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RESEARCH ARTICLE

Synthesis and Characterization of Some Adducts of *O*-Hexyl Dithiocarbonates of Nickel(II) with Heterocyclic Amines

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Abstract: A series of adducts of *o*-hexyl dithiocarbonate of nickel(II) [$(C_6H_{13}OCS_2)_2$ Ni] have been synthesized in 1:2 molar ratio by the reaction of aqueous solution of $NiCl_2.6H_2O$ with aqueous solution of potassium salt of *o*-hexyl dithiocarbonate. These complexes were further reacted with nitrogen donor ligands to obtain donor stabilized complex of the type [$(C_6H_{13}OCS_2)_2$ Ni.nL], (L=2-,3-,4-cyanopyridines and 2-,3-,4-aminopyridines, n=2). These adducts were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, IR and electronic spectral studies. The spectral studies revealed the trans octahedral geometry of the adducts around the Ni(II) metal ion. All the adducts were paramagnetic and non-electrolytic in nature. These complexes have also depicted the potential antifungal activity against the fungus *Curvularia lunata*.

Keywords: Nickel(II), *O*-hexyl dithiocarbonate, *Curvularia lunata*, Nitrogen donor ligands

Introduction

Xanthates, also known as *o*-alkyl/aryl dithiocarbonates, are one of the important members of 1,1-dithiolate family. Xanthates have been known for a long time[1,2] and many adducts of metal xanthates with different ligands have been prepared studied in the last several decades[3,4]. Xanthates of certain transition metals are used as accelerators in vulcanization of rubber, brought a new revolution in rubber industry[5]. Xanthates form a chelate with virtually all transition elements and has proved to be a versatile chelating agent for the separation and extraction of metal in analytical chemistry and mineral floating[6,7]. Xanthates have recently been shown to inhibit the replication of both DNA and RNA viruses *in vitro*. It was found that certain xanthate derivatives exhibit beneficial antimicrobial and antiviral effects[8]. In the present research work, we are reporting the synthesis and characterization of 1:2 adducts of *o*-hexyl dithiocarbonate of nickel(II) with substituted heterocyclic amines such as 2-,3-,4- cyanopyridines and 2-,3-,4-aminopyridies.

Experimental

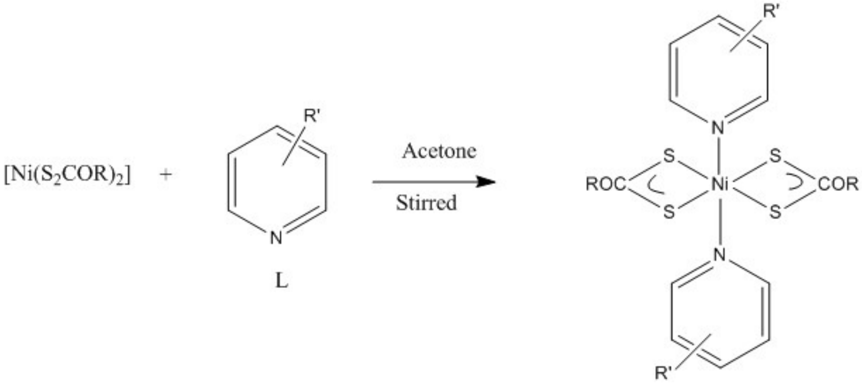
Potassium salt of hexyl xanthate was prepared by the method reported in literature[9]. In a 400 mL round bottomed flask, fitted with a reflux condenser, was placed 42 g (0.75 mol) of potassium hydroxide pellets and 265.66 g (323.9 mL, 2.6 mol) of *n*-hexanol was added. The reaction mixture was heated under reflux for 1 h. The mixture was then cooled and liquid from residual solid was decanted off into another dry 500 mL flask. To this flask, was added 52 g (45 mL, 0.75 mol) of carbon disulphide slowly with constant shaking. The residual solid mass was filtered (after cooling in ice) on a sintered glass funnel at the pump. It was washed with three 25 mL portions of ether. The resulting potassium *o*-hexyl dithiocarbonate (potassium salt of hexyl xanthate) was dried in a vaccum desiccator over anhydrous calcium chloride. It was then recrystallized from absolute ethanol.

Preparation of bis (O-hexyl dithiocarbonato)nickel(II)

The saturated aqueous solution of hydrated nickel chloride, $NiCl_2.6H_20$ (2.37 g, 0.01 mol) and potassium *o*-hexyl dithiocarbonate (4.32 g, 0.02 mol) were prepared separately and then mixed with constant stirring. Dark green precipitates were formed which were filtered immediately and were dried in a vaccum desiccator over anhydrous calcium chloride. The composition of the complex was established to be $Ni[S_2C(O\text{-}C_6H_{13})]_2$ by the elemental analysis.

Preparation of 1:2 adducts of bis(O-hexyl dithiocarbonato)nickel(II) with substituted heterocyclic amines

1:2 Addition complexes of bis(*o*-hexyl dithiocarbonato)nickel(II) with substituted heterocyclic amines were prepared by stirring $Ni[S_2C(O\text{-}C_6H_{13})]_2$ (1.073 g, 0.0026 mol) in acetone with heterocyclic amines [2-,3-,4-cyanopyridine = 0.541 g each; 2-,3-,4- aminopyridine = 0.489 g each (0.0052 mol)] for 30 min. The contents of the reaction mixture were allowed to stand for 20-24 h and the green adduct obtained was washed with the solvent used in their preparation and dried over calcium chloride at room temperature (Scheme 1).



Where R= C_6H_{13}; L=2-,3-,4-cyanopyridines; 2-,3-,4-aminopyridines; R' = CN or NH_2

Scheme 1. Method of preparation and proposed structure of 1:2 adducts

Methods

Carbon, hydrogen, nitrogen and sulfur were determined on elemental analyzer (CNN5-932, LECO Corporation, USA). Molar conductance was determined on their millimolar solutions in DMF using digital conductivity meter (century CC601). Magnetic moments were determined at room temperature by Gouy's method on magnetic susceptibility balance.

Infrared spectra of the complexes over the region 4,000-400 cm^{-1} were recorded using KBr pellets on infrared spectrophotometer (Perkin Flmer FT-IR). The electronic spectra of the adducts were recorded in DMF in the range 12500 cm^{-1} to 40000 cm^{-1} on T90 + UV-visible spectrophotometer.

Results and Discussion

The adducts of bis(*o*-hexyl dithiocarbonato)nickel(II) are microcrystalline solids. The adducts are shining green to blackish green in color and are soluble in common organic solvents like acetone, chloroform, dimethylformamide and dimethyl sulfoxide, but they are insoluble in benzene, carbon tetrachloride, nitrobenzene and water. The elemental analysis reveals that the adducts isolated have 1:2 stoichiometry depending upon the molar ratios of metal and ligand taken for their preparation (Table 1).

Table 1. Analytical data of 1:2 adducts of bis(*o*-hexyl dithiocarbonato)nickel(II) with substituted heterocyclic amines

S.No.	Name of the adduct	Analysis found (calculated) %			
		C	H	N	S
1.	Bis(*o*-hexyl dithiocarbonato) bis(2-cyanopyridine)nickel(II)	48.33 (50.26)	4.60 (5.47)	8.06 (9.02)	20.07 (20.62)
2.	Bis(*o*-hexyl dithiocarbonato) bis(3-cyanopyridine)nickel(II)	49.13 (50.26)	4.77 (5.47)	8.91 (9.02)	19.50 (20.62)
3.	Bis(*o*-hexyl dithiocarbonato) bis(4-cyanopyridine)nickel(II)	49.55 (50.26)	5.09 (5.47)	8.86 (9.02)	20.12 (20.62)
4.	Bis(*o*-hexyl dithiocarbonato) bis(2-aminopyridine)nickel(II)	46.97 (47.94)	5.83 (6.32)	8.76 (9.32)	20.68 (21.3)
5.	Bis(*o*-hexyl dithiocarbonato) bis(3-aminopyridine)nickel(II)	47.08 (47.94)	5.79 (6.32)	8.93 (9.32)	20.55 (21.3)
6.	Bis(*o*-hexyl dithiocarbonato) bis(4-aminopyridine)nickel(II)	47.12 (47.94)	5.90 (6.32)	9.02 (9.32)	20.70 (21.3)

The structures of the isolated complexes were established from their molar conductance and magnetic susceptibility measurements, electronic and infrared spectral data. The results of these investigations are tabulated and discussed. The molar conductance values of their millimolar solutions in DMF are found in the range of 21.38-34.63 ohm^{-1}mol^{-1}cm^{2}. These values are lower than the values expected for any uni-univalent electrolyte in these solvents suggesting that these complexes are neutral and non-ionic in character (Table 2). The Ni^{2+}cation, being d^8cation give rise to two spin unpaired electrons per nickel(II) ion giving a spin only magnetic moment of 2.83 B.M. In octahedral complexes, the observed magnetic moments lie in the range of 2.9-3.4 B.M. These lower values of magnetic moments in octahedral complexes of nickel(II) are due to almost complete quenching of orbital contribution in these complexes[12-14]. The 1:2 adducts of nickel(II) hexylxanthate with nitrogen donors fall in the range 2.87-3.24 B.M. (Table 2). These values are in accordance with the paramagnetic nature of these adducts due to the presence of two unpaired electrons. It also suggests that the adducts of nickel(II) have six coordinated octahedral structure. The higher value of magnetic moment may be due to the orbital contribution.

The infrared spectra of the adducts of nickel(II) xanthates exhibit absorption bands for xanthate ligands at 1270-1210 cm^{-1} and 1140 cm^{-1} which have been assigned to V_{as} (C-O-C) and V_{as} (C-O-C) vibrations while bands at 1030-1040 cm^{-1} belongs to the V (C-S) vibrations[15].

In the free aminopyridine ligands N-H streching frequencies fall at 3450, 3350 and 3175 cm^{-1} for 2-aminopyridine; 3335 and 3205 cm^{-1} for 3-aminopyridine and 3320 and 3185 cm^{-1} for 4-aminopyridine. In case the aminopyridine coordinated to a metal through its amino nitrogen, these peaks shift to a lower position. In the complexes prepared in the present work, these vibrations showed a small position shift. In the adducts of bis(*o*-hexyl dithiocarbonato) nickel(II), these peaks appear around 3450-3465, 3350-3390 and 3180-3230 cm^{-1} in the adducts with 2-aminopyridines. Similarly in case of adducts with 3-aminopyridines with N-H stretching frequencies occur about 3340-3370 and 3210-3235 cm^{-1} in the adducts with 4-aminopyridines, the N-H stretching frequencies occur around 3325-3350 and 3195-3220 cm^{-1}. The absence of negative shifts in the stretching frequencies on coordination implied that the interaction of the amino group with nickel(II) ion is ruled out. Thus, these ligands use their ring nitrogen atom for coordination to the metal ion. A negative shift is observed in C-H out of plane vibrations of 2-,3- and 4-aminopyridine adducts which confirms that these ligands interact with the metal ion through their ring nitrogen atom.

Table 2. Molar conductance and magnetic data of 1:2 adducts of bis(*o*-hexyl dithiocarbonato)-nickel(II) with substituted heterocyclic amines

S.No.	Name of the adduct	Molar conductance ($ohm^{-1}mol^{-1}cm^{-2}$)	Magnetic data (B.M)	Temp., K
1.	Bis(*o*-hexyl dithiocarbonato) bis(2-cyanopyridine)nickel(II)	34.63	3.18	308
2.	Bis(*o*-hexyl dithiocarbonato) bis(3-cyanopyridine)nickel(II)	21.38	3.15	308
3.	Bis(*o*-hexyl dithiocarbonato) bis(4-cyanopyridine)nickel(II)	25.50	3.20	308
4.	Bis(*o*-hexyl dithiocarbonato) bis(2-aminopyridine)nickel(II)	18.33	2.87	308
5.	Bis(*o*-hexyl dithiocarbonato) bis(3-aminopyridine)nickel(II)	19.72	3.24	308
6.	Bis(*o*-hexyl dithiocarbonato) bis(4-aminopyridine)nickel(II)	19.39	3.17	308

In cyanopyridines, there are two potential donor sites, the pyridine ring nitrogen and nitrile group nitrogen atom. In order to decide the coordination site in a particular cyanopyridine, a study of vibrations of pyridine ring and C≡N stretching frequencies can be of much help[16-18].

It is established that there should be an increase in v(C≡N) by at least 30 cm^{-1} if a cyanopyridne coordinates to the metal using nitrile nitrogen atom. On the other hand if –CN group coordinates using π-electrons v(C≡N) must show a negative shift[19-21]. The C≡N stretching frequencies in free 2-,3- and 4-cyanopyridnes fall at 2268 cm^{-1}, 2240 cm^{-1} and 2225 cm^{-1} respectively but in adducts of bis(*o*-hexyl dithiocarbonato) nickel(II), these vibrations occur around 2269 cm-^{1}, 2235 cm^{-1} and 2236 cm^{-1} respectively showing no appreciable shift in v(C≡N). (Figure 1) So, it can be concluded that 2-,3- and 4-cyanopyridines coordinate to metal through their ring nitrogen atom. The IR spectra of 1:2 adducts of bis(*o*-hexyl dithiocarbonato) nickel(II) with cyanopyridines and aminopyridines show absorption bands at 1210-1146 cm^{-1} and 1035-1082 cm^{-1} which are assigned to be v_{as}(C-O-C), v_s(C-O-C) and v(C-S) stretching vibrations respectively (Table 3). The appearance of a single band for v(C-S) its position indicates symmetrical bidentate binding of the xanthate moiety.

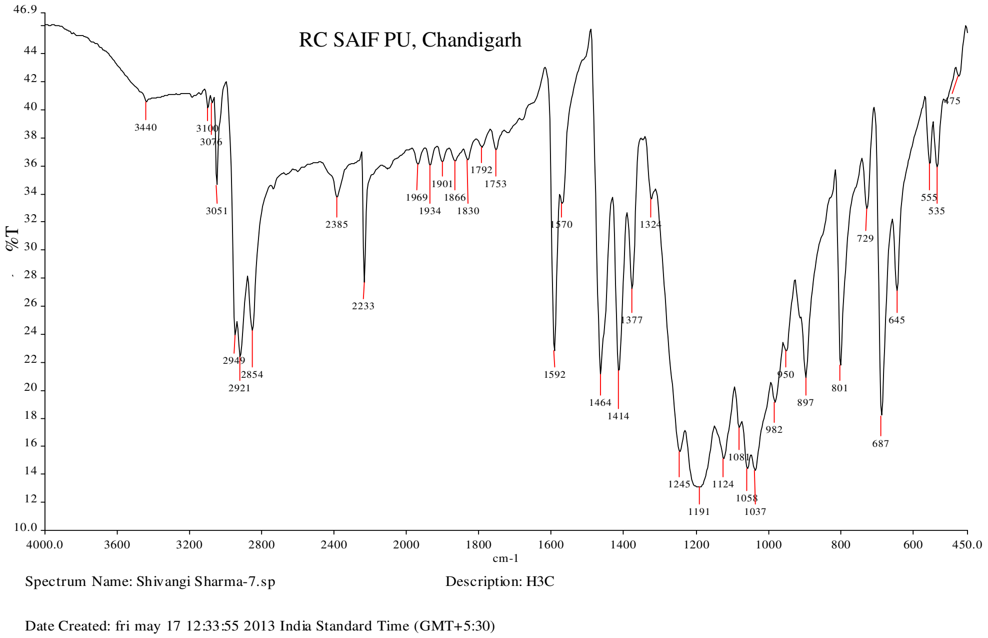


Figure 1. IR spectra of bis(*o*-hexyl dithiocarbonato bis(3-cyanopyridine)nickel(II)

Table 3. Infrared and electronic spectral data of 1:2 adducts of bis(*o*-hexyl dithiocarbonato) nickel(II) with substituted heterocyclic amines

S.No	Name of the adduct	Infrared spectral data, cm^{-1}			Electronic spectral data, cm^{-1}		
		vas (C-O-C)	vs (C-O-C)	v (C-S)	v1	v2	v3
1.	Bis(*o*-hexyl dithiocarbonato) bis(2-cyanopyridine)nickel(II)	1272	1126	1082	10466	18918	27672
2.	Bis(*o*-hexyl dithiocarbonato) bis(3-cyanopyridine)nickel(II)	1245	1124	1058	11671	18317	27717
3.	Bis(*o*-hexyl dithiocarbonato) bis(4-cyanopyridine)nickel(II)	1271	1128	1048	10317	17880	27875
4.	Bis(*o*-hexyl dithiocarbonato) bis(2-aminopyridine)nickel(II)	1264	1133	1052	10363	17388	26975
5.	Bis(*o*-hexyl dithiocarbonato) bis(3-aminopyridine)nickel(II)	1210	1125	1035	11896	17358	26952
6.	Bis(*o*-hexyl dithiocarbonato) bis(4-aminopyridine)nickel(II)	1291	1146	1052	11425	17978	27190

The electronic spectra of the adducts of nickel(II) xanthates with substituted heterocyclic amines, prepared in the present work recorded in dimethylformamide. The electronic spectral data of the 1:2 adducts of bis(*o*-hexyl dithiocarbonato)nickel(II) with cyano and aminopyridines show these bands in the range 10317-11896 cm^{-1}, 17358-18918 cm^{-1} and 26952-27875 cm^{-1} which are assigned to $^3A_{2g}\rightarrow{}^3T_{2g}(F)$ (v_1), $^3A_{2g}\rightarrow{}^3T_{1g}$ (F) (v_2) and $^3A_{2g}(F)\rightarrow{}^3T_{1g}$ (P) (v_3) transitions respectively are presented in Table 3. The appearance of these three broad bands along with shoulders show that the adducts are having trans octahedral geometry around the Ni(II) metal ion (Figure 2). The data is in consistent with the results for six coordinate octahedral complexes of Ni(II) ion[22].

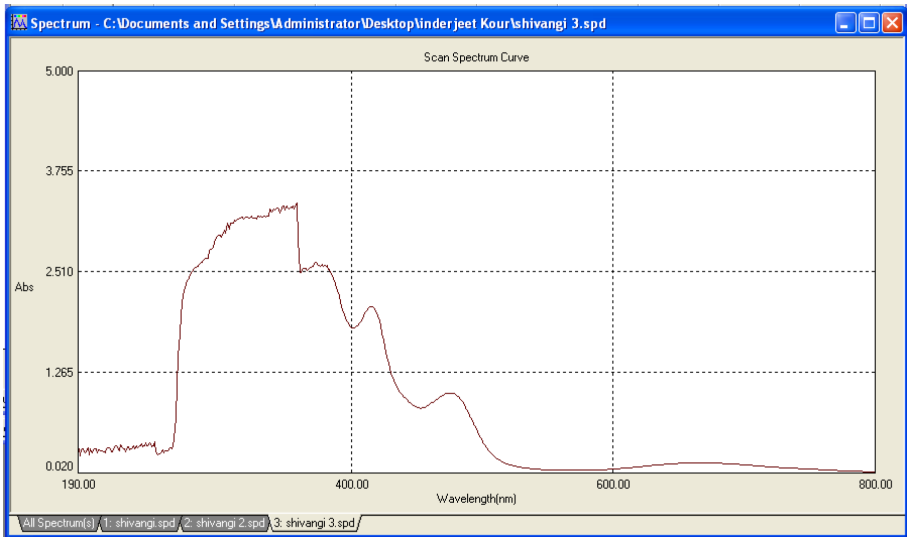


Figure 2. Electronic spectra of bis(*o*-hexyldithiocarbonato)bis(2-cyanopyridine)nickel(II)

Antifungal studies

The antifungal activity of the adducts was tested by poisoned food technique against the pathogenic fungus *Curvularia lunata*. The linear growth of the fungus in controlled manner was recorded at different concentrations of the adducts. The growth inhibition of *Curvularia lunata* over control was calculated (Table 4).

Table 4. *In vitro* evaluation of complexes against *Curvularia lunata*, mean colony diameter, C=90 mm

S.No.	Name of the adducts	Concentration, ppm	Colony diameter, mm	% Inhibition (I) = [C-T/C]x100
1.	Bis(*o*-hexyldithiocarbonato)-bis (4-aminopyridine)nickel(II)	10	75	17
		100	38	58
		200	14	84
2.	Bis(*o*-hexyldithiocarbonato)-bis (3-cyanopyridine)nickel(II)	10	81	10
		100	67	26
		200	50	44
3.	Bis(*o*-hexyldithiocarbonato)-bis(4-cyanopyridine)nickel(II)	10	79	13
		100	64	29
		200	52	42

It is found that on increasing the concentration of the adducts, the colony diameter of the fungus decreases and hence percent inhibition increases[23] (Figure 3a, 3b and 3c). The growth inhibition of fungus over control was calculated as:

$$\% \text{ Inhibition (I)} = [C\text{-}T/C]\text{x}100$$

Where I= percent inhibition, C= mean growth of fungus (in mm) in control and T= mean growth of fungus (in mm) in treatment.

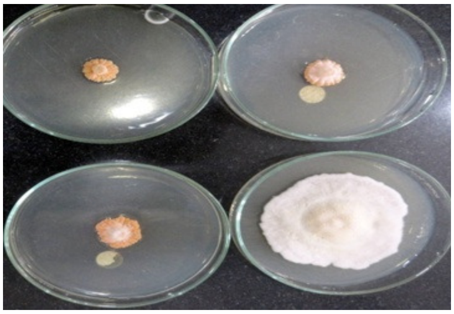


Figure 3(a). Antifungal activity of bis(*o*-hexyldithiocarbonato)bis(4-aminopyridine)-nickel(II)

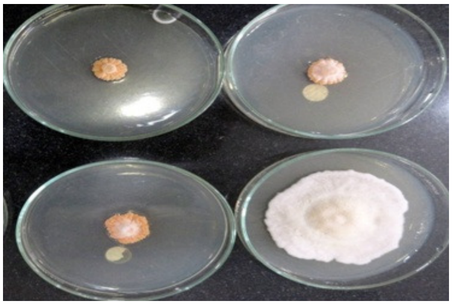


Figure 3(b). Antifungal activity of bis(*o*-hexyldithiocarbonato)bis(3-cyanopyridine)-nickel(II)

Figure 3(c). Antifungal activity of bis(*o*-hexyldithiocarbonato)bis(4-cyanopyridine)nickel(II)

Conclusion

On the basis of above studies, it is found that 1:2 adducts of Ni (*o*-hexyldithiocarbonato)$_2$ have trans octahedral geometry. The complexes analyzed are paramagnetic in nature and they show considerable antifungal activity.

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