362. *Nickel–Thiourea Complexes. Part I. Infrared Absorption Spectra*

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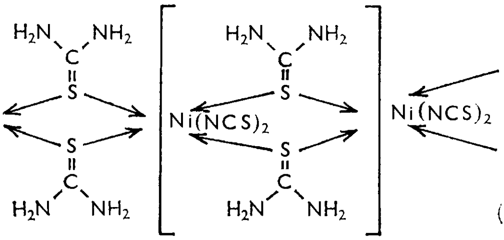
The infrared absorption spectra of nickel–thiourea complexes have been measured and interpreted. Regular shifts, found in some bands, depend on the sulphur atom of the thiourea being co-ordinated to zero, one, or two nickel atoms.

Although co-ordination of thiourea (tu) to nickel(II) was first reported in 1906 by Rosenheim and Meyer,[1] it is only in recent years that extensive work has been carried out. The original formulations [2] of the compounds as $Ni_2tu_7Cl_4$, Ni $tu_5(NO_3)_2$, and Ni $tu_2(NCS)_2$ have been reinvestigated, and only the last one, Ni $tu_2(NCS)_2$, has been verified.

The others [3,4] have been shown to be members of two series, Ni tu_6X_2 (X = Br, ClO_4, NO_3, or I) and Ni tu_4X_2 (X = Cl or Br). The formulation of the chloride reported by Rosenheim and Meyer [1] as Ni tu_4Cl_2 has been verified by a phase analysis of the system nickel dichloride–thiourea–water,[5] and by an *X*-ray structure determination.[6]

Using a Urey–Bradley potential function, Yamaguchi *et al.*[7] were able to calculate the A_1 and B_1 in-plane vibrational frequencies for the urea molecule. With the same method, and retaining five out of the ten force constants used for urea, Yamaguchi *et al.*[8] have predicted the A_1 and B_1 frequencies for thiourea and [$^2H_4$]thiourea. There are nine ($5A_1 + 4B_1$) of these normal modes, and good agreement with experiment was found for all frequencies.



(I)

Structural formulæ of Ni $tu_2(NCS)_2$, showing the bridge structure and the repeating [Ni tu_2] planar unit

These workers [8] compared the infrared absorption frequencies of a series of thiourea complexes of platinum, palladium, and nickel with those for free thiourea, and interpreted frequency-shifts in terms of bonding between the metal atom and the sulphur atom of the thiourea. The only nickel complex studied was Ni $tu_2(NCS)_2$, but, because of its unusual structure, involving thiourea bridges [see (I)],[9] it is not typical of nickel–thiourea complexes. All other known nickel–thiourea complexes involve monodentate thiourea bonding through the sulphur to give hexa- and tetra-thioureanickel(II) species. The nickel is invariably hexa-co-ordinated, this being achieved for tetrathiourea derivatives by co-ordination of the anion (chloride or bromide).

Co-ordination of thiourea will make the unpaired electrons on the sulphur atom less available for bonding with the thiourea molecule. This means that resonance contributors of the form $\overset{+}{N}H_2{:}C(S^-){\cdot}NH_2$ will assume increased importance over the unchanged

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[1] Rosenheim and Meyer, *Z. anorg. Chem.*, 1906, **49**, 13.

[2] Nardelli, Cavalea, and Braibanti, *Gazzetta*, 1957, **87**, 917.

[3] Šramko, *Chem. Zvesti*, 1961, **15**, 271.

[4] (*a*) Babaeva and Yan-Vei-da, *Russ. J. Inorg. Chem.*, 1960, **5**, 1320; (*b*) Babaeva and Chzhan Shou-gan, *ibid.*, pp. 1051, 1055; (*c*) Belova, Syrkin, and Babaeva, *ibid.*, 1961, **6**, 423.

[5] Nandelli, Cavalca, and Braibanti, *Gazzetta*, 1956, **86**, 867.

[6] Cavalca, Nandelli, and Braibanti, *Gazzetta*, 1956, **86**, 942; Lopez-Castro and Trutor, *J.*, 1963, 1309.

[7] Yamaguchi, *Nippon Kagaku Zasshi*, 1957, **78**, 1319, 1467; Yamaguchi, Miyazawa, Shimanouchi, and Mizushima, *Spectrochim. Acta*, 1958, **10**, 170.

[8] Yamaguchi, Penland, Mizushima, Lane, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1958, **80**, 527.

[9] Nardelli, Braibanti, and Fava, *Gazzetta*, 1957, **87**, 1209.

contributor $NH_2{\cdot}C(\dot{:}S){\cdot}NH_2$ in the ligand bond system. This would lead to an increase of the double-bond character in the C–N bonds, and a lowering of it in the C–S bond. The two extremes, free thiourea and Ni $tu_2(NCS)_2$, where the sulphur atom is, respectively, free and co-ordinated to two nickel atoms,[9] show this change in double-bond character.[8,10] The mono-co-ordinate thiourea complexes should then show intermediate bond-character, and data to support this are presented here.

EXPERIMENTAL

The compounds were prepared by the method of Šramko,[3] although, prior to the appearance of his Paper, analogous methods using different solvents had been used. All samples were recrystallised to constant analysis. As noted by Babeva and Chzhan Shou-gan,[4b] at least six recrystallisations of the tetrathiourea complexes were necessary before constant composition was obtained, although only one recrystallisation was usually necessary for hexathiourea complexes. The analytical data are given in Table 1.

TABLE 1

Complex	Found (%) Ni	Found (%) N	Found (%) S	Calc. (%) Ni	Calc. (%) N	Calc. (%) S
Ni $tu_6(ClO_4)_2$	7·8	23·2	—	8·2	23·5	—
Ni $tu_6(NO_3)_2$	9·1	27·0	29·8	9·2	26·2	30·0
Ni tu_6Br_2	8·1	24·4	27·2	8·7	24·9	28·4
Ni tu_4Cl_2	13·4	—	—	13·5	—	—
Ni tu_4Br_2	11·3	—	—	11·2	—	—
Ni $tu_2(NCS)_2$	17·6	—	39·7	17·9	—	39·3

The infrared absorption spectra were measured with a Beckman IR2 single-beam instrument, the samples being pressed in potassium bromide pellets. Although Stewart[10] has shown that " complex " formation between thiourea and potassium bromide may occur under these conditions, resulting in a splitting of the absorption bands, no such effect was observed. In fact, except in the 3-μ region, all bands are within ±5 cm.$^{-1}$ of those observed by Stewart for " pure " thiourea.

RESULTS AND DISCUSSION

The infrared absorption bands are listed in Table 2.

Free Thiourea.—The spectrum observed for free thiourea agrees very well with that reported by Stewart,[10] and by Yamaguchi *et al.*,[8] except in the 3-μ region, as may be seen from Table 3.

Stewart's analysis[10] gives the A_1 (a_1) and B_1 (b_2) NH_2 rocking modes as coincident at 1086 cm.$^{-1}$. The calculation of Yamaguchi *et al.*,[8] shows that they should be distinct,

TABLE 2

tu	Ni tu_4Cl_2	Ni $tu_6(NO_3)_2$	Ni tu_6I_2	Ni $tu_2(NCS)_2$
3400s	3420s	3400s		3390m
	3360s	3360s	3360s	3300m
3250s	3230s	3220s	3225s	3220m
2720m	2730m	2740m	2720m	—
2130w				2100s
1620s	1630s	1630s		1640s
	1726s	1620s	1621s	1630sh
1476s	1488s	1500s	1490s	1518s
			1441m	
				1420s
1416vs	1400s	1387vs	1399vs	1392vs
		1350sh		
1200wb				
				1183vw
1090s	1100m	1104s	1096s	1115m
				971w
	883w	832m	884m	933m
				812m
				722w
733s	718s	717s	717s	702s

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[10] Stewart, *J. Chem. Phys.*, 1957, **26**, 248, and references therein.

TABLE 3

Infrared absorption frequencies for thiourea in the range 700—2800 cm.$^{-1}$

Stewart [10]	Yamaguchi *et al.*[8]	Calc.[8]	This work	Stewart [10]	Yamaguchi *et al.*[8]	Calc.[8]	This work
A_1				B_1			
1617	1610	1619	1620	1617	1625	1623	1620
1413	1417	1450	1416	1473	1470	1473	1476
1086	1083	1059	1090	1086	1114	1153	1200
730	730	757	733	486	415	462	—
463	488	498	—				

and in fact a second band, although much weaker and broader, was observed at about 1200 cm.$^{-1}$. This band was not observed for any of the complexes.

The band at 2700 cm.$^{-1}$ (Stewart,[10] 2670 cm.$^{-1}$) was not reported by Yamaguchi *et al.*[8] This band is present, with enhanced intensity, in the complexes, except for Ni tu$_2$(NCS)$_2$, from which it is entirely absent. Stewart [10] lists this band as a combination [ν_4 (a_1) + $2\nu_{11}$ (b_1); calc. 2671, obs. 2670 cm.$^{-1}$] of C=S stretching and S–C–N bending modes. Such a combination would be expected to show a shift on co-ordination (see below). This does not appear to be so. Other possible combinations which will also give rise to an absorption in this region, *e.g.*, (i) $\nu_3(a_1) + \nu_5(a_1)$, and (ii) $\nu_{15}(b_2) + \nu_{17}(b_2)$ [(i) calc. 2710, obs. 2720 cm.$^{-1}$; (ii) calc. 2820, obs. 2720 cm.$^{-1}$], should therefore be considered. Both of these latter combinations involve only N–H bonds, and are thus relatively insensitive to co-ordination through sulphur.

Complexes.—Bands in the 3200—3500 cm.$^{-1}$ region are associated with the N–H bonds.[8, 10–12] They do not seem to be significantly shifted by co-ordination. By analogy with urea complexes, where both N- and O-co-ordination are found, this region of the spectrum can be used [12] to determine the donor atoms in a given complex; co-ordination by oxygen introduces little change in the spectrum with respect to that of free urea, but N-co-ordination causes a splitting of these bands into two groups and a decrease in their intensity.[12] The latter does not appear to happen for thiourea complexes, so that bonding through sulphur can be inferred in all cases.

The sharpening of these bands noticed by Yamaguchi *et al.*,[8] for Ni tu$_2$(NCS)$_2$ appears to be restricted to that compound. The broadening of these bands in pure thiourea is attributed to a considerable amount of hydrogen bonding,[10] which is absent in Ni tu$_2$(NCS)$_2$. The generally broad nature of these bands for the hexa- and tetra-thioureanickel(II) complexes is very similar to that observed in free thiourea, so that considerable hydrogen bonding must also be present in these compounds. Indeed, the structure of Ni tu$_4$Cl$_2$ [6] is such that Cl · · · H–N-type hydrogen bonding must occur, and in the other compounds it is possible to envisage similar situations. The structure of Ni tu$_2$(NCS)$_2$, with its planar [Ni tu$_2$] unit [9] [see (I)] allows very little scope for hydrogen bonding.

The band at about 2720 cm.$^{-1}$, mentioned above, is present, with increased intensity, in all the complexes except Ni tu$_2$(NCS)$_2$, from which it is entirely absent. If the alternative combinations given above are correct, this result is reasonable if the combining mechanism is associated with the formation of hydrogen bonds.

The B_1 N–C–N stretching mode, found at 1476 cm.$^{-1}$ in free thiourea, should be sensitive to co-ordination through sulphur, because of the increased double-bond character of the C–N bond. This is clearly seen in the series: free thiourea, 1476 cm.$^{-1}$; mono-co-ordinate thiourea [Ni tu$_6$(NO$_3$)$_2$, 1488; Ni tu$_4$Cl$_2$, 1500 cm.$^{-1}$]; bridging thiourea [Ni tu$_2$(NCS)$_2$, 1518 cm.$^{-1}$].

Three A_1 modes (C–S stretching, C–N stretching, and NH$_2$ rocking) give rise to absorption in free thiourea at 1416, 1090, and 733 cm.$^{-1}$. Co-ordination will lead to a decrease in the C–S stretching frequency, and an increase in the C–N stretching frequency. The

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[11] Badger and Waldron, *J. Chem. Phys.*, 1957, **26**, 255; Chibisov and Pentin, *J. Gen. Chem.* (*U.S.S.R.*), 1961, **31**, 11, 323.

[12] Quagliano, Svatos, and Curran, *Analyt. Chem.*, 1954, **26**, 429; Svatos, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1955, **77**, 6159.

experimental frequencies will result from " hybrids " of these three modes, and the effect of co-ordination on the frequency will depend on their relative weightings in each " hybrid." Thus the bands at about 1100 cm.$^{-1}$ show an increase on co-ordination (1090 $\rightarrow$ 1100 $\rightarrow$ 1115 cm.$^{-1}$), showing that the C–N stretching mode is more important than is the C–S stretching mode. In the 700-cm.$^{-1}$ region, the reverse is the case (733 $\rightarrow$ 718 $\rightarrow$ 702 cm.$^{-1}$) The 1400-cm.$^{-1}$ band is also lowered on co-ordination, but the presence of other absorption bands in this region makes interpretation difficult.

The intensity of the 1100-cm.$^{-1}$ band decreases noticeably on co-ordination, although not always to the extent noticed by Yamaguchi *et al.*;[8] at the same time, it is considerably broadened. They[8] have suggested that this is due to the increased frequency of the C–S stretching mode. It seems unlikely that a change in " the degree of mixing " of the three A_1 modes associated with this absorption band should give rise to a broadening of the band; instead, it should give rise to a shifting of the band. The broadening is possibly an effect of co-ordination, similar to that of hydrogen bonding in the 3-μ region. A similar, but smaller, effect is seen for the 730-cm.$^{-1}$ band.

The strong band at 2100 cm.$^{-1}$ in Ni $tu_2(NCS)_2$ is associated with the thiocyanate group. The ν_3 band of the thiocyanate ion (2066 cm.$^{-1}$) has been used to determine the mode of bonding of thiocyanato-groups in complexes,[13] terminal groups absorbing in the range 2100—2120 cm.$^{-1}$, and bridging groups in the range 2150—2182 cm.$^{-1}$. It is seen, therefore, that thiocyanato-bridges are absent in Ni $tu_2(NCS)_2$, a conclusion in accord with the known structure.[9]

Stewart[10] lists the A_1 and B_1 deformation modes of $-NH_2$ as being of equal frequency (1617 cm.$^{-1}$), but Yamaguchi *et al.*,[8] have separated them (1610 and 1625 cm.$^{-1}$, respectively). We have not separated these modes for pure thiourea, but, on co-ordination, the splitting has become clear. This may be due to changes in the hydrogen bonding affecting the two symmetry modes differently.

The bands at 1350 and 832 cm.$^{-1}$ for Ni $tu_6(NO_3)_2$ are associated with the nitrate group. As they are not shifted from the positions for normal ionic nitrates,[14] this group is not co-ordinated to the metal. This conclusion has also been reached by Cotton, Faut, and Mague.[15]

The 812-cm.$^{-1}$ band of Ni $tu_2(NCS)_2$ is associated with the thiocyanate group. Basolo, Burmeister, and Poe[16] have shown that N- and S-co-ordinated thiocyanate can be distinguished by the position of this band, being at 842—854 cm.$^{-1}$ for N-co-ordination, and at about 700 cm.$^{-1}$ for S-co-ordination. The present position, at 812 cm.$^{-1}$, is somewhat outside the range for N-co-ordination, but is much nearer to this range than to that for S-co-ordination.

Conclusions.—Co-ordination of thiourea to nickel causes shifts of certain infrared absorption frequencies, notably at about 1400, 1100, and 700 cm.$^{-1}$, which can be correlated with changes in double-bond character of the C–S and C–N bonds. Such changes imply increased importance of charged resonance-contributors of the type $\overset{+}{N}H_2{:}C(S^-){\cdot}NH_2$, and hence an effective movement of electron density towards the sulphur atom within the thiourea molecule. Such a situation implies considerable covalent character of the sulphur–nickel bonds. This conclusion is not unexpected for complexes with metal–sulphur bonds.

The author thanks Professor A. L. Odell for useful discussion, Dr. L. D. Colebrook for help in obtaining the infrared spectra, Professor D. R. Llewellyn for his continued interest, and the Research Committee of the N.Z. Universities Grants Committee for financial assistance.

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[*Received, June 29th*, 1964.]

[13] Chatt and Duncanson, *Nature*, 1956, **178**, 997.

[14] Bellamy, " Infra-red Spectra of Complex Compounds," 1st edn., Methuen, London, 1954, p. 255.

[15] Cotton, Faut, and Mague, *Inorg. Chem.*, 1964, **3**, 17.

[16] Basolo, Burmeister, and Poe, *J. Amer. Chem. Soc.*, 1963, **85**, 1700.