

## Spectral and magnetic studies of metal thiocyanate complexes with N-substituted thioureas

S B KOKATNUR† and A S R MURTY \*

Department of Chemistry, Karnatak University, Dharwad 580 003, India

†B K Arts and Science College, Chikodi, India

MS received 30 July 1981 ; revised 10 September 1982

**Abstract.** The complexes of the type  $ML_2(SCN)_2$  have been synthesised from  $M(SCN)_2$  [ $M = CO(II), Ni(II)$ ] and N-substituted thioureas (L) such as chlorophenyl (Cl-Ptu), tolyl (totu), methoxy phenyl (meo-ptu), nitrophenyl ( $NO_2$ -Ptu) and bromophenyl (Br-Ptu) thioureas. All the complexes are non-electrolytes in acetone. IR spectral studies reveal that thiourea and thiocyanate are bonded to the central metal through S and N respectively. Magnetic susceptibility studies at room temperature ( $25^\circ C$ ) and electronic spectral data confer octahedral symmetry to nickel (II) and tetrahedral symmetry to cobalt (II) complexes.

**Keywords.** Spectral ; magnetic ; nickel (II) ; cobalt (II) ; N-substituted thioureas.

### 1. Introduction

The replacement of halides by potentially ambidentate thiocyanate groups offers interesting bonding possibilities in metal complexes. The linear thiocyanate anion may coordinate to metal through either nitrogen  $M \leftarrow NCS$  or sulphur  $M \leftarrow SCN$  or both  $M \leftarrow NCS \rightarrow M$ .  $M \leftarrow NCS$  group is either linear or bent, while  $M \leftarrow SCN$  group is always bent. The  $\nu CS$  and  $\delta NCS$  frequencies are different between the two isomers (Turco and Pecile 1961 ; Lewis *et al* 1961 ; Sabatini and Bertini 1960). Epps and Mazili (1972) have reported the isolation of the first octahedral complex containing both N and S bonded thiocyanate.

The synthesis and characterization of the complexes of the composition  $[Ni L_2(SCN)_2]$  and  $[CO L_2(SCN)_2]$  have been reported by Yagupsky *et al* (1965) and Maharana *et al* (1970). According to the above authors, both thiourea (through S) and thiocyanate (through N) are bonded to the metal. No reports are available on the synthesis and characterization of cobalt (II) or nickel (II) thiocyanate complexes with N and N, N' substituted thioureas. So it is proposed to carry out systematic studies of the above complexes.

---

\* To whom all correspondence should be made.

## 2. Experimental

### 2.1. *Synthesis of ligands*

The ligands were synthesised from appropriate substituted amines, ammonium thiocyanate and hydrochloric acid utilizing published procedures (Kurzer 1958; Frank and Smith 1955).

### 2.2. *Synthesis of complexes*

The metal thiocyanate and the N-substituted thioureas were mixed in 1:1 ratio in hot ethanol. The mixture was refluxed for 30 min in the case of cobalt complex and was concentrated with constant stirring in the case of nickel complex. The solid thus obtained was filtered, washed with alcohol and ether and then dried in vacuum over  $P_2O_5$ . In some cases the solid was separated by vigorous stirring with petroleum ether (60–80° C) and the same was treated as above.

### 2.3. *Chemical analysis*

All complexes were analysed for cobalt (oxinate method-gravimetric), nickel (dimethylglyoxime-gravimetric), nitrogen, sulphur and chlorine (Vogel 1962).

### 2.4. *Physical measurements*

Conductance studies of complexes in acetone medium were made utilizing Elico conductivity bridge type CM-82 provided with a dip type conductivity cell having cell constant 0.61.

Molar magnetic susceptibility of the complexes was measured at room temperature (25° C) by Gouy method against  $Hg[Co(SCN)_4]$  as calibrant. It was corrected for diamagnetism from the data available in the table of pascal's constants (Mulay 1963).

The infrared spectra of ligands and complexes in KBr pellet were recorded on Perkin-Elmer model 257 spectrometer. The electronic spectra of the complexes in nujol mull were taken from Unicom 700 A instrument.

## 3. Results and discussion

### 3.1. *Physical properties*

The N-substituted thiourea complexes of cobalt (II) thiocyanate are blue to bluish green while those of nickel (II) are pale yellow to deep yellow powders. They are soluble in acetone. The elemental analysis favours 1:2 ratio for metal to ligand. (cf table 1). The molar conductance values fall into the range 4 to 38 mhos  $cm^{-2} mol^{-1}$  at 25° C indicating their non electrolytic nature.

### 3.2. *Infrared spectra*

The assignments of different bands in infrared region have been made according to the procedure laid down by Jensen and Nielsen (1966). The coordination

Table 1. Elemental analysis of complexes.

Sl. No.	Name of the complex	% Ni/Co	% N	% S
1.	[Ni (o-Cl Ptu) <sub>2</sub> (NCS) <sub>2</sub> ]	10·66 (10·70)	15·40 (15·33)	23·45 (23·56)
2.	[Ni (m-Cl Ptu) <sub>2</sub> (NCS) <sub>2</sub> ]	10·57 (10·70)	15·17 (15·33)	23·31 (23·56)
3.	[Ni (p-Cl Ptu) <sub>2</sub> (NCS) <sub>2</sub> ]	10·56 (10·70)	15·35 (15·33)	23·45 (23·56)
4.	[Ni (o-totu) <sub>2</sub> (NCS) <sub>2</sub> ]	11·20 (11·57)	16·36 (16·57)	25·39 (25·28)
5.	[Ni (m-totu) <sub>2</sub> (NCS) <sub>2</sub> ]	11·36 (11·57)	16·40 (16·57)	25·42 (25·28)
6.	[Ni (p-totu) <sub>2</sub> (NCS) <sub>2</sub> ]	11·43 (11·57)	16·38 (16·57)	25·07 (25·28)
7.	[Ni (o-meo Ptu) <sub>2</sub> (NCS) <sub>2</sub> ]	11·04 (10·89)	15·77 (15·59)	23·96 (23·78)
8.	[Ni (m-NO <sub>2</sub> Ptu) <sub>2</sub> (NCS) <sub>2</sub> ]	10·37 (10·31)	19·87 (19·69)	22·60 (22·52)
9.	[Ni (p-Br Ptu) <sub>2</sub> (NCS) <sub>2</sub> ]	9·09 (9·22)	13·39 (13·19)	19·94 (20·13)
10.	[Co (o-Cl Ptu) <sub>2</sub> (NCS) <sub>2</sub> ]	10·65 (10·78)	15·12 (15·33)	23·27 (23·39)
11.	[Co (m-Cl Ptu) <sub>2</sub> (NCS) <sub>2</sub> ]	11·05 (10·78)	15·04 (15·33)	23·40 (23·39)
12.	[Co (p-Cl Ptu) <sub>2</sub> (NCS) <sub>2</sub> ]	10·86 (10·78)	15·12 (15·33)	23·41 (23·39)
13.	[Co (o-totu) <sub>2</sub> (NCS) <sub>2</sub> ]	11·80 (11·61)	16·72 (16·56)	24·91 (25·27)
14.	[Co (m-totu) <sub>2</sub> (NCS) <sub>2</sub> ]	11·80 (11·61)	16·44 (16·56)	25·01 (25·27)
15.	[Co (p-totu) <sub>2</sub> (NCS) <sub>2</sub> ]	11·55 (11·61)	16·50 (16·56)	25·11 (25·27)
16.	[Co (o-me o-Ptu) <sub>2</sub> (NCS) <sub>2</sub> ]	11·10 (10·92)	15·33 (15·58)	23·52 (23·77)
17.	[Co (m-NO <sub>2</sub> Ptu) <sub>2</sub> (NCS) <sub>2</sub> ]	10·25 (10·35)	19·56 (19·68)	22·55 (22·52)
18.	[Co (p-Br Ptu) <sub>2</sub> (NCS) <sub>2</sub> ]	9·08 (9·25)	12·98 (13·19)	19·98 (20·12)

of central metal ion through S of the ligand ( $\nu$  C = S group) but not N of NH has been established on the basis of the following observations (cf. table 2)

- (i) No marked shift in the  $\nu$ NH region 3450-3000  $\text{cm}^{-1}$  on complexation,
- (ii) Slight positive shift for a strong band  $\nu$ NCN +  $\delta$ NH<sub>2</sub> in the region 1540-1480  $\text{cm}^{-1}$ ; (iii) A negative shift of the order 30  $\text{cm}^{-1}$ ; with reduction in intensity in a few complexes for the band  $\nu$ CS +  $\nu$ CN in the region 780-700  $\text{cm}^{-1}$  compared to free ligands and also a similar shift for the band  $\nu$ CS at 600-680  $\text{cm}^{-1}$ .

The appearance of  $\nu$ CN and  $\nu$ CS in the regions 2100-2000  $\text{cm}^{-1}$  and 820-750  $\text{cm}^{-1}$  respectively is indicative of linkage of NCS through N to the central

Table 2. IR absorption frequencies ( $\text{cm}^{-1}$ ) of ligands and complexes

Ligand/complex	$\nu$ NH	$\nu$ NCN + $\delta$ NH <sub>2</sub>	$\nu$ CS + $\nu$ NCN	NCS	
				$\nu$ CS	$\nu$ CS
o-Cl Ptu	3355 mbr	1504 s	725 s	670 s	...
[Ni L <sub>2</sub> (NCS) <sub>2</sub> ]	3350 mbr	1510 mbr	723 w	665 ms	805 mbr
[Co L <sub>2</sub> (NCS) <sub>2</sub> ]	3240 ms	1505 mbr	717 s	660 mbr	820 ms
m-Cl Ptu	3394 vs	1515 msh	706 vs	625 s	...
[Ni L <sub>2</sub> (NCS) <sub>2</sub> ]	3410 ms	1515 mbr	690 ms	635 vw	720 ms
[Co L <sub>2</sub> (NCS) <sub>2</sub> ]	3280 mbr	1510 br	710 ms	625 vw	800 s
p-Cl Ptu	3364 s	1496 sh	705 s	632 s	...
[Ni L <sub>2</sub> (NCS) <sub>2</sub> ]	3370 mbr	1518 ms	698 s	630 vw	800 msh
[Co L <sub>2</sub> (NCS) <sub>2</sub> ]	3238 mbr	1495 mbr	680 mbr	612 vw	815 ms
o-to tu	3328 s	1483 ms	754 s	631 s	...
[Ni L <sub>2</sub> (NCS) <sub>2</sub> ]	3380 ms	1503 ms	748 s	610 br	790 wsh
[Co L <sub>2</sub> (NCS) <sub>2</sub> ]	3290 mbr	1510 mbr	745 ms	2010 s	810 ms
m-to tu	3374 s	1508 ms	779 s	2050 w	...
[Ni L <sub>2</sub> (NCS) <sub>2</sub> ]	3350 br	1510 br	770 s	632 ms	...
[Co L <sub>2</sub> (NCS) <sub>2</sub> ]	3200 wbr	1520 mbr	769 s	610 wbr	800 wsh
p-to tu	3372 vs	1514 ms	745 s	610 vw	820 s
[Ni L <sub>2</sub> (NCS) <sub>2</sub> ]	3390 ms	1500-10 br	748 ms	643 ms	...
[Co L <sub>2</sub> (NCS) <sub>2</sub> ]	3400 ms	1510 mbr	752 wbr	640 vw	810 w
o-me o Ptu	3414 s	1489 ms	773 s	625 vw	800 s
[Ni L <sub>2</sub> (NCS) <sub>2</sub> ]	3390 mbr	1474 ms	760 s	692 vs	...
[Co L <sub>2</sub> (NCS) <sub>2</sub> ]	3400 ms	1498 ms	772 ms	680 mbr	770 wsh
m-No <sub>2</sub> Ptu	3374 s	1500 s	753 ms	690 vw	810 s
[Ni L <sub>2</sub> (NCS) <sub>2</sub> ]	3350 vs	1490 br	753 ms	660 ms	...
[Co L <sub>2</sub> (NCS) <sub>2</sub> ]	3270 w	1500 mbr	753 ms	670 ms	...
p-Br Ptu	3354 wsh	1510 ms	...	672 ms	810 s
[Ni L <sub>2</sub> (NCS) <sub>2</sub> ]	3365 wbr	1515 ms	...	640 w	...
[Co L <sub>2</sub> (NCS) <sub>2</sub> ]	3280 wsh	1506 mbr	...	640 vw	...
				2060 vs	...
				2055 s	810 mw

s = sharp ; br = broad ; vs = very sharp ; ms = medium sharp ; mbr = medium broad ; sh = shoulder.

Table 3. Electronic spectra of complexes (solid).

Sl. No.	$\nu_1$ kK	$\nu_2$ kK	$\nu_3$ kK	$\beta'$	$\beta'$	$\nu_2/\nu_1$	$\Delta$ cm <sup>-1</sup>	$\mu_{eff}$ BM
1.	8·477	14·930	22·779	892·6	0·845	1·76	8477	2·94
2.	8·696	15·620	26·666	1010·7	0·957	1·79	8696	2·89
3.	8·513	14·930	22·222	852·3	0·807	1·75	8513	3·01
4.		Diamagnetic						
5.	9·804	16·530	24·390	1007·6	0·954	1·69	9804	2·87
6.	8·510	14·930	25·000	1050·6	0·995	1·75	8510	2·94
7.	8·333	14·710	25·641	973·2	0·922	1·76	8333	2·85
8.	9·291	16·130	25·979	982·0	0·930	1·73	9291	3·00
9.	8·333	14·070	24·691	900·3	0·855	1·76	8333	2·80
10.		7·074	16·670	764·8	0·780	...	4092	4·64
11.		7·113	11·670	672·8	0·690	...	4114	4·72
12.		5·780	15·500	756·0	0·770	...	3314	4·54
13.		7·885	16·320	692·9	0·709	...	4590	4·50
14.		6·945	16·130	734·4	0·750	...	4020	4·64
15.		7·756	16·130	684·1	0·700	...	4541	4·41
16.		7·264	16·260	724·7	0·724	...	4217	4·81
17.		7·268	16·000	705·8	0·723	...	4227	4·62
18.		7·724	16·260	696·2	0·713	...	4514	4·48

cobalt (II) or nickel (II) ion (Nakamoto 1970 ; Mitchell and Williams 1960 ; Sabatini and Bertini 1965). However an extra band at 2140 cm<sup>-1</sup> exhibited by *m*-Cl Ptu and *m*-NO<sub>2</sub> ptu may tempt us to assign that for S bonding of NCS group, the position of  $\nu_{CS}$  band does not support the above view. If the thiocyanate complexes were to be S bonded, the  $\nu_{CN}$  should appear at a higher frequency side and  $\nu_{CS}$  at lower frequency (690–720 cm<sup>-1</sup>). Thus it can be concluded that in our complexes thiourea and thiocyanate are bonded through S and N respectively.

### 3.3. Electronic spectra

The solid state electronic spectra of the present nickel complexes exhibit three bands at  $\sim 8,500$  [ ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F) \nu_1$ ],  $\sim 15,000$  [ ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F) \nu_2$ ] and  $\sim 24,000$  [ ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F) \nu_3$ ]. The spectral parameters such as  $\Delta$  ( $10\Delta Dq$ ) and  $\beta$  have been calculated (Drago 1965). The octahedral nature of the complexes has been proved by the very weak intensity of the bands and the low value of  $\nu_2/\nu_1$  (1.73 to 1.79) [Sutton 1968]. The extent of covalency of the metal ligand bond can be estimated from  $\beta$  as shown in table 3.

In a tetrahedral ligand field, the frequencies of transition for cobalt (II) ion  ${}^4T_2(F) \leftarrow {}^4A_2(F)$ ,  ${}^4T_1(P) \leftarrow {}^4A_2(F)$  and  ${}^4T_1(F) \leftarrow {}^4A_2(F)$  are designated as  $\nu_1$  (not found)  $\nu_2$  ( $\sim 16,000$  cm<sup>-1</sup>) and  $\nu_3$  ( $\sim 7000$  cm<sup>-1</sup>) respectively in the increasing order of energies. The ligand field and Racah parameters have been calculated (Cotton and Goodgame 1961) and presented in table 3. The observed Dq (340–470 cm<sup>-1</sup>) and B' (670–700 cm<sup>-1</sup>) values for the present cobalt (II) complexes agree with the lower limits of the calculated values from

the rule of average environment  $\text{CoS}_2\text{Cl}_2$  chromophore-Dq ( $302\text{--}401\text{ cm}^{-1}$ ),  $B'$  ( $625\text{--}697\text{ cm}^{-1}$ ) and suggest that in these chloro-complexes, the ligand molecules are coordinated through S atom of the CS group.

### 3.4. Magnetic susceptibility data

It is observed that the  $\mu_{\text{eff}}$  values of Ni(II) complexes lie in the range 2.8 to 3.00 BM. As these values are slightly above the spin only value (2.83 BM), it is evident that the present complexes (1 to 9 excluding 4) are octahedral in nature and the complex 4 is square planar. The magnetic susceptibility values of Co(II) complexes lie in the range 4.4–4.8 BM which are higher than spin only value (3.87 BM). This indicates tetrahedral nature of the complexes.

## 4. Conclusion

On the basis of the above analytical, spectral and magnetic data, the tentative structure proposed for  $\text{NiL}_2(\text{SCN})_2$  is shown below.

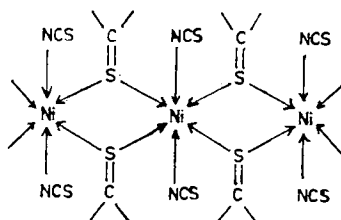


Figure 1. Structure of  $[\text{Ni}(\text{o-Cl Ptu})_2(\text{SCN})(\text{NCS})]$  complex.

Thus the octahedral nature of the central metal is indicated. However it is to be recognized that cobalt complexes exist as monomers with tetrahedral symmetry.

## Acknowledgements

The authors are thankful to Prof. H Sankegowda of Mysore University for providing facilities to carry out magnetic susceptibility studies of the complexes and are grateful to UGC, New Delhi for the award of Research fellowship to SBK.

## References

- Cotton F A, Goodgame D H L and Goodgame M 1961 *J. Am. Chem. Soc.* **83** 4691
- Drago R S 1965 *Physical Methods in Inorganic Chemistry* (New York : Reinhold) pp. 410
- Epps L A and Marzili L G 1972 *J. Chem. Soc. Chem. Comm.* 109
- Frank R I and Smith P V 1955 *Organic Synthesis Coll.* Vol. III (ed) Horning (New York : John Wiley) pp. 735
- Jensen K A and Nielsen P H 1966 *Acta Chem. Scand.* **20** 597

- Kurzer F 1958 *Organic Synthesis* Vol. 31 (ed) R S Seheriber, (New York : John Wiley) p. 21
- Lewis J, Nyholm R N and Smith P W 1961 *J. Chem. Soc.* 4590
- Maharana S N and Dash K C 1970 *Indian J. Chem.* 8 1023
- Mitchell P C H and Williams R J P 1960 *J. Chem. Soc.* 1912
- Mulay L N 1963 *Magnetic Susceptibility* (New York : John Wiley) p 1818
- Nakamoto K 1970 *Infrared Spectra of Inorganic Compounds* (New York : Wiley-Interscience) pp 189
- Sabatini A and Bertini I 1965 *Inorg. Chem.* 959
- Sutton D 1968 *Electronic Spectra of Transition Metal complexes* (London : McGraw Hill)
- Turco A and Pecile C 1961 *Nature (London)* 191 66
- Vogel A I 1962 *A Text Book of Quantitative Inorganic Analysis* 3rd edn, (London : ELBS Longmans) pp. 256, 462, 479, 389
- Yagupsky G and Lavitus R 1965 *J. Inorg. Nucl. Chem.*, 27 2603