

THIOCYANATO COMPLEXES OF Co (II), Ni (II), Zn (II), Cd (II), Cr (III) AND U (VI) CONTAINING UNIDENTATE AND BIDENTATE AUXILIARY LIGANDS

M.T.H. TARAFDER, M.A. AFFAN AND M.Q. ISLAM

Department of Chemistry, University of Rajshahi, Rajshahi, Bangladesh

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Several thiocyanato complexes of Co(II), Ni(II), Zn(II), Cd(II), Cr(III) and U(VI) containing some unidentate and bidentate auxiliary ligands have been synthesized and characterized by elemental analyses, magnetic and conductivity measurement, IR and electronic spectral studies. The complexes have the compositions $[\text{Co}(\text{SCN})_2.4\text{L}]$, $[\text{Ni}(\text{SCN})_2.2\text{L}. \text{H}_2\text{O}]$, $[\text{Zn}(\text{SCN})_2.2\text{L}]$, $[\text{Cd}(\text{SCN})_2.\text{L}']$, $[\text{Cd}(\text{SCN})_2.2\text{L}]$, H_2O , $[\text{UO}_2(\text{NCS})_2.3\text{L}]$ and $[\text{UO}_2(\text{NCS})_2.\text{L}'] \text{H}_2\text{O}$ where $\text{L} = \text{NH}_2\text{-NH}_2$; $\text{L}' = \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and $\text{C}_6\text{H}_4\text{-(NH}_2)_2$. The molar conductance data indicate that all the complexes behave as 2:1 electrolyte in DMSO. Magnetic and spectral data are in support of octahedral geometry for cobalt, nickel, chromium and uranium complexes whereas the zinc and cadmium complexes are probably tetrahedral in nature.

Key words: Donor, Acceptor, Interaction.

Introduction

There has been considerable interest in the investigation of the acceptor properties of transition metals [1-5]. In the case of ambidentate ligands the mode of coordination depends on the choice of both metal ions and auxiliary ligands [6-8]. As the thiocyanato ligand can coordinate either through the nitrogen or through the sulfur ends, its bonding sequences reveal the acceptor behaviour of the metal ions. The size of the metal ions and the nature of the auxiliary ligands both affect the coordination of the thiocyanato ligand. In general the electronic nature of the π -acid ligands renders class a acidity to the metal ions resulting in M-NCS bonding whereas σ -donor ligands render class b acidity in which case the bonding is profoundly M-SCN. In an earlier investigation it has been observed that the primary valencies of the higher valent (+4 state) metal ions determine its acidity [6-10]. In continuation of that study we have aimed to prepare thiocyanato complexes of both low and high valent lighter and heavier metal ions containing several bidentate ancillary ligands to see the bonding mode of the ambidentate ligand and the resultant geometry of the complexes. We report herein the synthesis and characterization of thiocyanato complexes of several transition metals ion containing hydrazine, O-phenylenediamine and ethylene diamine as ancillary ligands.

Experimental

Reagents. All chemicals used were of reagent grade and were used as supplied by Merck except for ethanol which was purified by refluxing the 99% crude with magnesium turnings and iodine and finally distilled and stored over molecular sieves.

Physical measurements and elemental analyses. IR spectra (as KBr pellets) were recorded on a Pye-Unicam SP3-300 IR spectrophotometer. Conductivities of 10^{-3}M

solutions in dimethyl sulfoxide (DMSO) were measured at room temperature using a WPA CM35 conductivity meter and a dip-type cell with platinized electrodes. Some of the conductivities were also measured in PTI-18 digital conductivity meter. Magnetic susceptibilities were obtained on a magnetic balance of Johnson Matthey catalytic systems Division Equipment, London. Electronic spectra were obtained on a LKB - Ultraspec K 4053 spectrophotometer.

Microanalysis for C, H and N were performed by the microanalytical Services at the Department of Chemistry, University of St. Andrews, Scotland. Metal estimation was done by standard methods [11,12].

Preparation of complexes. General method for the preparation of 1, 2, 4-9, $[\text{Ni}(\text{SCN})_2.2\text{L}. \text{H}_2\text{O}]$, $[\text{Zn}(\text{SCN})_2.2\text{L}]$, $[\text{Co}(\text{SCN})_2.4\text{L}]$, $[\text{Cd}(\text{SCN})_2.\text{L}']$, $[\text{Cd}(\text{SCN})_2.2\text{L}]$, $[\text{UO}_2(\text{NCS})_2.3\text{L}]$ and $[\text{UO}_2(\text{NCS})_2.\text{L}'] \text{H}_2\text{O}$ ($\text{L} = \text{NH}_2\text{-NH}_2$; ($\text{L}' = \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and $\text{C}_6\text{H}_4(\text{NH}_2)_2$).

These all compounds were prepared by the same general procedure. A solution of the appropriate hydrated metal nitrate (0.005 mol) in absolute ethanol (25 ml) was added to a solution of potassium thiocyanate (0.01 mol) in the same solvent (25 ml). The solution was filtered and to the filtrate, was added, a stoichiometric amount of L or L' in ethanol (25 - 75 ml). The mixture was boiled for 10 mins and cooled. The precipitated complexes were filtered, washed with hot ethanol and dried in vacuo over P_4O_{10} .

Preparation of 3, $[\text{Cr}(\text{SCN})_3.3\text{NH}_2\text{NH}_2]$. A solution of chromium nitrate monohydrate (0.003 mol) in absolute ethanol (20 ml) was added to a solution of potassium thiocyanate (0.009 mol) in the same solvent. The precipitated potassium nitrate was discarded and the filtrate added to an ethanolic solution of hydrazine hydrate (0.009 mol) (20 ml). The complex formed was separated and dried in vacuo over P_2O_5 .

TABLE 1. ANALYTICAL DATA AND OTHER PHYSICAL PROPERTIES OF THE COMPLEXES.

No.	Compound	Colour	mp (°C)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Metal (%)	Molar conduc- tance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Magnetic moment (BM)	Electronic spectral band maxima (λ_{max} in nm)
1.	[Ni(SCN) ₂ .2NH ₂ .NH ₂ .2H ₂ O]	Pale blue	240-242	8.6(8.7)	4.4(4.4)	30.4(30.6)	4.6(4.7)	69.0	3.01	840,550,330
2.	[Zn(SCN) ₂ .2NH ₂ .NH ₂]	White	205-207	9.8(9.8)	3.2(3.3)	34.1(34.2)	3.7(3.8)	66.0	diam	300
3.	[Cr(SCN) ₃ .3NH ₂ .NH ₂]	Pale blue	230-232	11.0(11.2)	3.7(3.7)	38.7(39.1)	6.1(6.2)	60.0	4.0	580,445,385
4.	[Co(SCN) ₂ .4.NH ₂ .NH ₂]	Pink	225-227	7.9(7.7)	5.2(5.3)	46.1(46.2)	5.1(5.0)	61.0	4.1	585,500
5.	[Cd(SCN) ₂ .C ₆ H ₄ (NH ₂) ₂]	Grey	235-237	28.3(28.6)	2.3(2.4)	16.5(16.7)	2.9(3.0)	62.0	diam	280
6.	[Cd(SCN) ₂ .NH ₂ CH ₂ CH ₂ NH ₂].H ₂ O	White	185-187	15.5(15.7)	3.3(3.3)	18.2(18.3)	2.7(2.7)	66.0	diam	290
7.	[Cd(SCN) ₂ .2NH ₂ .NH ₂].H ₂ O	White	210-212	7.6(7.7)	3.1(3.2)	26.7(27.1)	2.7(2.8)	62.0	diam	290
8.	[UO ₂ (NCS) ₂ .3NH ₂ .NH ₂]	Grey	228-230	4.9(5.0)	2.4(2.5)	23.0(23.2)	1.8(2.0)	68.0	diam	320
9.	[UO ₂ (NCS) ₂ .NH ₂ CH ₂ CH ₂ NH ₂].H ₂ O	Red yellow	190-192	10.1(10.2)	2.1(2.2)	12.0(12.1)	1.9(1.9)	62.0	diam	325

*Calculated values are in parenthesis.

Results and Discussion

Elemental analyses and other analytical data are presented in Table 1. The conductivity data for solutions in DMSO indicate that 1-9 are all 2:1 electrolytes [13]. This is because of solvation according to the scheme, $M(\text{SCN})_2 \cdot 2\text{L} + 2\text{DMSO} = [M(\text{DMSO})_2 \cdot 2\text{L}]^{++} + 2\text{SCN}^-$. The complexes 1-4, 7 and 8 exhibit IR bands characteristic of both coordinated and free amino moieties indicating that the ligand is unidentate in the complexes. O-phenylenediamine in 5 behaves as a bidentate ligand and shows bands at 3310 and 3240 cm^{-1} , considerably lower than the free ligand values (3400 and 3380 cm^{-1})⁵. Ethylene-diamine is potentially bidentate, coordinating through both the terminal nitrogens. In 6 and 9, the $\nu(\text{NH}_2)$ modes of the free ligand (3360, 3280 cm^{-1}) are shifted to lower wavenumbers at 3270-3320 and 3200-3260 cm^{-1} upon coordination. The presence of M-N coordinations in 1-9 are also evident from the appearance of $\nu(\text{M-N})$ bands at 472-260 cm^{-1} in the far IR spectra of the complexes [14-16]. The NCS moiety can coordinate either through the nitrogen or through the sulfur depending on the nature of the metal ions and the ancillary ligands used. The $\nu(\text{CN})$ appears at higher frequencies in M-S-C \equiv N complexes than those in M-N=C=S complexes [9,10]. The complexes 1-7 display $\nu(\text{CN})$ modes at 2080 - 2115 cm^{-1} characteristics of S-bonded thiocyanato moiety [18-20]. The metal ions in the above complexes are class b acceptors. In person's terminology these are soft acids. It is noteworthy that $\nu(\text{CS})$ modes appear at lower frequencies in M-S-C \equiv N complexes than those in M-N=C=S complexes [7,10,17]. 1-7 Display $\nu(\text{CS})$ at 745-795 cm^{-1} , arising from M-S-C \equiv N bonding sequence. That the thiocyanato ligands are S-bonded in 1-7 are also evident from the appearance of $\nu(\text{M-S})$ modes at 320-360 cm^{-1} in the far IR spectra of the complexes [19,20]. However, the $\nu(\text{CN})$ modes appear at 2070 and 2065 cm^{-1} in 8 and 9, respectively presumably arising

from U^{6+} -NCS coordination. The $\nu(\text{CS})$ bands appear at 860-870 cm^{-1} characteristic of M-N=C=S bonding sequence. These demonstrate that the electronic effect of σ donor ligands can not compete with the high primary valencies of U^{6+} . The metal ions in 8 and 9 exhibit class a acceptor property. 1 shows band at 3460 cm^{-1} , arising from the coordinated water molecule [21,22]. 6,7 and 9 show bands at 3400 cm^{-1} characteristic of lattice waters [23]. That water occupies a coordination position in 1 is also evident from the appearance of $\nu(\text{Ni-O})$ band at 562 cm^{-1} in the far IR spectrum of the complex [19,20]. The uranium complexes 8 and 9 display bands at 900 and 890 cm^{-1} , respectively attributable to $\nu(\text{U=O})$ stretch [18].

The complexes 2, 5-9 are diamagnetic. The complexes 1, 3 and 4 are paramagnetic, giving magnetic moments of 3.01, 4.0 and 4.1 B.M., respectively. The electronic spectra of all the complexes excepting 1, 3 and 4, show charge-transfer band only (Table 1). The nickel complex 1 exhibits bands at 840, 550 and 390 nm corresponding to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions in O_h symmetry, respectively. The chromium complex 3 shows absorption bands at 580, 445 and 385 nm assigned to the transitions ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$, ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions in O_h symmetry, respectively [24,25]. The complex 4 exhibits bands at 585 and 500 nm due to the transitions ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{F})$, respectively of octahedral cobalt (II) [25].

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