by extraction with alcohol [31] [Found: K, 11·9; C, 12·1; N, 13·3; H, 0·4. Calc. for K$_2$Pt(CNS)$_6$: K, 11·9; C, 10·95; N, 12·8; H, 0·6%]. This material and another sample prepared by Dr. M. Baldwin gave an identical infrared spectrum.

Dehydration.—(i) K$_3$Mo(CNS)$_6$,4H$_2$O: Weight loss on vacuum-treatment was assessed by plotting loss against time (dehydration was accompanied by a small amount of decomposition even in the absence of oxygen). The loss so found corresponded to removal of four mol. of water (11·4%. Calc. for 4H$_2$O: 11·4%). The buff-coloured dehydrated compound gave an

[26] Maas and Sand, *Ber.*, 1908, **41**, 1506.
[27] Palmer, " Experimental Inorganic Chemistry," Cambridge Univ. Press, 1954.
[28] Rosenheim and Garfunkel, *Ber.*, 1908, **41**, 2388.
[29] Barbieri, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1930, **12**, 55.
[30] Barbieri, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1931, **13**, 434.
[31] Buckton, *J. prakt. Chem.*, 1855, **64**, 65.

infrared spectrum similar to that of the tetrahydrate but lacking OH and H–O–H peaks. With another preparation a direct determination of the loss gave a value of 12·15% (without correction as above), but the product on storage over sodium carbonate decahydrate [27] showed an increase in weight corresponding to 11·45% of the original sample.

The splitting observed in the H–O–H frequencies in the infrared spectrum suggested the possibility of a non-equivalence of water molecules in the structure. Deuteration, performed by dehydrating the material as above and then exposing it to D_2O vapour, resulted, however, in an exactly similar pattern with the expected shift in frequencies (see Table 4).

(ii) $(NH_4)_3Mo(CNS)_6,4H_2O$. Dehydration over sulphuric acid or *in vacuo* did not produce a water-free product. The material so obtained when stored over sodium carbonate decahydrate increased in weight by 10·0%, corresponding with an uptake of 3 mol. of water. (Calc.: 10·5%). The infrared spectrum of the compound again displayed a splitting of the v_2 water band but with some shift of frequency.

TABLE 4.

Infrared frequencies observed for the v_2H_2O band (cm.$^{-1}$).

$K_3Mo(CNS)_6,4H_2O$	1653—1655 sh,	1626—1628 wm
$K_3Mo(CNS)_6,4D_2O$	~1640 w,	1208 sh, 1170 wm
$(NH_4)_3Mo(CNS)_6,4H_2O$	1621—1626 sh,	1608—1610 wm
$(NH_4)_3Mo(CNS)_6,HCl,H_2O$	~1621 w	
$(NH_4)_3Mo(CNS)_6,EtOH,H_2O$	1637—1639 w	

(iii) $(NH_4)_3Mo(CNS)_6,C_2H_5·OH,H_2O$. Vacuum-treatment resulted in loss of alcohol and retention of water [Found: loss, 7·9. Calc. for $(NH_4)_3Mo(CNS)_6,H_2O$: H_2O, 8·2%]. This result was confirmed by changes in the infrared spectrum.

(iv) $(NH_4)_3Mo(CNS)_6,HCl,H_2O$. The end-product on vacuum-treatment showed retention of water [Found: Mo, 18·6; S, 37·4. Calc. for $(NH_4)_3Mo(CNS)_6,H_2O$: Mo, 18·6; S, 37·2. Calc. for $(NH_4)_3Mo(CNS)_6,HCl$: Mo, 17·9; S, 34·8%].

Spectra.—Infrared spectra were obtained by using paraffin or hexachlorobutadiene mulls with sodium chloride or polystyrene-coated potassium bromide plates as necessary. Aceto-phenone was used as a solvent for the solution measurements. Evaporation of an acetone solution on a preheated plate was employed to produce a thin crystal film where desirable, to confirm other results. The spectrometer was a Grubb–Parsons grating instrument of type GS2A. Determinations of bending frequencies (in the 500—375 cm.$^{-1}$ region) were supplemented by measurements on a Unicam S.P. 100 spectrometer fitted with a potassium bromide prism.

Ultraviolet and visible spectra were determined with a Unicam S.P. 500 or Carey model 10 spectrophotometer. Magnetic-susceptibility measurements were carried out on the apparatus described earlier [32] and in calculations of magnetic moments the usual diamagnetic corrections were made.

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[32] Figgis and Nyholm, *J.*, 1959, 331.