

# Olylxanthate Complexes of Cobalt (II), Nickel(II), Copper(II), and Zinc(II) with nitrogen donor ligands

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## ABSTRACT

New complexes of Xanthate of the general formula  $[M(\text{oleyXant})_2]$  and  $[M(\text{oleyXant})_2.nL]$  Where  $M = \text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cu(II)}$  and  $\text{Zn(II)}$ , and  $(\text{oleyXant}) = \text{Olylxanthate}$ , and  $n = 2$  When  $L = \text{pyridine}$ ,  $\gamma\text{-picoline}$ ,  $3,5\text{-lutidine}$ ,  $n = 1$  When  $L = \text{ethylenediamine}$ ,  $(1,10)\text{-phenanthroline}$ , have been prepared and characterized by elemental analyses, infrared, conductance measurements, electronic absorption spectra, and susceptibility measurements. Magnetic moment and electronic spectra, indicate that the complexes of the type  $\{M(\text{oleyXant})_2\}$  where  $M = \text{Co(II)}$ ,  $\text{Ni(II)}$  and  $\text{Zn(II)}$ , are of tetrahedral geometry, and of a square planar geometry when  $M = \text{Cu(II)}$  while the complexes of the type  $[M(\text{oleyXant})_2.nL]$  have an octahedral geometry.

**Keyword:** Xanthate, Cobalt(II), Nickel(II), Copper(II), Zn(II).

## INTRODUCTION

Mateixanthate complexes and their reaction products with variety lewis bases have been extensively studied<sup>(1,2,3)</sup>. Xanthate,  $S_2COR$ , Comprise an important class of 1,1-dithiolate ligands with many applications ranging from flotation agents to radical polymerization<sup>(4-8)</sup>.

We describe here the syntheses and characterization of nitrogen donor base adducts of the starting bis(oleyxantheto)  $M(\text{II})$  Complexes where  $M = \text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cu(II)}$  and  $\text{Zn(II)}$ . The complexes were prepared by reaction of  $[M(\text{oleyXant})_2]$  with the ligand (nitrogen base donor) in a 1:1 and 1:2 molar ratio in ethanol as solvent.

## EXPERIMENTAL MATERIALS AND METHOD

All reagents and solvents were of analytical grade and used as supplied from Fluka or BDH chemical companies, Infrared spectra were recorded on a Brucker Tensor 27 co. FTIR spectrophotometer in the  $400\text{-}4000\text{ cm}^{-1}$  range using KBr discs. Conductivity measurements were carried out on  $10^{-3}\text{ M}$  solution of the complexes in DMF using conductivity meter PCM3 Jenway at ambient temperature. The electronic spectra were recorded on a Shimadzu UV-visible spectrophotometer UV-160 for  $10^{-3}\text{ M}$  solution of complexes in DMF as solvent at  $25^\circ\text{C}$  using 1 cm quartz cell. Metal content were determined spectrophotometrically using AA670atomic absorption. Melting points were recorded on an Electrothermal 9300 apparatus. The magnetic measurement was carried out at  $25^\circ\text{C}$  on the solids by Faraday's method using Brucker BM6 instrument.

### Synthesis of potassium oleyl Xanthate

To  $(63.2\text{ cm}^3, 0.2\text{ mol})$  of oleyl alcohol was added to aqueous solution  $(11.2\text{ g}, 0.2\text{ mol})$  of potassium hydroxide with stirring. The mixture was cooled in an ice bath, to this mixture  $(12.03\text{ cm}^3, 0.20\text{ mol})$  of disulfide was added drop wise with continuous stirring for 60 min. in ice salt bath, The precipitate formed was extracted with  $(150\text{ ml})$  diethyl ether, filtered off, washed with diethyl ether and dried under vacuum, a yellow precipitate formed.

### I.A. Synthesis of complex $[M(\text{oleyXant})_2]$ $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$

Ethanolic solution of  $\text{CoCl}_2.6\text{H}_2\text{O}$  (2.37 g, 0.01 mol) or  $\text{NiCl}_2.6\text{H}_2\text{O}$  (2.37 g, 0.01 mol) or  $\text{CuCl}_2.2\text{H}_2\text{O}$  (1.70 g, 0.01 mol) or  $\text{ZnCl}_2$ , anhydrous (1.26 g, 0.01 mol) was added drop wise to ethanolic solution of potassium oleylxanthate

(5.36 g, 0.02 mol) with stirring for 45 min. until complete precipitation. The precipitate was filtered off, washed with ethanol, then with diethyl ether and dried under vacuum.

**I.B. Synthesis of complex  $[M(\text{oleyXant})_2(L)_2]$   
L = Pyridine, 4-picoline, 3,5-lutidine**

Prepared similarly as in procedure (I.A.). the precipitate formed was treated with (0.02 mol) of (Pyridine,  $\gamma$ -picoline, 3,5-lutidine) drop wise with continuous stirring for 45 min., the precipitate formed, was filtered, washed with ethanol then dried under vacuum.

**I.C. Synthesis of complex  $[M(\text{oleyXant})_2(L)]$   
L = 1,10-phenanthroline, ethylenediamine**

Prepared similarly as in procedure (I.A.) precipitate formed was treated with (0.01 mol) from (1,10-phenanthroline, ethylenediamine) drop wise with continuous stirring for 45 min., the precipitate formed, was filtered, washed with ethanol then dried under vacuum.

## RESULTS AND DISCUSSION

The new ligand was prepared by the reaction of oleyl alcohol with potassium hydroxide and the added carbon disulphide; the complexes were prepared through direct reaction of the metal chlorides,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$  or anhydrous  $\text{ZnCl}_2$  with the above ligand in (1:2) molar ratio. The values of conductivity in dimethyl formamide solution of the complexes range from  $(14.92\text{-}36.27)\Omega^{-1} \text{cm}^2\text{mol}^{-1}$ , which are typical values for non-electrolyte type in the solvent used<sup>9</sup>.

### Infrared spectral studies:

The most important IR bands assignments of the ligand and complexes are listed in (Table 2).

The two bonds  $\nu(\text{C-O})$  and  $\nu(\text{C-S})$  of the ligand were observed at  $(1196\text{cm}^{-1})$  and  $(1055\text{cm}^{-1})$ , in all complexes these bond shift to appear at the region  $(1218\text{-}1267\text{cm}^{-1})$  and  $(1020\text{-}1050\text{cm}^{-1})$  respectively. The presence of only one band in the later region reports the bidentate coordination of the dithioligand<sup>(10)</sup>. IR spectra showed a new band at  $(411\text{-}461 \text{cm}^{-1})$  which is an evidence for the coordination of metal to sulfur  $\nu(\text{M-S})$ <sup>(11)</sup>.

### Electronic spectral studies:

The UV-Visible spectra of the ligands and their complexes in  $10^{-3}$  M in DMF solution, were recorded; the results were listed in (Table 2) the UV-Visible spectra of the Co(II) complex (1) exhibited an absorption band  $(15527 \text{cm}^{-1})$  region, which were assigned to  $({}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P}))$  transition<sup>12</sup>, in tetrahedral configuration of this complex and the absence of  $({}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F}))$  and  $({}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F}))$ , are due to the sensitivity of the instrument used. Complexes (2-6) show three absorption bands at the range  $(9852\text{-}10288 \text{cm}^{-1})$ ,  $(15535\text{-}16447 \text{cm}^{-1})$  and  $(20393\text{-}21532 \text{cm}^{-1})$  which were assigned to  $({}^4\text{T}_1(\text{g}(\text{F})) \rightarrow {}^4\text{T}_1(\text{g}(\text{F})))$ ,  $({}^4\text{T}_1(\text{g}(\text{F})) \rightarrow {}^4\text{A}_2(\text{g}(\text{F})))$  and  $({}^4\text{T}_1(\text{g}(\text{F})) \rightarrow {}^4\text{T}_1(\text{g}(\text{P})))$  transition in octahedral configuration<sup>(13)</sup>.

The Ni(II) complex (7) show two absorption bands at  $(95238 \text{cm}^{-1})$  and  $(12531 \text{cm}^{-1})$  which were assigned to  $({}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{A}_2(\text{F}))$  and  $({}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P}))$  transitions in a tetrahedral geometry<sup>14</sup>, respectively, the complexes (8-12) show three absorption bands in the range  $(10822 - 11252 \text{cm}^{-1})$ ,  $(15290 - 16235 \text{cm}^{-1})$  and  $(22321 - 24390 \text{cm}^{-1})$ , which were assigned to  $({}^3\text{A}_2(\text{g}(\text{F})) \rightarrow {}^3\text{T}_2(\text{g}(\text{F})))$ ,  $({}^3\text{A}_2(\text{g}(\text{F})) \rightarrow {}^3\text{T}_1(\text{g}(\text{F})))$ ,  $({}^3\text{A}_2(\text{g}(\text{F})) \rightarrow {}^3\text{T}_1(\text{g}(\text{P})))$  in octahedral geometry<sup>(15)</sup>.

The Cu(II) complex(13) give a broad absorption band at  $(15524\text{cm}^{-1})$ , which was assigned to the combination of  $({}^2\text{B}_1\text{g} \rightarrow {}^2\text{A}_1\text{g})$  and  $({}^2\text{B}_1\text{g} \rightarrow {}^2\text{E}_\text{g})$  transition in a square planar geometry<sup>(16)</sup>, the complexes (14-18) show a broad absorption band in the region  $(13895 - 14147 \text{cm}^{-1})$ , which was assigned to  $({}^2\text{E}_\text{g} \rightarrow {}^2\text{T}_2\text{g})$  transition in octahedral geometry that result from the combination of three transitions  $({}^2\text{B}_1\text{g} \rightarrow {}^2\text{A}_1\text{g})$ ,  $({}^2\text{B}_1\text{g} \rightarrow {}^2\text{B}_2\text{g})$  and  $({}^2\text{B}_1\text{g} \rightarrow {}^2\text{E}_\text{g})$ <sup>(17)</sup>. For all the compounds, the other band appear above  $(28,000 \text{cm}^{-1})$  refers to charge transfer band.

### Magnetic susceptibility measurements

The magnetic moments of the complexes (Table1) were measured at  $(25^\circ\text{C})$ . The magnetic moments for Co(II) and Ni(II) complexes (1 and 7) are (4.02 and 2.89 B.M.) respectively suggesting a tetrahedral geometry<sup>(14)</sup>. The magnetic moment values of the other Co(II) and Ni(II) complex (2-6, 8-12) were in the range (4.36-4.98 and 2.99 -3.30 B.M) respectively in an octahedral geometry<sup>(14)</sup>. Then high values of magnetic moments for complexes (8-12) are due to orbital contribution<sup>(18)</sup>.

The magnetic moment value for four coordinated Cu(II) complexes (13) is (2.14 B.M) correspond to the spin only value irrespective of the stereo chemistry, which suggest a square planar geometry around Cu(II) ion. The magnetic moments values for hexa coordinated Cu(II) complexes (14-18) (Table 1), are in the rang(1.68 – 2.26 B.M). The observed rang is similar to other reported values of octahedral Cu (II) complexes.

The Zn(II) complex (19) possess a diamagnetic property, as expected for  $d^{10}$  system, suggesting a tetrahedral geometry. All other hexa coordinated Zn(II) complexes (20-24) were diamagnetic suggesting an octahedral geometry.

**Table (1): Analytical and some physical properties of the prepared complexes**

No	Compound	Color	m.p	Molar conductivity $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	%M	%yield	$\mu_{\text{eff}}$ B.M
L	$\text{C}_{19}\text{H}_{35}\text{OS}_2\text{K}$	Yellow	232	-----	-----	-----	-----
1	$[\text{Co}(\text{oleylxant})_2]$	Green	182	22.14	8.11 (7.91)	74	4.02
2	$[\text{Co}(\text{oleylxant})_2(\text{py})_2]$	Green	196	33.74	6.72 (6.52)	86	4.76
3	$[\text{Co}(\text{oleylxant})_2(\gamma\text{-pico})_2]$	Green	175*	27.00	6.98 (6.33)	71	4.52
4	$[\text{Co}(\text{oleylxant})_2(3,5\text{-Lut})_2]$	Green	189	32.64	6.79 (6.14)	78	4.36
5	$[\text{Co}(\text{oleylxant})_2(\text{en})]$	Green	226	24.72	7.47 (7.32)	61	4.98
6	$[\text{Co}(\text{oleylxant})_2(1,10\text{-phen})]$	Green	215	33.85	6.79 (6.37)	83	4.45
7	$[\text{Ni}(\text{oleylxant})_2]$	Yellow	73*	31.04	8.15 (7.88)	79	2.89
8	$[\text{Ni}(\text{oleylxant})_2(\text{py})_2]$	Yellow	142	25.36	6.73 (6.50)	75	3.25
9	$[\text{Ni}(\text{oleylxant})_2(\gamma\text{-pico})_2]$	Brown	116	36.27	6.40 (6.30)	81	3.05
10	$[\text{Ni}(\text{oleylxant})_2(3,5\text{-Lut})_2]$	Yellow	136	20.85	6.43 (6.12)	90	3.30
11	$[\text{Ni}(\text{oleylxant})_2(\text{en})]$	green	194	27.53	7.52 (7.29)	67	2.99
12	$[\text{Ni}(\text{oleylxant})_2(1,10\text{-phen})]$	Yellow	128	31.61	6.50(6.34)	72	3.15
13	$[\text{Cu}(\text{oleylxant})_2]$	Brown	123*	16.24	9.29(8.47)	87	2.14
14	$[\text{Cu}(\text{oleylxant})_2(\text{py})_2]$	Green	147	24.20	7.25(7.00)	70	1.89
15	$[\text{Cu}(\text{oleylxant})_2(\gamma\text{-pico})_2]$	Yellow	139	22.80	6.92(6.79)	77	1.78
16	$[\text{Cu}(\text{oleylxant})_2(3,5\text{-Lut})_2]$	Green	128*	31.50	7.21(6.59)	69	1.68
17	$[\text{Cu}(\text{oleylxant})_2(\text{en})]$	Green	143	18.70	8.01(7.84)	73	1.96
18	$[\text{Cu}(\text{oleylxant})_2(1,10\text{-phen})]$	Brown	213	32.47	7.17(6.83)	82	2.26
19	$[\text{Zn}(\text{oleylxant})_2]$	White	>300	24.63	8.96(8.70)	64	Dia
20	$[\text{Zn}(\text{oleylxant})_2(\text{py})_2]$	White	>300	29.35	7.36(7.18)	92	Dia
21	$[\text{Zn}(\text{oleylxant})_2(\gamma\text{-pico})_2]$	White	>300	18.27	7.08(6.97)	76	Dia
22	$[\text{Zn}(\text{oleylxant})_2(3,5\text{-Lut})_2]$	White	>300	17.25	6.90(6.76)	60	Dia
23	$[\text{Zn}(\text{oleylxant})_2(\text{en})]$	White	>300	14.92	8.61(8.06)	88	Dia
24	$[\text{Zn}(\text{oleylxant})_2(1,10\text{-phen})]$	White	>300	16.48	7.35(7.01)	94	Dia

\*decomposition

**Table (2): IR bands ( $\text{cm}^{-1}$ ) and electronic spectral data of ligand and prepared complexes**

No.	Compound	UV bands ( $\text{cm}^{-1}$ )	IR spectra		
			$\nu(\text{C-O})$	$\nu(\text{C-S})$	$\nu(\text{M-S})$
L	$\text{C}_{19}\text{H}_{35}\text{OS}_2\text{K}$	-----	1196	1055	-----
1	$[\text{Co}(\text{oleylxant})_2]$	15527,28712	1235	1020	461
2	$[\text{Co}(\text{oleylxant})_2(\text{py})_2]$	9852, 15535, 20311,28411	1224	1047	414
3	$[\text{Co}(\text{oleylxant})_2(\gamma\text{-pico})_2]$	10244,16393,20393,28472	1227	1049	427
4	$[\text{Co}(\text{oleylxant})_2(3,5\text{-Lut})_2]$	9961, 16180, 21459,28585	1221	1053	430
5	$[\text{Co}(\text{oleylxant})_2(\text{en})]$	10162,16447,21929,28894	1238	1035	423
6	$[\text{Co}(\text{oleylxant})_2(1,10\text{-phen})]$	10288,16351,21532,28347	1232	1038	440
7	$[\text{Ni}(\text{oleylxant})_2]$	9237, 12531, 32258	1261	1026	445
8	$[\text{Ni}(\text{oleylxant})_2(\text{py})_2]$	10851,16235,24038,32029	1220	1032	411
9	$[\text{Ni}(\text{oleylxant})_2(\gamma\text{-pico})_2]$	11252,15290,24352,31527	1234	1048	417
10	$[\text{Ni}(\text{oleylxant})_2(3,5\text{-Lut})_2]$	10904,15527,23696,32033	1237	1036	433
11	$[\text{Ni}(\text{oleylxant})_2(\text{en})]$	10822,16037,22321,32676	1222	1043	439
12	$[\text{Ni}(\text{oleylxant})_2(1,10\text{-phen})]$	11227,15655,24390,33124	1218	1029	431
13	$[\text{Cu}(\text{oleylxant})_2]$	15524, 34674	1267	1043	446

14	[Cu(oleylxant) <sub>2</sub> (py) <sub>2</sub> ]	14147, 35714	1230	1050	415
15	[Cu(oleylxant) <sub>2</sub> (γ-pico) <sub>2</sub> ]	14052, 34671	1238	1047	421
16	[Cu(oleylxant) <sub>2</sub> (3,5-Lut) <sub>2</sub> ]	13895, 33557	1223	1042	433
17	[Cu(oleylxant) <sub>2</sub> (en)]	14071, 36571	1235	1045	419
18	[Cu(oleylxant) <sub>2</sub> (1,10phen)]	14127, 34258	1220	1041	424
19	[Zn(oleylxant) <sub>2</sub> ]	-----	1253	1035	435
20	[Zn(oleylxant) <sub>2</sub> (py) <sub>2</sub> ]	-----	1236	1030	415
21	[Zn(oleylxant) <sub>2</sub> (γ-pico) <sub>2</sub> ]	-----	1225	1046	418
22	[Zn(oleylxant) <sub>2</sub> (3,5-Lut) <sub>2</sub> ]	-----	1228	1050	429
23	[Zn(oleylxant) <sub>2</sub> (en)]	-----	1240	1037	431
24	[Zn(oleylxant) <sub>2</sub> (1,10-phen)]	-----	1238	1039	438

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