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Complexes of Esters of Pyridine Carboxylic Acids. Part I. Complexes with Ni(II) and Co(II) Thiocyanates

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The syntheses of Nickel(II) and Cobalt(II) thiocyanate complexes of type $ML_n(NCS)_2$ where M = Co or Ni and n = 2 for L = methyl picolinate (MP), ethyl picolinate (EP), isopropyl picolinate (IP) and n = 4 for L = ethyl nicotinate (EN) and ethyl isonicotinate (EIN), are described. The complexes have been characterised by elemental analyses, molar conductance, magnetic susceptibility, thermogravimetric, electronic and infrared spectral data. The complexes are non-electrolytes in nitrobenzene and have high spin distorted octahedral structure with N-bonded thiocyanate groups in trans-position. MP, EP and IP act as bidentate ligands coordinating through pyridine ring nitrogen and carbonyl oxygen while EN and EIN act as unidentate ligands and coordinate through ring nitrogen only. The values of splitting energy (10 Dq), Racah parameter (B) and nephelauxetic ratio (β) have been evaluated for the nickel complexes.

Introduction

A substantial array of nickel(II) and cobalt(II) thiocyanate complexes with the general formula ML_n $(NCS)_2$ where L = pyridine, α,β,γ-picolines, 2,6-lutidine or isoquinoline and n = 2 or 4, have been reported[1–10]. There are, however, few references concerning the use of esters of pyridine carboxylic acids as ligands. In this work we wish to report the synthesis and characterization of various complexes of esters of pyridine carboxylic acids. Specifically, complexes of nickel(II) and cobalt(II) thiocyanates with methyl picolinate (MP), isopropyl picolinate (IP), ethyl nicotinate (EN) and ethyl isonicotinate (EIN) are reported. In an earlier communication[11] we have reported some complexes of ethyl picolinate (EP). Part of the data given therein along with some additional results on nickel(II) and cobalt(II) thiocyanate complexes of ethyl picolinate is also being included for comparison.

Experimental

Reagents

Ethyl picolinate, methyl picolinate, isopropyl picolinate, ethyl nicotinate and ethyl isonicotinate were prepared from the corresponding acids by the general procedure described by Vogel[12]. Other reagents used were of BDH (AR) quality.

General Procedure for the Preparation of Metal Complexes

The nickel(II) and cobalt(II) thiocyanate complexes with various esters were prepared as follows. Solid potassium thiocyanate (0.02 mol) was dissolved in a solution of cobalt or nickel sulphate (0.01 mol in 50 ml distilled water). To this solution liquid ester (0.02 mol of EP, MP or IP and 0.04 mol of EN or EIN) was added dropwise with stirring and scratching the sides of the container. With EP, MP and IP, the solid complexes separated out quickly. They were washed successively with water, ether–alcohol mixture and pure ether and dried over calcium chloride. With EN and EIN instead a semisolid mass appeared which on keeping over anhydrous calcium chloride for 24 hours changed into an amorphous solid. For analysis of the complexes, Ni(II) was estimated as dimethylglyoxime complex and Co(II) as anthranilic acid complex. Thiocyanate content was estimated by Volhard's method and nitrogen by microanalytical techniques.

Magnetic and Conductance Measurements

Magnetic measurements were made at room temperature by the Gouy method using mercury tetrathiocyanatocobaltate(II) as standard. Conductivities were measured in nitrobenzene using precisely determined concentrations near 10^{-3} *M*, on a Toshniwal Conductivity Bridge type C1-0-1-/01.

Spectral Measurements

Infrared spectra, electronic spectra in solution and reflectance spectra were recorded on Perkin Elmer IR models 337 and 521, Specord UV– VIS, Cary 14 and Unicam 500 spectrophotometers.

Thermogravimetry

Thermogravimetric analysis was carried out on a Stanton Thermobalance Model AD-2.

Results and Discussion

The complexes synthesized in the investigations are listed in Table I along with their colour, physical appearance, melting point and molar conductance data. They correspond to the general formula $ML_n(NCS)_2$ where M = Ni(II) or Co(II) and n = 2 for L = EP, MP or IP and n = 4 for L = EN or EIN. All the compounds are stable to moisture and are soluble in organic solvents such as DMF, DMSO, nitrobenzene, nitromethane, acetonitrile, acetone and methanol. The molar conductivities of the millimolar solutions of the complexes in nitrobenzene (<6 ohm^{-1} cm^2 mol^{-1}) and in methanol (<50 ohm^{-1} cm^2 mol^{-1}) are considerably less than those for 1 : 1 electrolytes reported in the literature[13, 14] indicating that they behave almost as non-electrolytes in these solvents.

The vibrational bands of diagnostic value in the spectra of the ligands and the complexes are recorded in Table II. A perusal of Table II reveals that in the complexes of EP, MP and IP the pyridine ring vibrations are shifted to higher wavenumbers, while the C=O stretching vibrations get shifted to lower and the C–O stretching vibrations to higher spectral regions as compared to similar vibrations in the corresponding

TABLE I. Physico-chemical Data of the Complexes.

Complex	Colour and State	M. p. °C	Molar Conductance in Nitrobenzene[a]	Analytical Data					
				Metal (%)		Thiocyanate (%)		Nitrogen (%)	
				Found	Required	Found	Required	Found	Required
$Co(MP)_2(NCS)_2$	Pink violet powder	166	5.16	13.31	13.12	25.95	25.84	12.32	12.47
$Ni(MP)_2(NCS)_2$	Green powder	260	1.00	12.85	13.08	25.25	25.84	12.68	12.47
$Co(1P)_2(NCS)_2$	Pink powder	178	4.24	11.72	11.67	22.02	22.98	11.27	11.09
$Ni(IP)_2(NCS)_2$	Light green powder	188	1.00	11.48	11.63	22.33	22.98	11.03	11.09
$Co(EN)_4(NCS)_2$	Pink powder	107	5.84	7.51	7.56	14.75	14.89	10.54	10.77
$Ni(EN)_4(NCS)_2$	Bluish green crystal	115	1.46	7.48	7.54	14.80	14.89	10.40	10.78
$Co(EIN)_4(NCS)_2$	Buff powder	140	5.45	7.47	7.56	14.75	14.89	10.54	10.77
$Ni(EIN)_4(NCS)_2$	Bluish white powder	253	0.97	7.63	7.54	14.58	14.89	10.69	10.78

[a] Molar conductance of 1 : 1 electrolytes in nitrobenzene falls in the range 20–40 ohm^{-1}cm^{2}mol^{-1}.[13]

TABLE II. Pertinent Infrared Spectral Bands (cm^{-1}) of Ligands and Their Complexes.

Compound	$\nu_{C=O}$	ν_{C-O}	Pyridine Ring Vibrations						CN str.	CS str.	NCS bend
MP	1725	1250	1585	1575	1470	1433	1050	1000			
$Co(MP)_2(NCS)_2$	1690	1268	1600	1575	1480	1435	1068	1025	2080	823	477
$Ni(MP)_2(NCS)_2$	1675	1270	1595	1575	1475	1435	1055	1026	2075	800	476
EP	1723	1244	1590	1572	1465	1430	1045	995			
$Co(EP)_2(NCS)_2$	1685	1255	1600	1575	1468	1450	1050	1005	2075	820	472
$Ni(EP)_2(NCS)_2$	1668	1265	1604	1582	1470	1448	1043	1008	2078	818	473
IP	1720	1250	1595	1570	1475	1440	1050	1000			
$Co(IP)_2(NCS)_2$	1676	1265	1600	1581	1475	1450	1060	1020	2080	813	476
$Ni(IP)_2(NCS)_2$	1663	1255	1598	1578	1460	1445	1043	1020	2080	800	476
EN	1720	1290	1588	1464	1415	1037	1025				
$Co(EN)_4(NCS)_2$	1722	1290	1595	1475	1420	1020	1028		2068	815	485
$Ni(EN)_4(NCS)_2$	1725	1295	1595	1468	1418	1045	1018		2075	810	485
EIN	1720	1287	1592	1558	1460	1440	1020	992			
$Co(EIN)_4(NCS)_2$	1725	1288	1612	1565	1465	1450	1028	1018	2075	817	478
$Ni(EIN)_4(NCS)_2$	1720	1270	1608	1560	1455	1438	–	1008	2070	805	488

esters. This suggests that all the three esters coordinate to the metal atom through carbonyl oxygen and pyridine ring nitrogen, thus acting as bidentate ligands and forming five membered chelate rings with the metal atoms. In the complexes of ethylnicotinate and ethyl isonicotinate, on the other hand, no lowering of the C=O stretching frequency is observed. Rather there is a slight upward shift. The C–O stretching frequency is either slightly lowered or remains unaffected. This suggests that in the complexes of the two esters, carbonyl oxygen does not act as a donor atom. However, the pyridine ring vibrations in these complexes are shifted to higher spectral region indicating coordination of the pyridine ring nitrogen to the metal. Both EN and EIN, therefore, act as unidentate ligands in these complexes.

In the spectra of all these complexes the CN stretching vibrations appear as sharp or slightly broad bands in the range 2068–2080 cm^{-1} while CS stretching vibrations appear in 800–823 cm^{-1} region and NCS bending modes appear in the range 472–488 cm^{-1}. The position of these vibrational bands is suggestive of N-bonded thiocyanato groups[15–17]. Further, the non-splitting of CN stretching band is indicative of *trans* disposition of the thiocyanato groups in the complexes[18].

Cobalt(II) Complexes

Cobalt(II) complexes with all the esters are paramagnetic with the room temperature magnetic moments falling in the range 4.85–5.10 BM (Table III). These values are well within the range 4.7–5.2 BM generally observed for octahedral cobalt(II) complexes[19].

The electronic spectra of the complexes have been studied in methanol solutions in the region 25–12.5 kK. The results (Table III) indicate that in all these complexes the maximum absorption band is observed in the range 19.3–19 kK and the extinction coefficient is less than 50 which suggests that in all the complexes cobalt experiences an octahedral environment of the ligating atoms[9]. The band around 19 kK may be assigned to the transition $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ in octahedral stereochemistry. The reflectance spectra in the range 25–10 kK indicate that the complexes are octahedral even in the solid state and do not undergo any change in their stereochemistry on dissolution.

Thermogravimetry of the complexes (Figure 1) shows that each complex decomposes through the formation of an intermediate to finally give Co_3O_4. For $Co(MP)_2(NCS)_2$, the horizontal in the thermogravimetric curve, showing the formation of an intermediate, corresponds to the composition $Co(MP)(NCS)_2$. The composition of the intermediate in other cases could not be ascertained unambiguously. Curves further show that the ethyl picolinate complex is most stable and the ethyl isonicotinate complex is the least stable of all the complexes.

Nickel(II) Complexes

The room temperature magnetic moment of the nickel(II) complexes which fall in the range 3.16–3.23 BM, suggest octahedral geometry for the complexes[20]. Electronic spectra of all the complexes have been studied in methanolic solutions in the range 50–12.5 kK. Two of the three main bands now very well established for the majority of octahedral nickel(II) complexes have been observed to occur near 16 and 26 kK (Table III) in the spectra of all the complexes and have been assigned to the $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ transitions respectively. The ex-

TABLE III. Magnetic Moment, Electronic Spectral Data and Ligand Field Parameters of the Complexes.

Compound	μ_{eff} B.M.	Electronic Spectral Data			Dq cm^{-1}	B cm^{-1}	β
		Medium	Concentration	Bands observed in kK with ε in parentheses			
$Ni(MP)_2(NCS)_2$	3.17	solution, methanol	$8.8 \times 10^{-3} M$	25.50(18.3), 15.23(3.4)	936	842	0.78
$Ni(EP)_2(NCS)_2$	3.16	solution, methanol	$8.39 \times 10^{-3} M$	25.61(24.8), 15.31(4.8)	941	844	0.78
		solid, reflectance		15.87, 10.52			
$Ni(IP)_2(NCS)_2$	3.23	solution, methanol	$1.6 \times 10^{-2} M$	26.00(31.5), 15.46(7.6)	948	867	0.80
$Ni(EN)_4(NCS)_2$	3.21	solution, methanol	$1.0 \times 10^{-2} M$	27.00(13.4), 16.61(7.2)	1037	831	0.77
$Ni(EIN)_4(NCS)_2$	3.20	solution, methanol	$1.0 \times 10^{-2} M$	26.40(27.1), 15.69(5.8)	962	881	0.81
		solid, reflectance		16.80, 10.25			
$Co(MP)_2(NCS)_2$	4.85	solution, methanol	$4.4 \times 10^{-3} M$	19.00(26.9)			
$Co(EP)_2(NCS)_2$	4.88	solution, methanol	$4.2 \times 10^{-3} M$	19.31(14.5)			
		solid, reflectance		18.02			
$Co(IP)_2(NCS)_2$	4.91	solution, methanol	$8.0 \times 10^{-3} M$	19.17(37.8)			
$Co(EN)_4(NCS)_2$	5.10	solution, methanol	$2.5 \times 10^{-3} M$	19.00(23.3)			
		solid, reflectance		20.20			
$Co(EIN)_4(NCS)_2$	5.00	solution, methanol	$5.1 \times 10^{-3} M$	19.23(22.4)			
		solid, reflectance		20.83			

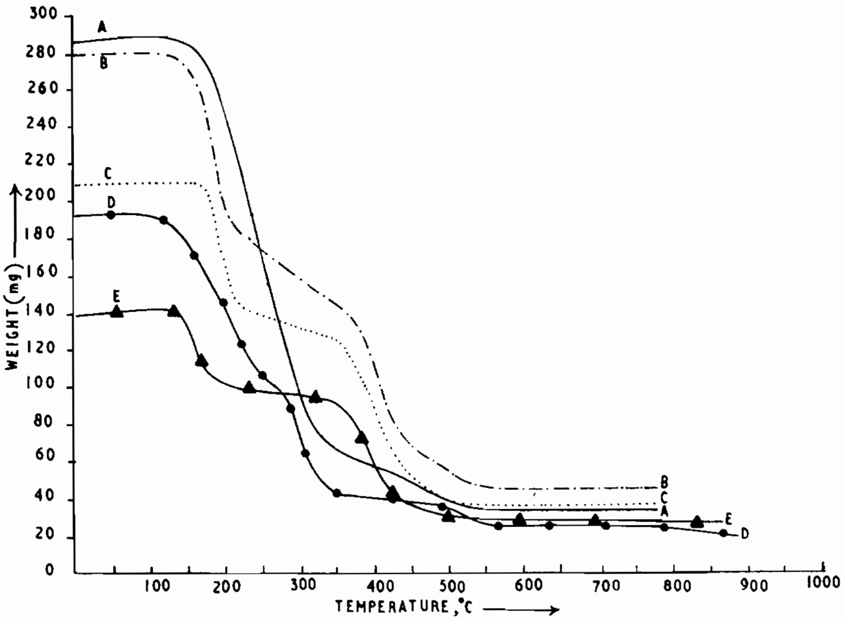

Figure 1. Thermogravimetric curves of $Co(EN)_4(NCS)_2$ (A), $Co(IP)_2(NCS)_2$ (B), $Co(EP)_2(NCS)_2$ (C), $Co(EIN)_4(NCS)_2$ (D) and $Co(MP)_2(NCS)_2$ (E).

tinction coefficient of the band around 16 kK in all cases is less than 10 l cm^{-1} mol^{-1}, which also favours an octahedral stereochemistry for these complexes[21].

The reflectance spectra of dithiocyanatobis(ethyl picolinate)nickel(II) and dithiocyanatobis(ethyl isonicotinate)nickel(II), recorded in the range 20–10 kK, show two bands with maximum absorption at 15.87 and 10.52 kK in the former and at 16.80 and 10.25 kK in the latter complex. These bands which correspond to the transitions ν_1 *i.e.* $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$ and ν_2 *i.e.* $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ respectively give the value $\frac{\nu_2}{\nu_1} = 1.51$ for the former and 1.64 for the latter complex. These values are within the range 1.5–1.7 generally reported for octahedral complexes[22]. From the electronic and infrared spectral data and magnetic and conductivity measurements, it can thus be concluded that all the complexes have *trans* octahedral configurations.

The value of splitting energy (10Dq) in octahedral nickel(II) complexes is usually taken directly from the first energy transition ν_1. However, this method gives only approximate values. In the present investigations, 10Dq and the Racah parameter B have been calculated from the observed positions of ν_2 and ν_3 by using the equations for the d^8 system[23].

In calculating the Dq values only data for solution spectra were used since in these spectra the band maximum could be located more accurately as compared to the reflectance spectra. These values (Table III) lead to the following spectrochemical series: MP < EP < IP < EIN < EN.

The Dq values reported for the complexes $NiL_4(NCS)_2$, where L = pyridine, 3-methyl pyridine, 4-methylpyridine and isoquinoline, fall in the range 1040–1050 cm^{-1} [24]. The esters used in the present studies should, therefore, be placed below the above mentioned nitrogen bases in the spectrochemical series.

In pyridine and its derivates, the nitrogen atom is in an aromatic ring system with delocalized π orbitals so that there is a possibility of transmission of some electron density from the metal to the π orbitals of the ligand through the donor atom. Evidence for the moderate degree of π bonding in six coordinate cobalt(II) pyridine complexes[25,26] and nickel(II) complexes of pyridine and its derivatives[24] has been reported. It can, therefore, be inferred that in the complexes of MP, EP, IP, EN or EIN with nickel(II) thiocyanate, one of the important factors influencing Dq values must the π-acceptor tendency of these ligands. Although thiocyanate is also known to have relatively high π-acceptor capacity, its effect on the variation in Dq values can be neglected since this effect will be of the same magnitude in all the complexes.

The values of B found in the complexes are less than the value of 1041 cm^{-1} found for the free ion. The reduction in B as represented by the ratio B in the complex/B in the free ion $= \beta$ can be taken as directly related to the covalent character in the metal–ligand bond. The following nephelauxetic series then results by placing the ligands in order of decreasing value of β: EIN > IP > EP > MP > EN. Since the nephelauxetic series reflect the net result of inductive and polarization factors, an appropriate explanation for the values is rather difficult.

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