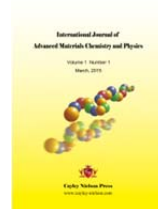




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Synthesis of adducts of nickel(II) thioxanthates with oxygen donor ligands

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ABSTRACT

Eight new 1:2 Adducts of Nickel(II)thioxanthates with dimethylsulphoxide and hexamethylphosphoramide have been prepared. The resulting adducts have been characterized by elemental analysis, molar conductance, magnetic susceptibility measurement, biological studies, thermal gravimetric analysis, mass, IR and UV-visible spectral studies. Analytical data reveals that Ni(II) complexes forms 1:2 adducts. Antifungal activities of some of these adducts have been carried out against the fungal strain *Sclerotium rolfsii*. Electronic and magnetic measurements indicate distorted octahedral geometry for the 1:2 adducts of Ni(II) adducts.

Keywords: Nickel(II)thioxanthates, Dimethylsulphoxide, Hexamethylphosphoramide and *Sclerotium rolfsii*.

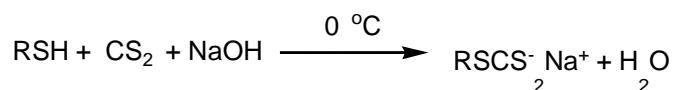
INTRODUCTION

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]. Thioxanthate complexes have received much 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 [2-3]. . These 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, plant defoliant and rust inhibitor. [4-5]. However, very few trithiocarbonato metal complexes have been synthesized and fully characterized [6-14]. 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 nickel(II)thioxanthates with Dimethylsulphoxide and Hexamethylphosphoramide.

EXPERIMENTAL SECTION

Preparation of sodium salt of alkylthioxanthate ligand [NaS₂CSR]

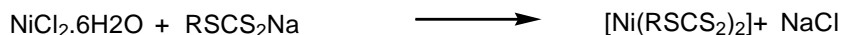
The sodium salt of alkylthioxanthate (where alkyl = ethyl, isopropyl, tertiarybutyl and benzyl) was prepared as reported in literature. [15] by the dropwise addition of the alkanethiol (1mol) to a saturated solution of sodium hydroxide at 0°C, followed by the addition of excess carbon disulfide (1.2 mol). The yellow precipitate formed immediately was collected by filtration and twice recrystallized from water-acetone mixture. The salt was characterized by its unpleasant odour and was stored in a vacuum dessicators over phosphorus pentoxide.



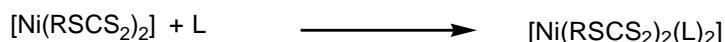
Where R = Ethyl, isopropyl, tertiarybutyl and benzyl

Synthesis of bis(alkylthioxanthato)nickel(II) complex:

To Sodium salt of alkylthioxanthate (0.02 mol) an aqueous solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (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 $[\text{Ni}(\text{S}_2\text{CSR})_2]$ by the elemental analysis.

**Synthesis of adducts of bis(ethylthioxanthato)nickel(II) with dimethylsulphoxide and hexamethyl phosphoramidate :**

Bis(alkylthioxanthato)nickel(II) (0.01 mol) was dissolved in acetone (60-80 mL) and stirred for about 10-20 minutes. To the resulting solution, dimethylsulphoxide and hexamethylphosphoramidate (0.02 mol) 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 desiccator over anhydrous calcium chloride. The composition of the adduct was established to be $[\text{Ni}(\text{S}_2\text{CSR})_2\text{L}_2]$.



Where L=Dimethylsulphoxide and Hexamethylphosphoramidate

RESULTS AND DISCUSSION

The adducts were analyzed by various analytical and physico – chemical techniques and the results shows that bis(alkylthioxanthato)nickel(II) (where alkyl =ethyl, isopropyl and tertiarybutyl or benzyl) forms 1:2 adducts with dimethylsulphoxide and hexamethylphosphoramidate . The analytical data (**Table 1**) reveals that 1:2 adduct have general formula $[\text{Ni}(\text{S}_2\text{CS}(\text{R}))_2\text{L}_2]$ (where R= ethyl, isopropyl, tertiarybutyl or benzyl and L= dimethylsulphoxide and hexamethylphosphoramidate) . 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 $[\text{Ni}(\text{S}_2\text{CS}(\text{R}))_2\text{L}_2]$ measured in 10^{-3} M DMF solution are found to be in the range of $59.63\text{-}59.78 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (**table2**). These values supports the neutral and non-ionic nature of the complexes. [16-17].

Magnetic susceptibility measurement:

The 1:2 adducts of bis(alkylthioxanthato)nickel(II) with dimethylsulphoxide and hexamethylphosphoramidate exhibit magnetic moment values in the range of 3.18-3.24 B.M (**Table2**) which is in agreement with magnetic moment values observed for paramagnetic octahedral complexes of nickel(II) [18].

Table(1): Analytical data of 1:2 adducts of Bis(alkylthioxanthato)nickel(II) with dimethylsulphoxide and hexamethyl phosphoramidate

S.no	Name of the adduct	% found				% calculated			
		C	H	N	S	C	H	N	S
1	Bis(ethylthioxanthato)bis(dimethylsulphoxide) nickel(II)	24.23	3.95	-	52.02	24.56	4.50	-	52.38
2	Bis(ethylthioxanthato)bis(hexamethylphosphoramidate)nickel(II)	31.02	5.98	11.86	27.43	31.28	6.66	12.16	27.80
3	Bis(isopropylthioxanthato)bis(dimethylsulphoxide)nickel(II)	27.17	4.73	-	49.16	27.87	5.03	-	49.55
4	Bis(isopropylthioxanthato)bis(hexamethylphosphoramidate) nickel (II)	33.06	6.34	11.17	26.42	33.39	6.96	11.69	26.72
5	Bis(tertiarybutylthioxanthato)bis(dimethylsulphoxide)nickel(II)	30.53	5.19	-	46.49	30.84	5.51	-	46.99
6	Bis(tertiarybutylthioxanthato)bis(hexamethylphosphoramidate)nickel (II)	35.06	6.86	11.05	25.14	35.36	7.23	11.25	25.72
7	Bis(benzylthioxanthato)bis(dimethylsulphoxide)nickel (II)	38.85	3.98	-	41.43	39.17	4.24	-	41.78
8	Bis(benzylthioxanthato)bis(hexamethylphosphoramidate)nickel (II)	40.92	5.87	10.03	23.18	41.25	6.14	10.31	23.57

Table 2: Colour, Molar conductance and magnetic susceptibility measurement data of 1:2 adducts of Bis(alkylthioxanthato)nickel(II) with dimethylsulphoxide and hexamethylphosphoramidate

S.no	hexamethylphosphoramidate	Colour	Molar conductance ($\text{ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$)	μ_{eff} (B.M.) at 293 K
1	Bis(ethylthioxanthato)bis(dimethylsulphoxide) nickel(II)	Green	59.67	3.19
2	Bis(ethylthioxanthato)bis(hexamethylphosphoramidate)nickel(II)	Green	59.72	3.23
3	Bis(isopropylthioxanthato)bis(dimethylsulphoxide)nickel(II)	Green	59.69	3.20
4	Bis(isopropylthioxanthato)bis(hexamethylphosphoramidate)nickel(II)	Green	59.78	3.22
5	Bis(tertiarybutylthioxanthato)bis(dimethylsulphoxide)nickel(II)	Green	59.72	3.18
6	Bis(tertiarybutylthioxanthato)bis(hexamethylphosphoramidate)nickel(II)	Green	59.76	3.21
7	Bis(benzylthioxanthato)bis(dimethylsulphoxide)nickel (II)	Green	59.63	3.21

Infrared spectra:

The most relevant bands in the IR spectra of the adducts of $\text{Ni}[\text{S}_2\text{CS}(\text{R})]_2 \cdot \text{L}_2$ (where R= ethyl, isopropyl, tertiarybutyl or benzyl and L= dimethylsulphoxide(DMSO) and hexamethylphosphoramide(HMPA) are shown in (Table 3). The IR spectra of the free ligand and the complexes were obtained in the range of $4000\text{-}300\text{ cm}^{-1}$. 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(alkylthioxanthato)nickel(II) show characteristic bands corresponding to $\nu(\text{C-S-C})_{\text{asym}}$ and $\nu(\text{C-S-C})_{\text{sym}}$ vibrations in the range of $689\text{-}703\text{ cm}^{-1}$ and $656\text{-}663\text{ cm}^{-1}$. An intense band corresponding to $\nu(\text{C-S})$ vibration is also observed in the range of $1031\text{-}1043\text{ cm}^{-1}$ for all the adducts synthesized which suggests that thioxanthate is binding as symmetrical bidentate chelating ligand [19-20]. 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. A band of medium to strong intensity observed in the region $380\text{-}395\text{ cm}^{-1}$ may be assigned due to (Ni-S) stretching mode [21].

Electronic Spectra:

The electronic spectral data of adducts are given in (Table 3). The spectra of 1:2 adducts were recorded in DMF in the range of $12500\text{-}4000\text{ cm}^{-1}$. These adducts show three bands in the range of $\nu_1(13290\text{-}13303\text{ cm}^{-1})$, $\nu_2(19785\text{-}19793\text{ cm}^{-1})$ and $\nu_3(24589\text{-}24597\text{ cm}^{-1})$, which corresponds to the d-d transitions $3A_{2g}(\text{F}) \rightarrow 3T_{2g}(\text{F})$, $3A_{2g}(\text{F}) \rightarrow 3T_{1g}(\text{F})$ and $3A_{2g}(\text{F}) \rightarrow 3T_{1g}(\text{P})$, respectively (Table 3). These three bands shows that adducts is having trans octahedral geometry around Ni (II) metal ion.[22].

Table 3: Electronic and vibrational spectral data of 1:2 adducts of Bis(alkylthioxanthato)nickel(II) with DMSO and HMPA

S.no	Name of the adduct	Electronic data			Infrared data			
		$\nu_1(\text{ cm}^{-1})$	$\nu_2(\text{ cm}^{-1})$	$\nu_3(\text{ cm}^{-1})$	$\nu(\text{C-S})$	$\nu(\text{C-S-C})_{\text{as}}$	$\nu(\text{C-S-C})_{\text{s}}$	$\nu(\text{Ni-S})$
1	Bis(ethylthioxanthato)bis(dimethylsulphoxide)nickel(II)	13303	19788	24597	1043	703	659	395
2	Bis(ethylthioxanthato)bis(hexamethylphosphoramide)nickel(II)	13300	19786	24595	1041	701	656	393
3	Bis(isopropylthioxanthato)bis(dimethylsulphoxide)nickel(II)	13299	19793	24596	1035	692	661	391
4	Bis(isopropylthioxanthato)bis(hexamethylphosphoramide)nickel(II)	13295	19791	24593	1032	689	659	388
5	Bis(tertiarybutylthioxanthato)bis(dimethylsulphoxide)nickel(II)	13296	19792	24594	1038	693	662	387
6	Bis(tertiarybutylthioxanthato)bis(hexamethylphosphoramide)nickel(II)	13294	19790	24591	1035	690	659	385
7	Bis(benzylthioxanthato)bis(dimethylsulphoxide)nickel(II)	13292	19786	24590	1032	693	663	383
8	Bis(benzylthioxanthato)bis(hexamethylphosphoramide)nickel(II)	13290	19785	24589	1031	691	661	380

Thermal studies:

TGA of bis(ethylthioxanthato)bis(hexamethylphosphoramide)nickel(II) shows a continuous weight loss with increasing temperature (Fig 1). At 187.3°C a major weight loss of 53.4% occurs which may be due to the loss of two molecules of coordinated hexamethylphosphoramide. After this a rapid weight loss is observed at which may be due to the loss of both the molecules of thioxanthato ligand. At 678.4°C the decomposition becomes complete with weight loss of 94.9% leaving NiS as a stable end product. [23].



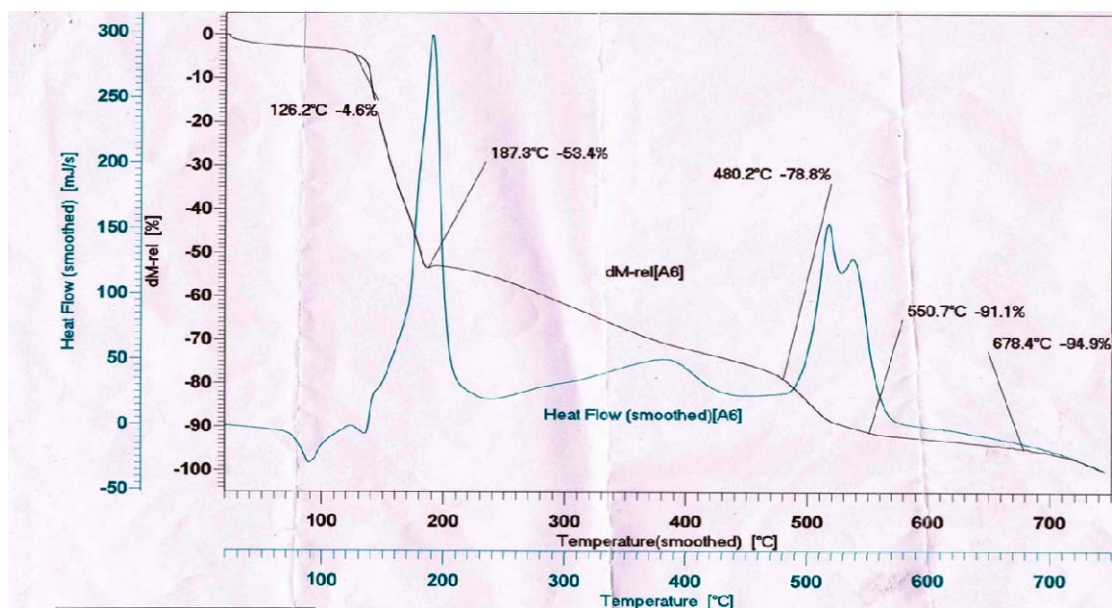


Figure1: TGA-DTA curve of bis(ethylthioxanthato)bis(hexamethylphosphoramidate) nickel(II)

Mass spectra:

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(ethylthioxanthato)bis(dimethylsulphoxide) 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 $\text{Ni}[(\text{S}_2\text{CSC}_2\text{H}_5)_2]^+$. 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.

Table(4): Mass spectra of Bis(ethylthioxanthato)bis(dimethylsulphoxide))nickel(II)

Mass m/z	possible formulae of the fragment
486	$\text{Ni}[(\text{S}_2\text{CSC}_2\text{H}_5)_2(\text{C}_2\text{H}_6\text{SO})_2]^+$.
323	$\text{Ni}[(\text{S}_2\text{CSC}_2\text{H}_5)_2]^+$.
195	$\text{Ni}[(\text{S}_2\text{CSC}_2\text{H}_5)]^+$.
134	$[(\text{S}_2\text{CSC}_2\text{H}_5)]^+$.
108	$[(\text{S}_2\text{CS})]^+$.
76	$[\text{S}_2\text{C}]^+$.

Table 5. Antifungal activities of some adducts mean colony diameter in the control=93.5 mm

S.no.	Name of the adduct	concentration,ppm	colony diameter,mm	% inhibition (I) = $[(\text{C}-\text{T})/\text{C}]\times 100$
1	Bis(ethylthioxanthato)bis(dimethylsulphoxide)nickel(II)	100	92	8
		200	87	56.5
		400	30	92.5
		800	5	99.37
2	Bis(isopropylthioxanthato)bis(hexamethylphosphoramidate)nickel(II)	100	94	6
		200	83	58.5
		400	27	93.25
		800	7	99.12
3	Bis(tertiarybutylthioxanthato)bis(dimethylsulphoxide)nickel(II)	100	96	4
		200	86	57
		400	29	92.75
		800	8	99
4	Bis(benzylthioxanthato)bis(hexamethylphosphoramidate)nickel(II)	100	91	9
		200	79	60.5
		400	31	92.25
		800	9	98.88

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**)[26]. 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.

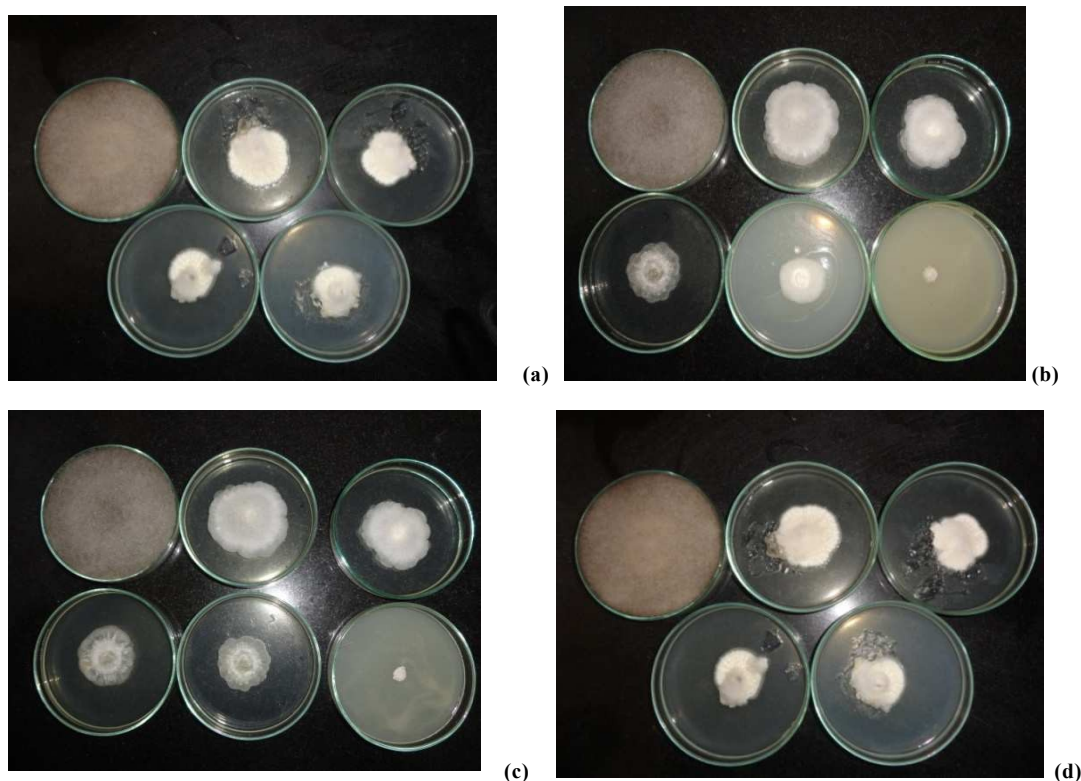


Figure 2: Antifungal activity of the adducts of (a) Bis(ethylthioxanthato)bis(dimethylsulphoxide)nickel(II), (b) Bis(isopropylthioxanthato)bis(hexamethyl phosphoramidate)nickel(II), (c) Bis(tertiarybutylthioxanthato)bis(dimethylsulphoxide)nickel(II) and (d) Bis(benzylthioxanthato)bis(hexamethylphosphoramidate)nickel(II)

CONCLUSION

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

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