

Synthesis, Spectroscopy and magnetic characterization of Cu (II) complexes with bis (o-ethylthiocarbonato), alkylpyridine as ligands.

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Abstract: The complexes of bis (o-ethylthiocarbonato) cu (II) of general formula Cu (C₂H₅OCS₂)₂(L), [L=2-,3-,4 methylpyridines and 2-,3-,4 ethylpyridines] have been synthesized and characterized by chemical analysis, IR and electronic spectroscopy, magnetic conductivity measurement. Analytical results show that the complexes have 1:1 stoichiometry. The complexes were found to be paramagnetic and their magnetic moments at room temperature lie within the 1.81-1.94 B.M range and this indicates the presence of one unpaired electron. All the complexes have distorted square pyramidal geometry.

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Key words: bis (o-ethylthiocarbonato), alkylpyridine, complexes of copper.

1. Introduction

O-Alkylthiocarbonates popularly known as xanthates derivatives, have found a wide practical application as addition. To lubricating oils, antioxidants for polyolefins, and so forth. However, alkylxanthates are mainly used in flotation concentration of nonferrous sulfides ores. These are extensively used as pharmaceuticals, fungicides and quite recently in therapy for HIV infections [1-3]. Divalent transition metals xanthates are partly unsaturated and can therefore form 1:1 complexes with electron donors such as neutral nitrogen, oxygen, phosphorous or sulfur donors in which the coordination geometry ranges from square pyramidal to trigonal bipyramidal [4]. Such complexes of many transition metals such as Ni, Zn, Mn, V, Pt and Pd are studied but little attention has been paid to the xanthates of copper owing to their instability. Here, we report synthesis and investigation of the 1:1 complexes of Cu (II) xanthates with alkyl pyridines such as 2-, 3-, 4-methylpyridines and 2-,3-,4 ethylpyridines.

2. Experimental

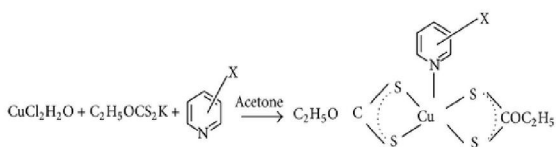
2.1. Preparation of potassium salt of o- ethyl di thiocarbonate

Potassium salt of ethyl xanthate was prepared by the method reported in literature [5]. Into a 500 ml round Bottomed flask, fitted with a reflux condenser, was placed 0.75 mole of potassium hydroxide pellets and 120 g of Ethanol. The reaction mixture was heated under reflux for 1 hour. The mixture was then

cooled and liquid from the residual solid was decanted off into another dry 500 ml flask. To this flask was added 45 ml (0.75 moles) of Carbon disulfide slowly with constant shaking. The residual solid yellow 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 salt of ethyl xanthate was dried in vacuum desiccator over anhydrous calcium chloride. The yield was about 75 kg. It was then recrystallised from ether.

2.2. Preparation of complexes of bis (O-ethyl dithiocarbonate) Copper II with alkyl- pyridines

The yellow coloured parent compound copper (II) xanthate could not be isolated because it changed rapidly into brown coloured Copper (II) xanthate. The addition complexes were prepared by the direct reaction of solution of metal salt, solution of potassium salt of ethylxanthate and substituted pyridine. About 20 ml solution of cupric chloride dehydrate (0.0025 mole) in acetone was prepared. To this solution, a solution of potassium salt of ethylxanthate (0.005 mole) and alkyl pyridine (0.0025 mole) [2-methyl pyridine=0.235g, 3-methyl pyridine=0.235g, 4-methyl pyridine=0.235g, 2-ethyl pyridine=0.27g, 3-ethyl pyridine=0.27g and 4-ethyl pyridine=0.27g] prepared in 50ml of acetone was added slowly with constant stirring. Dark green coloured precipitates so obtained were filtered, washed with acetone and dried over anhydrous calcium chloride in a vacuum desiccator at room temperature. A scheme of the proposed structure is shown in scheme 1.



Scheme 1: Scheme of the proposed structure, where $x = \text{---CH}_3, \text{---C}_2\text{H}_5$

3. Result and Discussion:

The addition complexes of bis (o- ethyl dithiocarbonate) Cu (II) are microcrystalline solids which are light green in colour. These are insoluble in common organic solvents such as ethanol, acetone and benzene. However, these are soluble in

dimethylformamide and dimethylsulfoxide. On the basis of elemental analysis (Table-1). They have been assigned the general formula $\text{Cu}(\text{S}_2\text{COC}_2\text{H}_5)_2\text{L}$ [L=2-,3-,4-methyl and 2-,3-,4-ethylpyridine]. Conductance values of these complexes in DMF fall in the range of $3.50\text{-}5.00\text{ ohm}^{-1}\text{mol}^{-1}\text{cm}^2$ (Table-1). These values are lower than the values expected for any uni-univalent electrolytes in this solvent suggesting that these complexes are neutral and non-ionic in character [6,7]. The magnetic moments of 1:1 complexes of bis (o- ethyl dithiocarbonate) copper (II) with substituted pyridines fall in the range 1.81-1.94 B.M (Table-1) which is in agreement with magnetic moment values observed for distorted square pyramidal complexes of copper [8-10].

Table 1: Molar conductance, magnetic moments and analytical data of 1:1 complexes of bis (o- ethyl dithiocarbonate) copper (II) with alkyl pyridines.

SL N O.	Name of the compounds	Molar Conductance $\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2$	μ (B.M) at 293K	% found				% calculated			
				C	H	N	S	C	H	N	S
1	Bis (ethylxanthato 2-methylpyridine) copper (II)	3.49	1.88								
				33.0	3.02	3.0	32.7	34.4	3.91	3.64	33.3
2	Bis (ethylxanthato 3-methylpyridine) copper (II)	3.85	1.92	34.8	3.98	2.78	31.9	36.2	4.27	3.51	32.2
3	Bis (ethylxanthato 4-methylpyridine) copper (II)	4.35	1.93	35.5	3.55	2.98	30.8	36.2	4.27	3.51	32.2
4	Bis (ethylxanthato 2-ethylpyridine) copper (II)	3.89	1.76	36.6	4.01	3.15	30.7	37.9	4.61	3.40	31.1
5	Bis (ethylxanthato 3-ethylpyridine) copper (II)	3.97	1.82	36.2	4.00	3.32	30.6	37.9	4.61	3.40	31.1
6	Bis (ethylxanthato 4-ethylpyridine) copper (II)	4.74	1.85	36.6	3.98	3.20	30.2	37.9	4.61	3.40	31.1

Free dithiocarbonate shows vibrations due to C-O-C stretching in the range of $1270\text{-}1280\text{ cm}^{-1}$ and the C-S stretching vibrations appear as two bands in the range of $1057\text{-}1070\text{ cm}^{-1}$. In the present work a single sharp band of high intensity has been observed in all the complexes in the range of $1011\text{-}1035\text{ cm}^{-1}$ (Table-2).

The appearance of the only C-S band suggests symmetrical bidentate binding of the dithiocarbonate

moiety. There is a positive shift of $10\text{-}30\text{ cm}^{-1}$ in comparison to the free ligands. This indicates that dithiocarbonate ligand co-ordinates with metal through sulphur atoms. Moreover, the complexes show a band in the region $1190\text{-}1220\text{ cm}^{-1}$ which is attributed to $\nu(\text{C-O})$ of dithiocarbonate moiety. In these complexes C-H out of plane bands occur at lower energy positions on complexation, indicating red shifts, which confirm that these ligands interact with the metal ion through their respective ring

nitrogen atom. A new band of medium to strong intensity observed in the range of $320-352\text{ cm}^{-1}$, may be attributed to Cu-S stretching mode (II). The electronic spectra of 1:1 addition complexes of bis (O-ethyl dithiocarbonato) copper (II) have been recorded in DMF. The copper (II) five co-ordinated complexes are expected to show a strong broad band appearing in the region $12000-17500\text{ cm}^{-1}$ (Table-2). The band

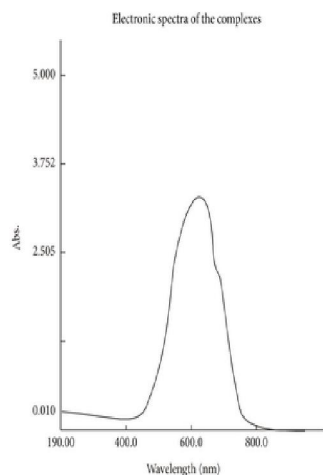
maximum appears around 16000 cm^{-1} and is assigned to $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition. A weak shoulder is associated with it due to $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. Third possible transition is orbitally forbidden and merges with the broad band. The relative energy order of these transitions depends upon the extent of axial ligand-metal interaction.

Table-2: Electronic and vibrational spectral data of bis (O-ethyl dithiocarbonato) copper (II) with alkyl-pyridines.

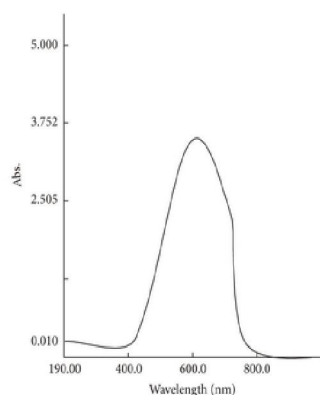
SL. No.	Name of the complexes	Yield (melting point)	ν_1 (cm^{-1})	ν (C-S)	ν (C-O)	ν (Cu-S)
1	Bis (ethylxanthato (2-methylpyridine) copper (II))	62% (89° c)	16421	1012	1199	324
2	Bis (ethylxanthato (3-methylpyridine) copper (II))	68% (87° c)	16623	1022	1210	335
3	Bis (ethylxanthato (4-methylpyridine) copper (II))	70%(80.5° c)	16858	1032	1200	330
4	Bis (ethylxanthato (2-ethylpyridine) copper (II))	65%(86.8° c)	16990	1020	1202	327
5	Bis (ethylxanthato (3-ethylpyridine) copper (II))	68%(86.8° c)	16400	1034	1198	324
6	Bis (ethylxanthato (4-ethylpyridine) copper (II))	69%(87.4° c)	15890	1037	1200	338

The complexes under observation show an intense band in the range of ($15500-17500\text{ cm}^{-1}$) which is attributed to d-d transition observed in most of the Copper complexes (ν_1). This main absorption band around 16000 cm^{-1} can be assigned to d_{xz} ,

$d_{yz} \rightarrow d_{x^2-y^2}$ (Table-2). The appearance of one band with the intensity pattern suggests square pyramidal geometry around Copper (II) ion in these 1:1 complexes [12] figure-1.



(a)



(b)

Figure 1

- Instrument performance
Model: UV-VIS spectrophotometer
Number: 18-1901-01-0103
Spectral bandwidth: 2.00nm
- Scan spectrum performance
Scan range: 190.00 to 800.00nm
Measure mode: Abs
Interval: 1.00nm
Speed: fast
Data file: i7.spd
Create data/time: Thursday, March 27, 2014 11:28:40 AM
Data type: original
Method file:
- Analyse note
Analyser: administrator
Sample name.

- Instrument performance
Model: UV-VIS spectrophotometer
Number: 18-1901-01-0103
Spectral bandwidth: 2.00nm
- Scan spectrum performance
Scan range: 190.00 to 800.00nm
Measure mode: Abs
Interval: 1.00nm
Speed: fast
Data file: Shengl.spd
Create data/time: Thursday, March 27, 2014 11:20:50 AM
Data type: original
Method file.
- Analyse note
Analyser: administrator
Simple name.

Conclusion:

The results obtained from various physicochemical and spectral techniques suggest that the complexes of bis (O-ethyl dithiocarbonate) Copper (II) with alkyl pyridines have 1:1 Stoichiometry with square pyramidal geometry around Copper (II) ion.

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