



Synthesis and characterization of adducts of bis(tertiarybutylthioxanthato)nickel(II) with ethylpyridines and chloropyridines and their antifungal activities

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ABSTRACT

A series of six coordinated adducts of bis(tertiarybutylthioxanthato)nickel(II) with general formula $[Ni(S_2CSC_4H_9)_2(L)_2]$ (Where L = ethylpyridines and chloropyridines) were synthesized and characterized by elemental analysis, molar conductivity measurements, magnetic susceptibility measurements, TGA-DTA, mass, IR and UV spectroscopy. All the adducts have 1:2 stoichiometry, are non ionic and paramagnetic in nature. TGA-DTA studies show the formation of NiS as the stable end product of the decomposition. The electronic and magnetic susceptibility studies are consistent with the distorted octahedral geometry for the adduct. Antifungal activities of these adducts have been carried out against the fungal strain *Sclerotium rolfsii*.

Key words: Bis(tertiarybutylthioxanthato)nickel(II), ethylpyridines, chloropyridines and *Sclerotium rolfsii*

INTRODUCTION

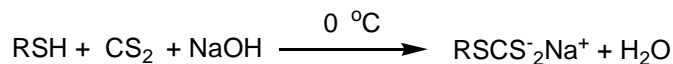
Thioxanthates also known as S-alkyltrithiocarbonates constitute an important class of compounds which have been used for various applications, especially as pesticides in agriculture and as lubricating additives^[1] They have been used extensively as pharmaceuticals, intermediates in organic synthesis, for protection of thiol functionality, in free radical polymerization reactions, in material science, in froth flotation, for the recovery of minerals from their ores. Moreover, they are useful synthons for the preparation of various compounds such as sulfines, ketenes, trithiocarbonate-S-oxides, thiols, dithiocarboxylate derivatives, thioacetates, olefins, nitro 1,3-benzodithiole-2-thiones, phosphite ylides and in various C-C bond forming reactions^[2-18]. Trithiocarbonate complexes have received attention because of the dual nature of metal-CS₃ moiety as an electrophilic and nucleophilic reagents, which makes them versatile intermediates for the synthesis of other oil thio species. These are used in the treatment of rheumatic diseases, leishmanial diseases and HIV or activity tumor cell^[19-20]. However, very few trithiocarbonato metal complexes have been synthesized and fully characterized^[21-29]. In view of the potential biological activity and practical applications of the thioxanthates, we have reported the synthesis and characterization of 1:2 adducts of bis(tertiarybutylthioxanthato)nickel(II) with ethylpyridines and chloropyridines.

EXPERIMENTAL SECTION

The Elemental analysis was performed on elemental analyzer (Elemental vario EL III, carlo Erba 1108). Molar conductance was measured in DMF using CC 601 Conductivity Bridge. The IR spectra was recorded on a Infrared spectrophotometer (Perkin Elmer FT-IR) over the region 4000-300 cm⁻¹ using KBr pellets. The electronic absorption spectra were recorded on Systronic 119 UV-Vis spectrophotometer. The magnetic susceptibility was measured at room temperature by Guoy's method using Hg[Co(CNS)₄] as calibrant.. Thermo gravimetric analysis (TGA) of the present complex was determined on Linseis STA-PT-1000 at 10°C/min.

2.1 Synthesis of sodium salt of tertiarybutylthioxanthate ligand [NaS₂CSC₄H₉]

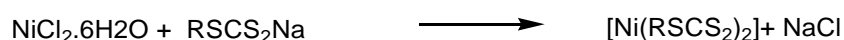
The sodium salt of tertiarybutylthioxanthate was prepared (as reported in literature)^[30] by the dropwise addition of the tertiarybutyl mercaptan (1mol) to a saturated solution of sodium hydroxide at 0°C, followed by the addition of excess carbon disulfide (1.2mol). The yellow precipitate formed immediately was collected by filtration and twice recrystallized from water-acetone mixture. The salt was characterized by its unpleasant odour and was stored in a vacuum dessicator over phosphorus pentoxide.



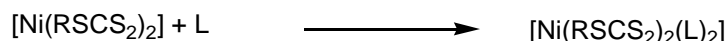
Where R = Tertiarybutyl

2.2 Synthesis of complex bis(tertiarybutylthioxanthato)nickel(II)

To Sodium salt of tertiarybutylthioxanthate(0.02 mol) an aqueous solution of NiCl₂.6H₂O (0.01mol) 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(S₂CSC₄H₉)₂] by the elemental analysis.

**2.3 Synthesis of adducts of bis(tertiarybutylthioxanthato)nickel(II) with ethylpyridines and chloropyridines:**

Bis(tertiarybutylthioxanthato)nickel(II) (0.0026mol) was dissolved in acetone (60-80mL) and stirred for about 10-20 minutes. To the resulting solution ethylpyridines and chloropyridines (0.0052mol) was added. The mixture was stirred for two to three days and kept overnight. Green coloured precipitates were formed. The product so obtained was filtered and dried in vacuum dessicator over anhydrous calcium chloride. The composition of the adduct was established to be Ni[(S₂CSC₄H₉)₂L₂].



Where L = ethylpyridines and chloropyridines

RESULTS AND DISCUSSION

The adducts were analyzed by various analytical and physico – chemical techniques and the results shows that bis(tertiarybutylthioxanthato)nickel(II) forms 1:2 adducts with ethylpyridines and chloropyridines. The analytical data (**Table 1**) reveals that 1:2 adduct have general formula Ni[S₂CS(C₄H₉)₂L₂] (L = ethylpyridines and chloropyridines) . All the adducts are coloured and stable in air. Conductance measurements were done to ascertain the electrolytic/ non-electrolytic nature of the metal complexes. The molar conductivity values of 1:2 adducts of Ni[S₂CS(C₄H₉)₂L₂] measured in 10⁻³ M DMF solution are found to be in the range of 58.92-58.98 ohm⁻¹cm²mol⁻¹(**table2**). These values supports the neutral and non-ionic nature of the complexes.^[31-32]

3.1 Magnetic susceptibility measurement:

The 1:2 adducts of bis(tertiarybutylthioxanthato)nickel(II) with ethylpyridines and chloropyridines exhibit magnetic moment values in the range of 3.10-3.20 B.M (**Table2**) which is in agreement with magnetic moment values observed for paramagnetic octahedral complexes of nickel(II)^[33].

Table 1: Analytical data of 1:2 adducts of bis(tertiarybutylthioxanthato)nickel(II) with ethylpyridines and chloropyridines

S.no	Name of the adduct	C% found	H	N	S	C% calc.	H	N	S
1	Bis(tertiarybutylthioxanthato)bis(2-ethylpyridine)nickel(II)	47.19	5.32	4.18	31.21	47.79	5.97	4.65	31.86
2	Bis(tertiarybutylthioxanthato)bis(3-ethylpyridine)nickel(II)	47.37	5.38	4.23	31.29	47.79	5.97	4.65	31.86
3	Bis(tertiarybutylthioxanthato)bis(4-ethylpyridine)nickel(II)	47.29	5.36	4.27	31.24	47.79	5.97	4.65	31.86
4	Bis(tertiarybutylthioxanthato)bis(2-chloropyridine)nickel(II)	38.15	3.78	4.17	30.86	38.99	4.22	4.55	31.19
5	Bis(tertiarybutylthioxanthato)bis(3-chloropyridine)nickel(II)	38.18	3.73	4.13	30.89	38.99	4.22	4.55	31.19

Table 2: Colour, Molar conductance and magnetic moment data of 1:2 adducts of bis(tertiarybutylthioxanthato)nickel(II) with ethylpyridines and chloropyridines

S.no.	Name of the adduct	Colour	Molar conductance (ohm ⁻¹ mol ⁻¹ cm ²)	μ _{eff} (B.M.) at 293k
1	Bis(tertiarybutylthioxanthato)bis(2-ethylpyridine)nickel(II)	Green	58.92	3.10
2	Bis(tertiarybutylthioxanthato)bis(3-ethylpyridine)nickel(II)	Green	58.97	3.13
3	Bis(tertiarybutylthioxanthato)bis(4-ethylpyridine)nickel(II)	Green	58.95	3.11
4	Bis(tertiarybutylthioxanthato)bis(2-chloropyridine)nickel(II)	Green	58.94	3.19
5	Bis(tertiarybutylthioxanthato)bis(3-chloropyridine)nickel(II)	Green	58.98	3.20

3.2 IR spectra

The IR spectra of the free ligand and the complexes were obtained in the range of 4000-300cm⁻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(tertiarybutylthioxanthato)nickel(II) with ethylpyridines and chloropyridines show characteristic bands corresponding to ν(C-S-C)_{asym} and ν(C-S-C)_{sym} vibrations in the range of 694-704 and 657-665 cm⁻¹. An intense band corresponding to ν(C-S) vibration is also observed in the range of 1036- 1041cm⁻¹ for the adducts synthesized which suggests that thioxanthate is binding as symmetrical bidentate chelating ligand (**table 3**). 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^[34-35].

3.3 UV-Visible spectra

The electronic spectra of adducts of bis(tertiarybutylthioxanthato)nickel(II) with ethylpyridines and chloropyridines show three absorption bands in the range of 13298-13309cm⁻¹, 19791-19798 cm⁻¹ and 24594-24608 cm⁻¹ (**Table 3**). These three bands may be assigned to three spin allowed transitions: ³A_{2g}→³T_{2g}(F)(ν₁), ³A_{2g}→³T_{1g}(F)(ν₂) and ³A_{2g}→³T_{1g}(P)(ν₃) respectively. The appearance of these bands along with shoulders suggest that the adducts synthesized have distorted octahedral geometry around Ni(II) metal ion^[36].

Table 3: Electronic and vibrational spectral data of 1:2 adducts of bis(tertiarybutylthioxanthato)nickel(II) with ethylpyridines and chloropyridines

S.No	Name of the adduct	Electronic spectral data in cm ⁻¹			Vibrational spectral data in cm ⁻¹		
		ν ₁	ν ₂	ν ₃	ν C-S	ν (C-S-C) _{As}	ν (C-S-C) _S
1	Bis(tertiarybutylthioxanthato)bis(2-ethylpyridine)nickel(II)	13309	19793	24604	1036	694	659
2	Bis(tertiarybutylthioxanthato)bis(3-ethylpyridine)nickel(II)	13298	19797	24608	1041	704	665
3	Bis(tertiarybutylthioxanthato)bis(4-ethylpyridine)nickel(II)	13299	19795	24606	1039	698	661
4	Bis(tertiarybutylthioxanthato)bis(2-chloropyridine)nickel(II)	13298	19791	24597	1041	703	659
5	Bis(tertiarybutylthioxanthato)bis(3-chloropyridine)nickel(II)	13300	19798	24594	1038	699	657

3.4 Thermal Studies:

The adducts were subjected to TG analysis from 25°C to 1000°C in nitrogen atmosphere and the results of the novel investigated adducts is as given below. The TG curve of the adduct show a continuous weight loss and a stable sulfide, NiS, is formed as an end product. An initial weight loss of 35.14% is observed at around 350°C due to the loss of two ethylpyridine molecules (calculated weight loss = 35.50%). Then a continuous weight loss of 83.7% is observed, which may be due to the loss of C₁₀H₁₈S₅ moiety, till a stable sulfide NiS is formed^[37] (**Figure 1**).



1.5. 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. Mass spectra of one of these adducts, bis(tertiarybutylthioxanthato) bis(4-ethylpyridine)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 base peak, corresponding to the fragment Ni[(S₂CSC₄H₉)₂]⁺. This indicates, in both cases, the strong chelating property of thioxanthates. The various fragments observed are in agreement with the molecular formula of the complexes^[38-39] .

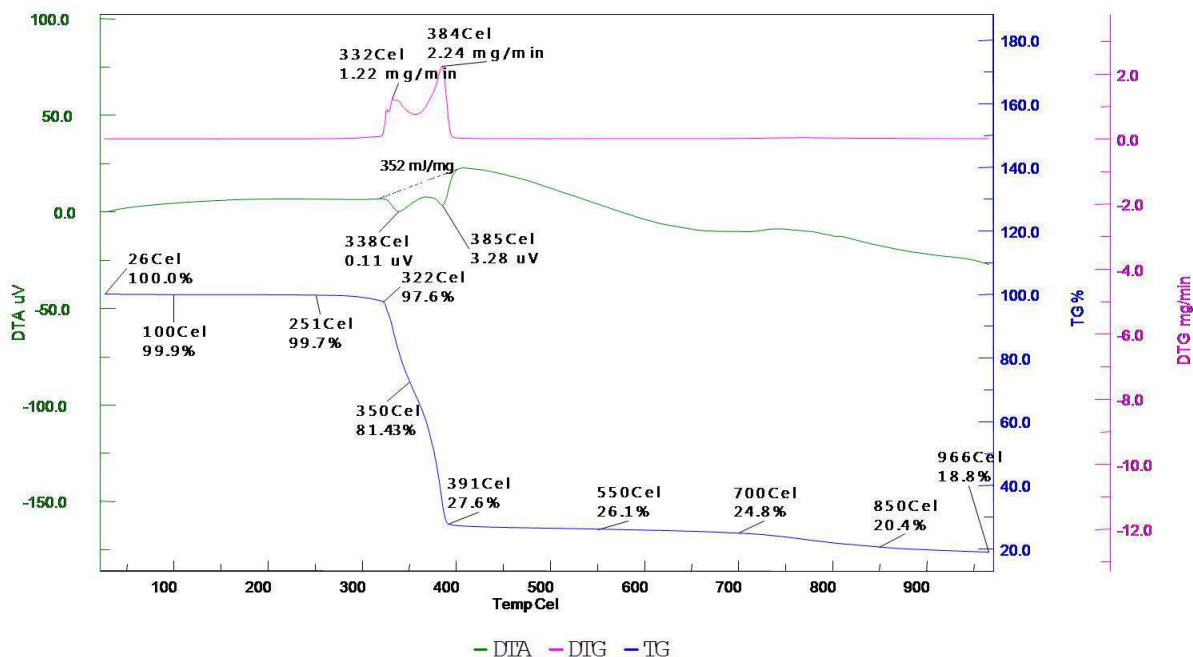


Fig. No. 1 TGA-DTA curve of bis(tertiarybutylthioxanthato)bis(3-ethylpyridine) nickel(II)

Table No 4. mass fragments of bis(tertiarybutylthioxanthato)bis(4-ethylpyridine) nickel(II)

Mass m/z	possible formulae of the fragment
602	$\text{Ni}[(\text{S}_2\text{CSC}_4\text{H}_9)_2(\text{C}_7\text{H}_9\text{N})_2]^+$
388	$\text{Ni}[(\text{S}_2\text{CSC}_4\text{H}_9)_2]^+$
222	$\text{Ni}[(\text{S}_2\text{CSC}_4\text{H}_9)]^+$
163	$[(\text{S}_2\text{CSC}_4\text{H}_9)]^+$
108	$[(\text{S}_2\text{CS})]^+$
76	$[\text{S}_2\text{C}]^+$

1.6 Biological studies:

The antifungal activity of the complex was tested by Poisoned Food Technique against the pathogenic fungus, *Sclerotium rolfsii*. The linear growth of fungus in controlled manner was recorded at different concentrations of the complexes. The growth inhibition of fungus over control was calculated (Table 5) and it shows that on increasing the concentration of the complexes, the colony diameter of the fungus decreases and hence percent inhibition increases (Fig.2)^[40]. The growth inhibition of *Sclerotium rolfsii* over control was calculated as:

$$\% \text{ inhibition (I)} = \frac{C-T}{C} \times 100$$

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

Table 5. Antifungal activities of some adducts mean colony diameter in the control=92 mm

S.no.	Name of the adduct	concentration, ppm	colony diameter, mm	% inhibition (I) = [(C-T)/C]×100
1	Bis(tertiarybutylthioxanthato)bis(4-ethylpyridine)nickel(II)	100	91	9
		200	78	61
		400	29	92.75
		800	4	99.5
2	Bis(tertiarybutylthioxanthato)bis(3-chloropyridine)nickel(II)	100	93	7
		200	83	58.5
		400	31	92.25
		800	3	99.63

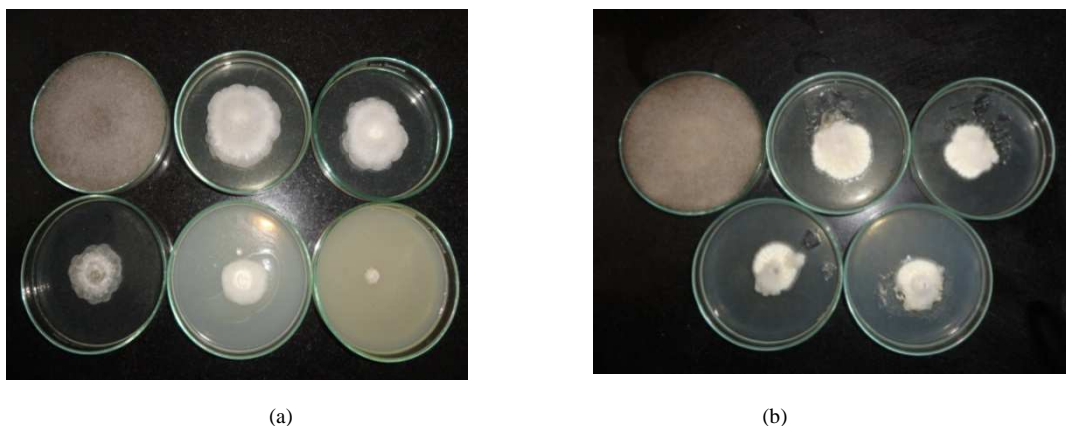


Figure 2: Antifungal activity of the adducts of (a) Bis(tertiarybutylthioxanthato)bis(4-ethylpyridine)nickel(II) and (b) Bis(tertiarybutylthioxanthato)bis(3-chloropyridine)nickel(II)

CONCLUSION

On the basis of above studies it is found that 1:2 adducts of bis(tertiarybutylthioxanthato)nickel(II) with ethylpyridines and chloropyridines have distorted octahedral geometry.

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