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RESEARCH ARTICLE

Synthesis, Characterization and Biological Application of Adducts of Bis(*S*-ethyltrithiocarbonato)nickel(II) with Heterocyclic Amines

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Abstract: Eleven new adducts of bis(*S*-ethyltrithiocarbonato)nickel(II) with heterocyclic amines have been described. Structural features of adducts isolated in the solid state are established by several techniques using elemental analysis, molar conductance, magnetic measurements, TGA-DTA and spectroscopic studies which include FTIR, UV-Vis, mass. These studies suggest that adducts have the general formula $[Ni(S_2CSC_2H_5)_2L_2]$ where L = cyano-, amino-, chloro-, ethylpyridine. Antifungal activities of these adducts have been carried out against the fungal strain *Sclerotium rolfsii* and *Fusarium oxysporium* and some of these adducts showed noticeable activity against the fungus. Various studies support the distorted octahedral geometry around Ni(II) ion.

Keywords: Bis(*S*-ethyltrithiocarbonato)nickel(II), Heterocyclic amines, Antifungal studies

Introduction

1,1-Dithiolates form an interesting family of sulfur donor ligands. They have been extensively used in classical and organometallic chemistry for several years[1-3]. Among these much work has been done on alkyl dithiacarbamates, dithiocarboxylates, dithiocarbonates but little attention has been paid to alkyl trithiocarbonates[4-10]. Trithiocarbonates are used as antioxidant additives to lubricate oil and greases[11], against human tumor[12]. Trithiocarbonate complexes have received attention because of the dual nature of metal -CS_3 moiety as an electrophilic and nucleophilic reagents, which makes them versatile intermediates for the synthesis of other oil thio species. Although the main application is the treatment of a variety of rheumatic diseases, some of these compounds have shown to have antileshmanial activity *in vitro* inhibitory effect on HIV or activity tumor cell[13-14]. Organotrithiocarbonates have found many applications in various fields such as in analysis, organic synthesis, medicine, industry and agriculture some of these applications are as flotation agents, vulcanization accelerators, pesticides, plant defoliants, rust inhibitor, lubricant oil additives, and some have recently reported to possess activity as antiradiation drugs[15-16]. *S*-alkyltrithiocarbonates commonly known as thioxanthates coordinate with a number of transition metals to form stable complexes. In order to investigate the ability of these stable complexes to extend their coordination sphere, here in this paper we report the synthesis and characterization of a new series of adducts of bis(*S*-ethyltrithiocarbonato)nickel(II) with various nitrogen donors.

Experimental

The sodium salt of *S*-ethyltrithiocarbonate was prepared (as reported in literature)[17] by the drop wise addition of the ethanethiol (1 mol) to a saturated solution of sodium hydroxide at 0 °C, followed by the addition of excess carbon disulfide (1.2 mol). The yellow precipitate formed immediately was collected by filteration and twice recrystallized from water-acetone mixture. The salt was characterized by its unpleasant odour and was stored in vacuum desiccators over phosphorus pentoxide.

$$C_2H_5SH + CS_2 + NaOH \xrightarrow{0\,^{o}C} C_2H_5SCS_2Na^+ + H_2O$$

Synthesis of complex bis(S-ethyltrithiocarbonato)nickel(II)

To the sodium salt of *S*-ethyltrithiocarbonate(0.02 mol) an aqueous solution of $NiCl_2.6H_2O$ (0.01 mol) was added. The mixture was immediately extracted with several portions of ether and the combined extracts were dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure and shiny black crystals were isolated. The composition of the complex was established to be $[Ni(S_2CSC_2H_5)_2]$ by the elemental analysis.

$$NiCl_22H_2O + C_2H_5SCS_2Na \longrightarrow [Ni(S_2CSC_2H_5)_2] + 2NaCl$$

Synthesis of adducts of bis(S-ethyltrithiocarbonato)nickel(II) with nitrogen donors

Bis(*S*-ethyltrithiocarbonato)nickel(II) (0.0026 mol) was dissolved in chloroform (60-80 mL) and stirred for about 10-20 minutes. To the resulting solution, nitrogen donor ligand (0.0052 mol) was added. The mixture was stirred for two to three days and kept overnight. Blackish green coloured precipitates were formed. The product so obtained was filtered and dried *in vacuum* desiccator over anhydrous calcium chloride. The composition of the adduct was established to be $Ni[(S_2CSC_2H_5)_2L_2]$ as confirmed by analytical data (Table 1) where L=2-, 3-, 4-ethylpyridine, 2-, 3-chloropyridine, 2-, 3-, 4-cyanopyridine, 2-, 3-, 4-aminopyridine.

$$[Ni(S_2CSC_2H_5)_2] + C_5H_5NX \longrightarrow [Ni(S_2CSC_2H_5)_2(C_5H_5NX)_2]$$

Where X = CN, Cl, C_2H_5, NH_2

Results and Discussion

The adducts isolated are green to blackish green in colour. Molar conductance of the adducts suggest their non-electrolytic nature[18]. All the adducts are paramagnetic as suggested by their magnetic moments[19] (Table 2).

IR spectra

The IR spectra of the free ligand and the complexes were obtained in the range of 4000-300 cm^{-1}. All the bands present in the IR spectra of the free ligand were also observed in the spectra of the complexes. In the present work IR spectra of the adducts of bis(*S*-ethyltrithiocarbonato)nickel(II) show characteristic bands corresponding to $\nu(C\text{-}S\text{-}C)_{asym}$ and $\nu(C\text{-}S\text{-}C)_{sym}$ vibrations in the range of 650-710 cm^{-1}. An intense band corresponding to ν(C-S) vibration is also observed for all the adducts synthesized which suggests that thioxanthate is binding as symmetrical bidentate chelating ligand[20-21]. On formation of adducts, there is a shift in the stretching frequencies, because of donation of electrons by the Lewis bases which weakens the metal sulfur bond that leads to corresponding weakening of C-S bond. Moreover it has been observed that the shift of frequency is much more pronounced in case of electron rich bases as compared to electron poor bases. Some of the important bands are given in Table 3.

Table 1. Analytical data of the adducts

Compound		Percentage calculated				Percentage Found			
		C	H	N	S	C	H	N	S
1	Bis(*S*-ethyltrithiocarbonato)bis (2-ethylpyridine)nickel(II)	35.45	4.35	3.18	43.64	34.86	3.85	2.76	41.98
2	Bis(*S*-ethyltrithiocarbonato) bis (3-ethylpyridine)nickel(II)	35.45	4.35	3.18	43.64	33.98	4.12	3.08	42.37
3	Bis(*S*-ethyltrithiocarbonato)bis (4-ethylpyridine)nickel(II)	35.45	4.35	3.18	43.64	34.27	4.22	3.00	41.95
4	Bis(*S*-ethyltrithiocarbonato) bis (2-chloropyridine)nickel(II)	29.24	3.13	3.10	42.52	28.78	2.96	2.74	40.89
5	Bis(*S*-ethyltrithiocarbonato)bis (3-chloropyridine)nickel(II)	29.24	3.13	3.10	42.52	27.74	2.88	2.82	41.22
6	Bis(*S*-ethyltrithiocarbonato)bis (2-cyanopyridine)nickel(II)	32.95	3.22	6.40	43.94	31.87	3.18	5.83	42.64
7	Bis(*S*-ethyltrithiocarbonato)bis (3-cyanopyridine)nickel(II)	32.95	3.22	6.40	43.94	30.91	3.09	6.03	43.78
8	Bis(*S*-ethyltrithiocarbonato)bis (4-cyanopyridine)nickel(II)	32.95	3.22	6.40	43.94	32.09	2.98	5.94	42.15
9	Bis(*S*-ethyltrithiocarbonato)bis (2-aminopyridine)nickel(II)	30.91	3.77	6.55	44.96	28.78	3.23	6.12	42.87
10	Bis(*S*-ethyltrithiocarbonato)bis (3-aminopyridine)nickel(II)	30.91	3.77	6.55	44.96	29.13	3.44	6.23	43.00
11	Bis(*S*-ethyltrithiocarbonato)bis (4-aminopyridine)nickel(II)	30.91	3.77	6.55	44.96	29.22	3.48	6.43	43.12

Table 2. Melting point, Magnetic moment and Molar Conductance of the isolated adducts

Compound name		Melting point in °C	Magnetic moment in B.M.	Molar conductance in $\Omega^{-1}mol^{-1}cm^{2}$
1	Bis(*S*-ethyltrithiocarbonato)bis(2-ethylpyridine)nickel(II)	82	2.98	50.45
2	Bis(*S*-ethyltrithiocarbonato) bis(3-ethylpyridine)nickel(II)	88	3.21	46.28
3	Bis(*S*-ethyltrithiocarbonato)bis (4-ethylpyridine)nickel(II)	87	3.45	52.18
4	Bis(*S*-ethyltrithiocarbonato)bis(2-chloropyridine)nickel(II)	78	2.91	56.98
5	Bis(*S*-ethyltrithiocarbonato)bis(3-chloropyridine)nickel(II)	75	3.22	60.12
6	Bis(*S*-ethyltrithiocarbonato)bis(2-cyanopyridine)nickel(II)	83	3.34	58.87
7	Bis(*S*-ethyltrithiocarbonato)bis(3-cyanopyridine)nickel(II)	87	3,16	49.90
8	Bis(*S*-ethyltrithiocarbonatobis (4-cyanopyridine)nickel(II)	86	3.02	47.76
9	Bis(*S*-ethyltrithiocarbonato)bis(2-aminopyridine)nickel(II)	81	2.98	60.12
10	Bis(S-ethyltrithiocarbonato)bis(3-aminopyridine)nickel(II)	84	3.02	48.88
12	Bis(S-ethyltrithiocarbonato)bis(4-aminopyridine)nickel(II)	86	3.13	45.56
13	Bis(*S*-ethyltrithiocarbonato)bis(2-ethylpyridine)nickel(II)	82	2.98	50.45

Table 3. Electronic and Vibrational Spectral data of the adducts

	Compound name	Electronic spectra data			Vibrational spectral data		
		C-S	(C-S-C)$_{as}$	(C-S-C)$_s$	ν_1	ν_2	ν_3
1	Bis(*S*-ethyltrithiocarbonato)bis(2-ethylpyridine)nickel(II)	1032	698	659	13735	19000	23476
2	Bis(*S*-ethyltrithiocarbonato)bis(3-ethylpyridine)nickel(II)	1031	704	660	12578	18200	24536
3	Bis(*S*-ethyltrithiocarbonato)bis(4-ethylpyridine)nickel(II)	1044	688	652	10883	19987	24520
4	Bis(*S*-ethyltrithiocarbonato)bis(2-chloropyridine)nickel(II)	1033	692	658	13500	18870	26450
5	Bis(*S*-ethyltrithiocarbonato)bis(3-chloropyridine)nickel(II)	1031	700	662	13654	18765	25800
6	Bis(*S*-ethyltrithiocarbonato)bis(2-cyanopyridine)nickel(II)	1030	702	655	13780	18989	24900
7	Bis(*S*-ethyltrithiocarbonato)bis(3-cyanopyridine)nickel(II)	1043	687	651	12788	20050	24978
8	Bis(*S*-ethyltrithiocarbonato)bis(4-cyanopyridine)nickel(II)	1042	693	656	13314	19700	26340
9	Bis(*S*-ethyltrithiocarbonato)bis(2-aminopyridine)nickel(II)	1048	694	662	13453	19239	24300
10	Bis(*S*-ethyltrithiocarbonato)bis(3-aminopyridine)nickel(II)	1044	701	669	12546	18670	24563
11	Bis(*S*-ethyltrithiocarbonato)bis(4-aminopyridine)nickel(II)	1040	708	660	13800	19830	25348

UV-Visible spectra

The electronic spectra of adducts of bis(*S*-ethyltrithiocarbonato)nickel(II) show three absorption bands in the range of 12500-13800 cm^{-1}, 18500-20000 cm^{-1} and 23000-25000 cm^{-1}. These three bands may be assigned to three spin allowed transitions: $^3A_2g \rightarrow {}^3T_2g(\nu^1)$, $^3A_2g \rightarrow {}^3T_1g(\nu^2)$ and $^3A_2g \rightarrow {}^{-3}T_1g(P)(\nu^3)$ respectively[22]. The appearance of these bands along with shoulders suggest that the adducts synthesized have distorted octahedral geometry around Ni(II) metal ion (Table 3).

Thermal studies

The thermal behavior of one of the representing complex $Ni[(S_2CSC_2H_5)_2(C_6H_4N_2)_2]$ was studied under inert atmosphere in the range of 200-900 ^oC and is shown in Figure 1 and it displays weight loss in three steps with different time intervals at different temperatures. These losses indicate decomposition and evaporation of the volatile part of the sample. The curved portion indicates the weight loss during the process of heating. TGA curve of the addition complex bis(*S*-ethyltrithiocarbonato)(3-chloropyridine) nickel(II) shows an initial weight loss of 59.6% at 157.7 ^oC which can be correlated with the loss of two molecules of chloropyridine (Calculated=58.5%). At a temperature of 517 ^oC both the coordinated thioxanthate molecules are lost (observed wt.loss=86.2%; Calculated=88%) and a stable sulfide, NiS is obtained as an end product[23].

$$\left[\mathbf{Ni(S_2CSC_2H_5)_{2}.\ (3\text{-}chloropyridine)_2}\right] \xrightarrow[\text{-2 molecules of 3-chloropyridine}]{\text{100-200}^o\text{C}} \left[\mathbf{Ni(S_2CSC_2H_5)_{2}.}\right] \xrightarrow{\text{200-500}^o\text{C}} \mathbf{NiSO_4} \xrightarrow{\text{810}^o\text{C}} \mathbf{NiS}$$

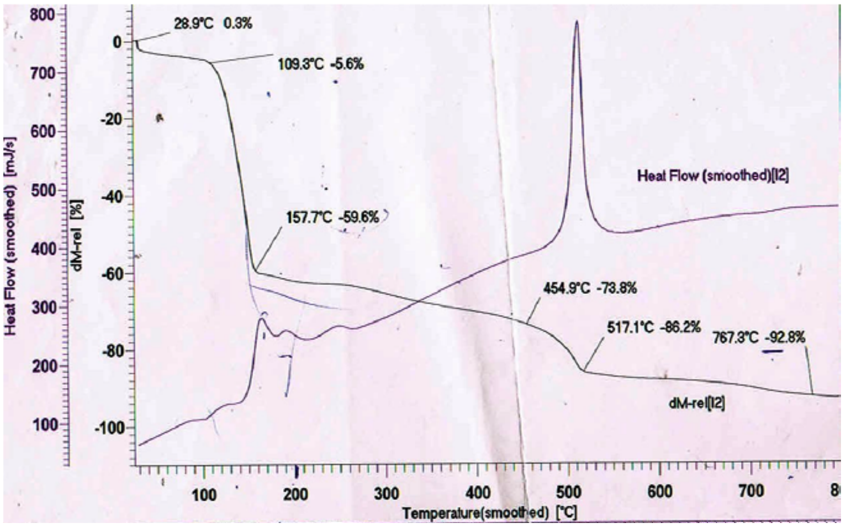


Figure 1. TGA-DTA curve of bis(*S*-ethyltrithiocarbonato)bis(3-chloropyridine) nickel(II)

Mass spectroscopy

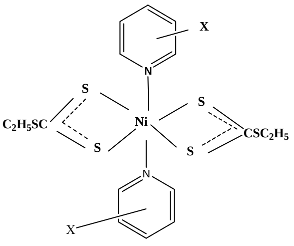
Mass spectroscopy is one of the most important methods to determine molecular weight of the complexes and to identify the fragments formed during bombardment, which reveal composition and properties of the particular moiety of the complexes[24-25]. Mass spectra of one of these adducts, bis(*S*-ethyltrithiocarbonato)bis(4-cyanopyridine)nickel(II) has been recorded. The possible formulae of the fragments and their *m/z* ratios are shown in Table 4.

Two important peaks were observed in the mass spectrum: the molecular ion peak, indicating the molecular mass of the complex, which is very weak in case of the complexes investigated and the base peak, corresponding to the fragment $Ni[(S_2CSC_2H_5)_2]^{+}$. This indicates, in both cases, the strong chelating property of trithiocarbonates. The various fragments observed are in agreement with the molecular formula of the complexes.

Table 4. Mass fragments of bis(*S*-ethyltrithiocarbonato)bis(4-cyanopyridine) nickel(II)

Mass *m/z*	Relative abundance	Possible formulae of the fragment
545	22%	$Ni[(S_2CSC_2H_5)_2(C_6H_4N_2)_2]^{+}$.
336	100%	$Ni[(S_2CSC_2H_5)_2]^{+}$.
199	35%	$Ni[(S_2CSC_2H_5)]^{+}$.
136	58%	$[(S_2CSC_2H_5)]^{+}$.
108	17%	$[(S_2CS]^{+}$.
73	24%	$[S_2C]^{+}$.

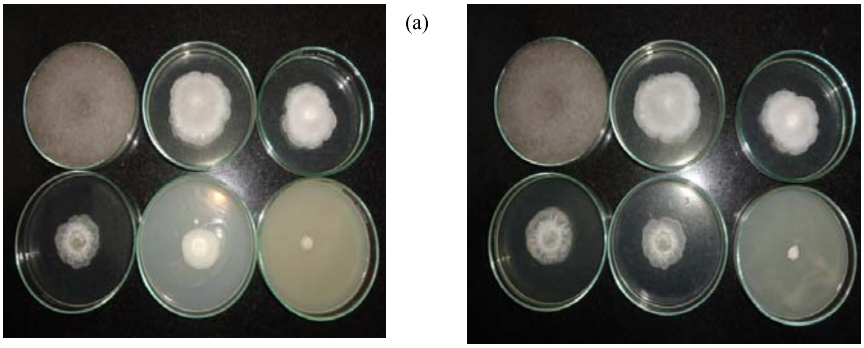
On the basis of above mentioned studies, following structure can be assigned to the adducts



where X= 2-, 3-, 4-cyano
2-, 3-, 4-amino
2-, 3-, 4-ethyl
2-, 3-chloro

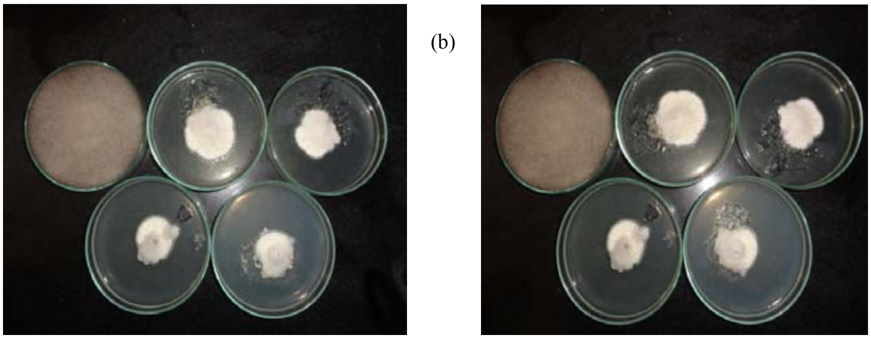
Antifungal activities

The antifungal activity of some novel investigated 1:2 addition complexes were carried out against two fungal strains "*Fusarium oxysporium and Sclerotium rolfsii'* by the poisoned food method using potato Dextrose Agar (PDA) as the nutrient medium[26]. The complexes were dissolved in DMF and were added to potato dextrose agar medium[27]. These were then poured into sterile Petri-dishes and were left to solidify. Using a cork borer (6 mm in diameter), the spores of the fungus were suspended on the medium at the centre. Finally the dishes were incubated at 27 °C for four days. The linear growth of the fungus in controlled manner was recorded at different concentrations of the complexes and a clear inhibition was noticed with all the complexes. Antifungal activities of the addition complexes bis(*S*-ethyltrithiocarbonato) bis(4-ethylpyridine)nickel(II), bis(*S*-ethyltrithiocarbonato)bis(3-chloropyridine)nickel(II) were recorded against *Fusarium oxysporium* while the antifungal activities of the adducts bis(S-ethyltrithiocarbonato)bis(4-cyanopyridine)nickel(II) and bis(*S*-ethyltrithiocarbonato)bis(4-aminopyridine)nickel(II) were recorded against *Sclerotium rolfsii* and are shown in Figure 2. The screening results are summarized in Table 5. The results obtained from these studies suggest that as the concentration of the complex increases the colony diameter decreases and hence the percentage inhibition increases.



Bis(*S*-ethyltithiocarbonato)bis(4-ethylpyridine) nickel(II)

Bis(*S*--ethyltrithiocarbonato)bis(3-chloropyridine) nickel(II)



Bis(*S*-ethyltrthiocarbonato)bis(4-aminopyridine) nickel(II)

Bis(*S*-ethyltrithiocarbonato)bis(4-cyanopyridine) nickel(II)

Figure 2. Antifungal activities of some adducts of bis(*S*-ethyltrithiocarbonato)nickel(II) with nitrogen donor ligands against (a) *Fusarium oxosporium* and (b) *Sclerotium rolfsii*

Table 5. Antifungal activities of some adducts of bis(s-ethyltrithiocarbonato)nickel(ii) with heterocyclic amines against *Fusarium oxosporium* and *Sclerotium rolfsii* Colony Diameter in control=80 mm

S.No	Adittion complex	Colony Diameter, mm	Concentration	Colony diameter, mm	%Inhibition I = [(CT)/C]×100
1	bis(*S*-ethyltrithiocarbonato) bis(4-ethylpyridine) nickel(II)	80	50	72	10.0
			100	60.5	24.37
			150	45.1	43.62
			200	20.2	74.75
2	bis(S-ethyltrithiocarbonato) bis(3-chloropyridine) nickel(II)	80	50	88	8.88
			100	53.5	40.55
			150	22.9	74.58
			200	14	84.44
3	bis(S-ethyltrithiocarbonato) bis(4-aminopyridine) nickel(II)	80	50	72.8	9.0
			100	55.5	30.6
			150	30.0	62.5
			200	12.6	84.25
4	bis(S-ethyltrithiocarbonato) bis(4-cyanopyridine) nickel(II)	80	50	78.0	2.5
			100	62.7	21.6
			150	40.1	49.87
			200	20.3	74.62

Conclusion

The adducts of bis(*S*-ethyltrithiocarbonato)nickel(II) with nitrogen donors are synthesized and on the basis of various physico-chemical techniques and spectroscopic studies are proposed to have distorted octahedral geometry. Some of these are found to be active against fungal strains.

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