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Synthesis and Characterization of the adducts of Bis(*O*-ethyldithiocarbonato)nickel(II) with substituted pyridines

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ABSTRACT

A series of adducts of Bis(*O*-ethyldithiocarbonato)nickel(II) with substituted pyridines have been synthesized by treating bis(*O*-ethyldithiocarbonato)nickel(II) with substituted pyridines in acetone. Analytical results show that the adducts have 1:1 and 1:2 stoichiometry with general formula $M(Xan)_2 L$ and $M(Xan)_2 L_2$ (M = Ni, Xan = *O*-ethyldithiocarbonate, L = 2-, 3- and 4- amino pyridines, 3- and 4- cyano pyridines). These addition complexes have been characterized by elemental analysis, conductivity measurements, magnetic susceptibility measurements, infrared and electronic spectral studies.

Key words: Adducts, *O*-alkyldithiocarbonates(xanthates) and substituted pyridines.

INTRODUCTION

The coordination compounds in which the dithio-ligands form a ring with the metal ion have been reported for a great number of metal ions and display interesting and often quite novel properties and structures. Many of them have been used in the analytical chemistry. They have also been used as fungicides, pesticides, vulcanization accelerators, floatation agents and high pressure lubricants[1,2]. *O*-alkyldithiocarbonates(xanthates) are among the more frequently considered sulphur containing ligands that have been studied from past may years. Xanthates are formed by the reaction between a metal alkoxide and carbondisulphide. A variety of alcohols have been xanthated in this manner. Xanthates form a variety of complexes with transition metals which have been the subject of detailed physico-chemical studies. The transition metal xanthates have been extensively studied over the several previous decades for their broad application in the manufacture of synthetic textiles, as collectors for flotation of sulphide minerals and in agriculture[3,4]. Several mixed ligand complexes of Mn(II), Fe(II), Ni(II), Zn(II), Cd(II) and Hg(II) with xanthates have been synthesized and characterized[5-7]. Although the reports on metal complexes containing dithiocarbonates (xanthates) are extensive, the studies on transition metal complexes containing both dithiocarbonate moiety and substituted pyridine ligands are scarce. This prompted us to prepare and investigate the adducts of bis(*O*-ethyldithiocarbonato)nickel(II) with substituted pyridines such as 2-, 3- and 4-amino pyridines and 3- and 4- cyano pyridines.

EXPERIMENTAL

Preparation of Potassium ethylxanthate

The potassium salt of *O*-ethyldithiocarbonate was prepared by the standard published method[8].

Into a 500 ml RBF, fitted with a reflux condenser, placed 42g (0.75 mol) of KOH pellets and 120 g (152 mL) of absolute ethanol. The resulting solution was heated under reflux for 1 h. It was allowed to cool and decanted the liquid from the residual solid into another dry 500 ml flask; added 57g (45 ml, 0.75 mol) of CS_2 slowly and with constant shaking. Filtered the resulting almost solid yellow mass, after cooling in ice, on a sintered glass funnel at the pump and washed with three 25 ml portions of ether. Dried the potassium *O*-ethyldithiocarbonate in a vacuum dessicator over silica gel. The yield was 74 g.

Preparation of bis(*O*-ethyldithiocarbonato) nickel(II) or nickel(II) ethylxanthate

The complex bis(*O*-ethyldithiocarbonato) nickel(II) was prepared by mixing and constant stirring of the aqueous solutions of nickel chloride (2.36 g, 0.01 mol) and potassium ethylxanthate (3.20 g, 0.02 mol). Brown precipitates were formed which were filtered immediately and were dried in a vacuum dessicator over anhydrous calcium chloride. The composition of the complex was established to be $[Ni(S_2COCH_2CH_3)_2]$ by the elemental analysis. (Nickel: found 18.53%, calculated : 19.43%).

Preparation of the adducts of bis(*O*-ethyldithiocarbonato) nickel(II) with substituted pyridines

1:1 addition complexes of nickel(II)ethylxanthate i.e. $Ni(S_2OCH_2CH_3)_2$ with substituted pyridines (nitrogen donors) were prepared by direct mixing of $Ni(S_2OCH_2CH_3)_2$ (0.78 g, 0.0026 mol) in acetone (60 mL) with substituted pyridines [2-aminopyridine = 0.244 g, 3-aminopyridine = 0.244 g, 4-aminopyridine = 0.244 g, 3-cyanopyridine = 0.270 g and 4-cyanopyridine = 0.270 g (0.0026 mol)].

The 1:2 addition complexes of nickelII) ethylxanthate with substituted pyridines were also pepared by direct mixing of $Ni(S_2OCH_2CH_3)_2$ (0.78 g, 0.0026 mol) in acetone (60 ml) with substituted pyridines [2-aminopyridine = 0.488 g, 3-aminopyridine = 0.488 g, 4-aminopyridine = 0.488 g, 3-cyanopyridine = 0.541 g and 4-cyanopyridine = 0.541 g (0.0052 mol). The resulting solutions were concentrated by distillation to obtain the maximum yield. The contents of the reaction mixture were allowed to stand for 20-24 hours, deposited green solid the solvent used in their preparation and dried over calcium chloride at room temperature.

METHODS

Carbon, Hydrogen, Nitrogen and Sulfur were determined on elemental analyzers (elemental vario EL III, Carlo Erba 1108). Molar conductance was determined on the millimolar solution in DMF using (centuary CC60 conductivity bridge). Infrared spectra of the complexes over the region 4000-200 cm^{-1} were recorded using KBr pellets on Infrared spectrometer (Perkin Elemer FT-IR Spectrometer). The electronic spectra of the adducts were recorded in DMF on systronics 119 UV-visible spectrophotometer. Magnetic moments were determined at room temperature by VSM method (Princeton Applied Research-Model No. 155). The analytical data, molar conductance and magnetic moments of the adducts isolated are presented in Table 1. Important IR bands and electronic spectral data are cited in Table 2.

RESULTS AND DISCUSSION

The complexes of Ni(II)ethylxanthates with amino and cyano pyridines are microcrystalline solids which are dark green or blackish-green. These adducts are soluble in acetone, chloroform dimethylformamide and dimethylsulphoxide. On the basis of elemental analysis (Table 1) the adducts isolated having 1:1 and 1:2 stoichiometry are assigned the formula $Ni(S_2OCH_2CH_3)_2$ L and $Ni(S_2OCH_2CH_3)_2\ L_2$ (where L = 2-, 3- and 4-aminopyridines, 3- and 4- cyanopyridines). The molar conductance are found in the range of 18.96-33.75 $ohm^{-1}\ mol^{-1}\ cm^2$ (Table 1). These values are lower than the values which can be expected for uni-univalent electrolytes in the solvent suggesting that these complexes are neutral and non-ionic in nature[9,10]. The 1:1 adducts of nickel(II)ethylxanthate with amino and cyanopyridines exhibit the magnetic moments around zero which is in agreement with magnetic moment values observed in many low spin square pyramidal complexes of nickel(II)[11]. The 1:2 adducts of nickel(II)ethylxanthate show magnetic moment values of 2.98 to 3.21 B.M. which is in agreement with magnetic moment values observed for octahedral complexes of nickel(II)[12,13].

A comparison of the infrared spectra of the present complexes with those of the

Table 1: Analytical, molar conductance and magnetic susceptibility data of the adducts of bis(*O*-ethyldithiocarbonato)nickel(II) with substituted pyridines

S. No.	Adducts	Formula	% found				% calculated				Molar Cond. (ohm^{-1} mol^{-1} cm^{2})	μ_{eff} (B.M.)
			C	H	N	S	C	H	N	S		
1	$Ni(S_2OCH_2CH_3)_2$(2-aminopyridine)	$C_{11}H_{16}O_2N_2S_4Ni$	32.40	3.07	6.18	31.02	33.43	4.08	7.08	32.45	19.21	-
2	$Ni(S_2OCH_2CH_3)_2$(3-aminopyridine)	$C_{11}H_{16}O_2N_2S_4Ni$	32.45	4.02	6.23	31.12	33.43	4.08	7.08	32.45	21.34	-
3	$Ni(S_2OCH_2CH_3)_2$(4-aminopyridine)	$C_{11}H_{16}O_2N_2S_4Ni$	32.43	3.05	6.27	31.24	33.43	4.08	7.08	32.45	22.42	-
4	$Ni(S_2OCH_2CH_3)_2$(3-cyanopyridine)	$C_{12}H_{14}O_2N_2S_4Ni$	34.21	2.89	5.67	30.13	35.56	3.48	6.91	31.65	22.47	-
5	$Ni(S_2OCH_2CH_3)_2$(4-cyanopyridine)	$C_{12}H_{14}O_2N_2S_4Ni$	34.14	2.19	5.32	30.15	35.56	3.48	6.91	31.65	22.34	-
6	$Ni(S_2OCH_2CH_3)_2$(2-aminopyridine)$_2$	$C_{16}H_{22}O_2N_4S_4Ni$	38.18	3.46	10.81	25.11	39.27	4.53	11.45	26.21	18.67	2.99
7	$Ni(S_2OCH_2CH_3)_2$(3-aminopyridine)$_2$	$C_{16}H_{22}O_2N_4S_4Ni$	38.13	3.57	10.44	25.13	39.27	4.53	11.45	26.21	19.76	3.20
8	$Ni(S_2OCH_2CH_3)_2$(4-aminopyridine)$_2$	$C_{16}H_{22}O_2N_4S_4Ni$	38.26	3.78	10.54	25.23	39.27	4.53	11.45	26.21	19.38	3.17
9	$Ni(S_2OCH_2CH_3)_2$(3-cyanopyridine)$_2$	$C_{18}H_{18}O_2N_4S_4Ni$	41.52	2.56	10.01	24.31	42.44	3.56	11.00	25.18	22.58	3.15
10	$Ni(S_2OCH_2CH_3)_2$(4-cyanopyridine)$_2$	$C_{18}H_{18}O_2N_4S_4Ni$	41.45	2.83	10.13	24.26	42.44	3.56	11.00	25.18	24.37	3.19

Table 2: Infrared and electronic spectral data of the adducts of bis(*O*-ethyldithiocarbonato)nickel(II) with substituted pyridines

S. No.	Adducts	IR Spectra Data			Electronic Spectral Data		
		ν(C–O)	ν(C–S)	ν(M–S)	ν_1(cm^{-1})	ν_2(cm^{-1})	ν_3(cm^{-1})
1	$Ni(S_2OCH_2CH_3)_2$(2-aminopyridine)	1189	1034	319	13620	21600	-
2	$Ni(S_2OCH_2CH_3)_2$(3-aminopyridine)	1184	1040	312	13320	21410	-
3	$Ni(S_2OCH_2CH_3)_2$(4-aminopyridine)	1193	1038	315	13700	21940	-
4	$Ni(S_2OCH_2CH_3)_2$(3-cyanopyridine)	1182	1030	313	13573	21010	-
5	$Ni(S_2OCH_2CH_3)_2$(4-cyanopyridine)	1187	1039	310	14490	21600	-
6	$Ni(S_2OCH_2CH_3)_2$(2-aminopyridine)$_2$	1196	1035	316	10356	17388	26959
7	$Ni(S_2OCH_2CH_3)_2$(3-aminopyridine)$_2$	1195	1030	317	10389	17342	26952
8	$Ni(S_2OCH_2CH_3)_2$(4-aminopyridine)$_2$	1197	1040	310	10425	17978	27182
9	$Ni(S_2OCH_2CH_3)_2$(3-cyanopyridine)$_2$	1191	1036	318	10674	18320	27723
10	$Ni(S_2OCH_2CH_3)_2$(4-cyanopyridine)$_2$	1194	1035	313	10312	17888	27826

corresponding free ligands reveals that most of the absorption bands of free ligands are shifted in their respective complexes. Amino and cyanopyridines have two possible coordinating cites. It has been established that N-H and C-N frequencies must show negative shift if the coordination occurs through amino group or cyanogroup nitrogen atom. But in the pesent complexes, they show no appreciable negative shift. Thus the possibility of coordination of 2-, 3- and 4-aminopyridines, 3- and 4 cyanopyridines through their amino or cyano nitrogen atom with metal is ruled out. This has been confirmed by examining the C-H out of plane deformation vibrations. In amino and cyanopyridine complexes C-H out of the plane bands occur at lower energy positions on complexation indicating negative shifts which confirms that these ligands interact with the metal ion through their respective ring nitrogen atom.

Electronic spectra of 1:1 adducts of nickel(II)ethylxanthate have been recorded in the range 13000-25000 cm^{-1}. It shows two main bands presented in the Table 2. The broad intense band centred around 21000 cm^{-1} is assigned to $^1A \rightarrow {}^1E$ (d_{xz}, d_{yz} $\rightarrow d_{x2-y2}$) transition (ν_2). The weak band around 14000 cm^{-1} is assigned to spin allowed orbitally forbidden transition (ν_2) viz., $^1A_1 \rightarrow {}^1B_1$ ($d_{z2} \rightarrow d_{x2-y2}$). This data is consistent with the results for five-coordinate adducts of nicke(II) suggesting that adducts are having square pyramidal geometry around the nicke(II) metal ion[14,15]. The electronic spectra of 1:2 adducts of nickel(II)ethylxanthate have been recorded in DMF in the range 8000-45000 cm^{-1} and show three broad bands ν_1, ν_2 and n_3 around 10,000 cm^{-1}, 18000 cm^{-1} and 28000 cm^{-1} respectively. The bands can be assigned to $^3B_{1g} \rightarrow {}^3E_g$ ($^3A_{2g} \rightarrow {}^3T_{2g}$), $^3B_{1g} \rightarrow {}^3E_g$ ($^3A_{2g} \rightarrow {}^3T_{1g}$) and $^3B_{1g} \rightarrow {}^3E_g$ (P) ($^3A_{2g} \rightarrow {}^3T_{1g}$ (P)) transitions respectively. Appearance of these three broad bands along with shoulders show that adducts are having trans octahedral geometry around the nickel(II) metal ion. This data is consistent with the results for six-coordinate octahedral complexes of nickel(II) ion[16].

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