

INTRODUCTION

Transition metal complexes in which a 1,1-dithio ligand form a four membered ring with the metal ion have been extensively investigated and thoroughly reviewed (Coucouvani, 1979; Bond and Martin, 1984; Cox, *et al.*, 1997; Therm, 1994). The four membered ring metal complexes expand their coordination number by interaction with a Lewis base. This may take place by adduct formation with other ligands of comparable ligating ability. The resulting complex is significantly different from those of the complex not having the expanded coordination number (Magnus *et al.*, 1994; Coucouvani, 1979).

2-Butoxyethylxanthates, S_2COR , comprise an important class of 1,1-dithiolate ligands with many applications ranging from flotation agent to radical polymerization (Coucouvani, 1970; Coucouvani, 1979; Coote and Radom, 2004; Wan, *et al.*, 2005; Tiekink and Haiduc, 2005).

Thus, we have described the preparation of some Fe(II), Co(II), Ni(II), Cu(II), Zn(II) complexes containing 2-butoxyethylxanthate ligand and their adducts with nitrogen bases. The nitrogen bases stabilize the binary complexes. The isolated products are stable in air but their stability decreased markedly when dissolved in organic solvents.

EXPERIMENTAL

Materials and Methods

All reagents and solvents were of analytical grade and used as supplied from Fluka or BDH chemical companies. Infrared spectra were recorded on a Bruker Tensor 27co. FTIR spectrophotometer in the 400-4000 cm^{-1} range using KBr discs. Conductivity measurements were carried out on a 10^{-3} 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} M solution of complexes in DMF as solvent at 25°C using 1cm quartz cells. Metals content was determined using AA670 atomic absorption. Melting points were recorded on an Electrothermal 9300 apparatus and were uncorrected. The magnetic measurement was carried out at 25°C on the solids by Faraday's method using Bruker BM6 instrument.

Synthesis of potassium 2-Butoxyethylxanthate

2-Butoxyethanol (11.80g, 0.10 mol) was added to aqueous solution (5.61g, 0.10mol) of potassium hydroxide with stirring. The mixture was cooled in an ice bath, to this mixture (7.60cm³, 0.10mol) of carbon disulfide was added dropwise with continuous stirring for 30 min. in ice bath, the yellow precipitate formed was filtered off, washed with diethylether and dried under vacuum.

I.A. Synthesis of complexes [M (2-BuoEtxant)₂]

M=Fe(II),Co(II),Ni(II),Cu(II),Zn(II)

An ethanolic solution of FeCl₂.4H₂O (1.98g, 0.01mol) or CoCl₂.6H₂O (2.37g, 0.01mol) or NiCl₂.6H₂O (2.37g, 0.01mol) or CuCl₂.2H₂O (1.70g, 0.01mol) or ZnCl₂ (1.36g, 0.01mol) was added dropwise to an ethanolic solution of potassium 2-butoxyethylxanthate (2.36g, 0.02 mol) with stirring for 30 min until complete precipitation. The precipitate was filtered off, washed with ethanol, then with diethylether and dried under vacuum.

I.B. Synthesis of complexes [M (2-BuoEtxant)₂(L)₂]**L= pyridine, isoquinoline, γ -picoline, 3,5-lutidine**

Prepared similarly as in (I.A.). The precipitate formed was treated with (0.02 mol) of (pyridine, isoquinoline, γ -picoline, 3,5-lutidine) dropwise with continuous stirring for 30 min., the precipitate formed was filtered off and washed with ethanol then dried under vacuum.

I.C. Synthesis of complexes [M (2-BuoEtxant)₂(L)]**L=1,10-phenanthroline, ethylenediamine**

Prepared similarly as in (I.A.) and the precipitate formed was treated with (0.01 mol) of (1,10-phenanthroline, ethylenediamine) dropwise with continuous stirring for 30 min., the precipitate formed was, filtered, washed with ethanol, then dried under vacuum.

RESULTS AND DISCUSSTION

The new ligand was prepared by the reaction of 2-butoxyethanol with potassium hydroxide and carbon disulphide: the complexes were prepared through direct reaction of the metal chlorides, FeCl₂.4H₂O, CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂. 2H₂O or anhydrous ZnCl₂ with the above ligand in (1:2) molar ratio. The values of conductivity measurement in dimethylformamide solution of the complexes are in the range (2.30-38.30) $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, which are typical values for non electrolyte type (Geary, 1971).

Magnetic susceptibility measurements

The magnetic moments of the complexes Table (1) were measured at (25 °C). The magnetic moments for Fe(II), Co(II), Ni(II) and Cu(II) complexes (1, 8, 15 and 22) (2.00-4.98 B.M) suggested a tetrahedral geometry (Nicholls, 1973). The magnetic moments values of the other complexes (2-7, 9-14, 16-21, 23-28) were in the range (1.58-5.36 B.M.) in an octahedral geometry. The high values of magnetic moments of some octahedral Co(II) complexes from the spin only value are due to the orbital contribution. (Nicholls, 1973).

Electronic spectral studies

The UV-Visible spectra of the ligand and its complexes of 10⁻³ M solution in DMF were recorded; the results were listed in Table (2). the UV-Visible spectra of the Fe(II) complex (1) gives absorption band at (9842cm⁻¹), which corresponds to (⁵E → ⁵T₂) transition in a tetrahedral geometry (Nicholls, 1973). Complexes (2-7) show absorption band at the range (10217-11037.cm⁻¹), which were assigned to (⁵T_{2g}→⁵E_g) transition these observations indicating an octahedral geometry around Fe(II) ions (Coucouvani and Fackler, 1967).

The Co(II) complex (8) exhibited an absorption band at (15544cm⁻¹) region, which was assigned to (⁴A₂(F)→⁴T₁(P)) transition (Siddiqi and Nishat, 2000), in a tetrahedral configuration of this complex and the absence of (⁴A₂(F) →⁴T₂(F))and(⁴A₂(F)→⁴T₁(F)), are due to the sensitivity of the instrument used. Complexes (9-14) show three absorption bands at the range (9823-11086cm⁻¹), (14124-16339cm⁻¹) and (20024-21777cm⁻¹), which were assigned to (⁴T_{1g}(F)→⁴T_{2g}(F)), (⁴T_{1g}(F) → ⁴A_{2g}(F)) and (⁴T_{1g}(F)→⁴T_{1g}(P)) transition respectively in an octahedral configuration (Martel, 1971 ; Onwudiwe and Ajibade, 2010).

The Ni(II) complex (15) show two absorption bands at (9433cm⁻¹) and (15290cm⁻¹) which were assigned to (³T₁(F) →³A₂(F)) and (³T₁(F)→³T₁(P)) transitions respectively in a

tetrahedral geometry (Nicholls, 1973), the complexes (16-21) show three absorption bands in the range (9363-10460 cm^{-1}), (15197-16447 cm^{-1}) and (21739-27472 cm^{-1}), which were assigned ($^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$), ($^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$) and ($^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$) respectively, which are characteristic for an octahedral geometry Ni(II) complexes (Singh *et al.*, 1989).

The Cu(II) complex (22) gives an absorption band at (9823 cm^{-1}), corresponds to ($^2T_2 \rightarrow ^2E$) transition in a tetrahedral geometry (Cookson *et al.*, 2010), while the complexes (23-28) show a broad absorption band in the region (13054-13886 cm^{-1}), which was assigned to ($^2E_g \rightarrow ^2T_{2g}$) transition which may be formed from the combination of three transitions ($^2B_{1g} \rightarrow ^2A_{1g}$), ($^2B_{1g} \rightarrow ^2B_{2g}$) and ($^2B_{1g} \rightarrow ^2E_g$) in distorted octahedral Cu(II) complexes. (Lever *et al.*, 1984 ; Sarwar *et al.*, 2007).

For all compounds the other bands are referring to charge transfer and ligand transitions.

Infra-red spectral studies

The important IR bands of the ligand (2-BuoEtXant)K and their complexes are listed in Table (2). The two bonds $\nu(C-O)$ and $\nu(C-S)$ of the ligand were observed at 1028 cm^{-1} and 1099 cm^{-1} , in all complexes these bond shift to appear at the region (1130-1269) cm^{-1} and (1028-1072) cm^{-1} respectively. The presence of only one band in the later region reports the bidentate coordination of the dithio ligand (Serrano, 2003).

IR spectra showed a new band at (415-440) cm^{-1} which may be an is the evidence for the coordination of metal to sulfur $\nu(M-S)$. This behavior may be attributed to the electron-releasing of the alcohol, which forces high electron density towards the sulfur atoms (Rathore *et al.*, 2007).

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

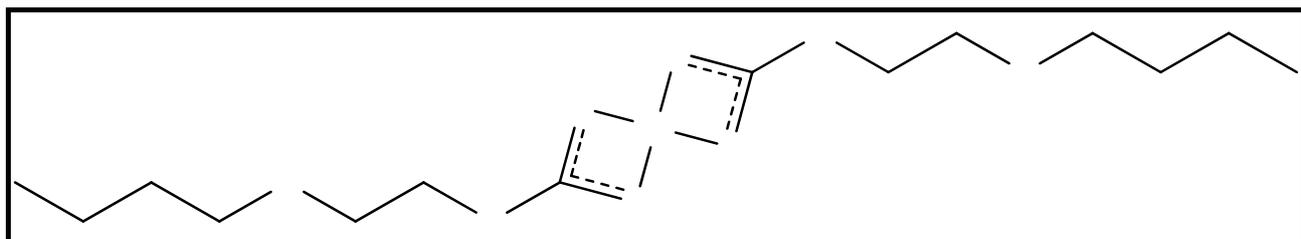
No.	Compound	Color	m.p (°c)	Molar conductivity $\Omega^{-1}.\text{cm}^2.\text{mol}^{-1}$	%M	μ_{eff}	
						% yield	B.M
	(2-BuoEtXant)K	yellow		----	----	----	---
1	[Fe(2-BuoEtXant) ₂]	Orange	240	24.5	12.99 (12.63)	18	4.98
2	[Fe(2-BuoEtXant) ₂ .(py) ₂]	Orange	200	38.3	9.86 (9.31)	56	5.30
3	[Fe(2-BuoEtXant) ₂ .(4-pic) ₂]	Light brown	185	25.3	9.55 (8.89)	70	5.03
4	[Fe(2-BuoEtXant) ₂ .(iso-Q) ₂]	Orange	100*	35.7	8.45 (7.98)	87	5.36
5	[Fe(2-BuoEtXant) ₂ .(3,5-lut) ₂]	Orange	260*	31.3	9.01 (8.51)	57	5.19
6	[Fe(2-BuoEtXant) ₂ .(1,10-phen)]	Brown	180	18.5	9.63 (8.98)	65	4.95
7	[Fe(2-BuoEtXant) ₂ .(en)]	Light purple	160	35.3	11.89 (11.13)	97	4.83
8	[Co(2-BuoEtXant) ₂]	Dark green	270	8.5	11.92 (11.31)	71	3.99
9	[Co(2-BuoEtXant) ₂ .(py) ₂]	Dark brown	240	2.3	9.05 (8.58)	82	4.67
10	[Co(2-BuoEtXant) ₂ .(4-pic) ₂]	Dark brown	190	4.3	8.79 (8.21)	78	4.50

11	[Co(2-BuoEtXant) ₂ . (iso-Q) ₂]	Dark brown	200*	24.6	7.94 (7.43)	76	4.36
12	[Co(2-BuoEtXant) ₂ . (3,5-lut) ₂]	Dark brown	270	8.6	8.56 (7.89)	57	4.73
13	[Co(2-BuoEtXant) ₂ . (1,10-phen)]	Black	280	3.6	8.88 (8.29)	83	4.77
14	[Co(2-BuoEtXant) ₂ . (en)]	Dark brown	220*	6.5	10.67 (10.08)	59	4.15
15	[Ni(2-BuoEtXant) ₂]	Dark green	200*	12.9	13.86 (13.25)	37	3.35
16	[Ni(2-BuoEtXant) ₂ .(py) ₂]	Orange	65*	13.7	10.33 (9.77)	88	2.88
17	[Ni(2-BuoEtXant) ₂ .(4-pic) ₂]	Dark green	140	16.6	10.23 (9.34)	86	3.13
18	[Ni(2-BuoEtXant) ₂ .(iso-Q) ₂]	Dark green	125*	18.6	9.12 (8.38)	77	2.94
19	[Ni(2-BuoEtXant) ₂ .(3,5-lut) ₂]	Dark green	110*	25.6	9.67 (8.94)	90	2.82
20	[Ni(2-BuoEtXant) ₂ .(1,10-phen)]	Light purple	125*	7.1	9.94 (9.43)	46	2.97
21	[Ni(2-BuoEtXant) ₂ .(en)]	Dark green	220	6.3	11.97 (11.67)	69	3.00
22	[Cu(2-BuoEtXant) ₂]	Dark brown	155*	3.3	12.12 (11.86)	81	2.00
23	[Cu(2-BuoEtXant) ₂ .(py) ₂]	Light yellow	140	11.4	9.45 (8.99)	70	1.84
24	[Cu(2-BuoEtXant) ₂ .(4-pic) ₂]	Green yellow	170*	5.4	9.01 (8.63)	37	2.52
25	[Cu(2-BuoEtXant) ₂ .(iso-Q) ₂]	Brown	140*	27.1	8.44 (7.81)	26	1.65
26	[Cu(2-BuoEtXant) ₂ .(3,5-lut) ₂]	Brown	120	31.8	8.74 (8.29)	68	2.10
27	[Cu(2-BuoEtXant) ₂ .(1,10-phen)]	Light brown	172*	7.6	9.61 (8.71)	77	1.58
28	[Cu(2-BuoEtXant) ₂ .(en)]	Yellow	110	12.5	10.89 (10.58)	80	2.22
29	[Zn(2-BuoEtXant) ₂]	White	120**	8.2	13.65 (13.20)	63	Dia
30	[Zn(2-BuoEtXant) ₂ .(py) ₂]	White	300**	34.7	10.49 (9.74)	76	Dia
31	[Zn(2-BuoEtXant) ₂ .(4-pic) ₂]	Light yellow	300**	10.7	9.74 (9.31)	26	Dia
32	[Zn(2-BuoEtXant) ₂ .(iso-Q) ₂]	White	300*	33.7	8.90 (8.35)	86	Dia
33	[Zn(2-BuoEtXant) ₂ .(3,5-lut) ₂]	Light yellow	75*	2.8	9.47 (8.90)	38	Dia
34	[Zn(2-BuoEtXant) ₂ .(1,10-phen)]	Yellow	160*	31.1	9.81 (9.39)	46	Dia
35	[Zn(2-BuoEtXant) ₂ .(en)]	Light yellow	220	29.9	11.97 (11.63)	27	Dia

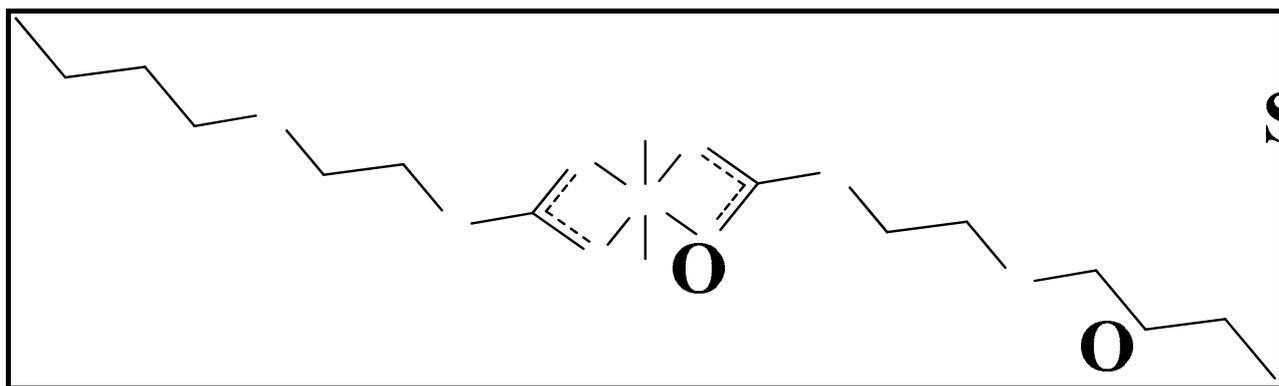
*decomposition

Table 2: IR bands and electronic spectral data of ligand and prepared complexes

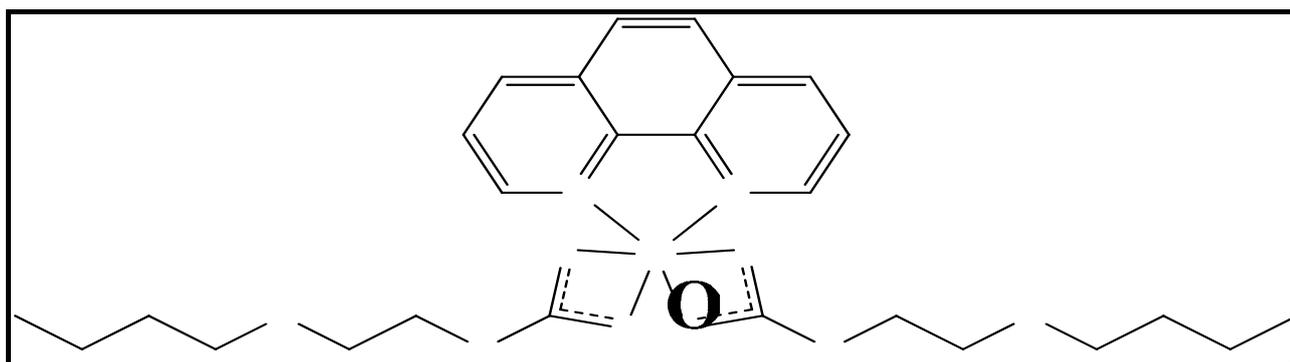
No.	Compound	U-Vis. bands (cm ⁻¹)	IR spectra (cm ⁻¹)		
			$\nu(\text{C}-\text{O})$	$\nu(\text{C}=\text{S})$	$\nu(\text{M}-\text{S})$
	(2-BuoEtXant)K	---	1028	1099	---
1	[Fe(2-BuoEtXant) ₂]	9842, 35714, 38167	1259	1039	437
2	[Fe(2-BuoEtXant) ₂ .(py) ₂]	11037, 34482, 35714	1200	1039	435
3	[Fe(2-BuoEtXant) ₂ .(4-pic) ₂]	11037, 28248, 34965, 37593	1188	1053	430
4	[Fe(2-BuoEtXant) ₂ .(iso-Q) ₂]	10224, 28409, 32051	1182	1059	434
5	[Fe(2-BuoEtXant) ₂ .(3,5-lut) ₂]	11037, 35460, 37313	1244	1070	432
6	[Fe(2-BuoEtXant) ₂ .(1,10-phen)]	10823, 30120, 31645	1188	1065	422
7	[Fe(2-BuoEtXant) ₂ .(en)]	10217, 34482, 35714	1180	1043	434
8	[Co(2-BuoEtXant) ₂]	15544, 32051, 35211	1250	1031	430
9	[Co(2-BuoEtXant) ₂ .(py) ₂]	10183, 15708, 21777, 34722	1221	1057	415
10	[Co(2-BuoEtXant) ₂ .(4-pic) ₂]	11037, 15915, 20455, 31250, 32051	1219	1041	426
11	[Co(2-BuoEtXant) ₂ .(iso-Q) ₂]	11086, 15845, 20595, 31055, 35211	1217	1039	420
12	[Co(2-BuoEtXant) ₂ .(3,5-lut) ₂]	9823, 15708, 21472, 32467, 37593	1219	1057	419
13	[Co(2-BuoEtXant) ₂ .(1,10-phen)]	11061, 16339, 20024, 34722	1159	1057	421
14	[Co(2-BuoEtXant) ₂ .(en)]	10224, 14124, 21624, 30674	1165	1059	420
15	[Ni(2-BuoEtXant) ₂]	9433, 15290, 28571, 30864	1269	1051	440
16	[Ni(2-BuoEtXant) ₂ .(py) ₂]	9363, 15197, 24752, 29761, 32896	1201	1057	438
17	[Ni(2-BuoEtXant) ₂ .(4-pic) ₂]	9398, 15723, 26069, 31847	1194	1061	430
18	[Ni(2-BuoEtXant) ₂ .(iso-Q) ₂]	9433, 15243, 25510, 29940	1186	1061	434
19	[Ni(2-BuoEtXant) ₂ .(3,5-lut) ₂]	9433, 15290, 26041, 29585	1203	1061	426
20	[Ni(2-BuoEtXant) ₂ .(1,10-phen)]	10460, 16447, 27472, 29411	1188	1063	424
21	[Ni(2-BuoEtXant) ₂ .(en)]	9609, 16037, 21739, 30674, 31847	1157	1028	425
22	[Cu(2-BuoEtXant) ₂]	9823, 27777, 34246	1209	1038	432
23	[Cu(2-BuoEtXant) ₂ .(py) ₂]	13157, 29585, 32467	1132	1039	418
24	[Cu(2-BuoEtXant) ₂ .(4-pic) ₂]	13157, 32258, 33112	1130	1038	420
25	[Cu(2-BuoEtXant) ₂ .(iso-Q) ₂]	13054, 25000, 31847	1130	1038	422
26	[Cu(2-BuoEtXant) ₂ .(3,5-lut) ₂]	13477, 29940, 31847	1132	1038	424
27	[Cu(2-BuoEtXant) ₂ .(1,10-phen)]	13886, 25641, 32679	1132	1038	430
28	[Cu(2-BuoEtXant) ₂ .(en)]	13376, 24154, 34965	1188	1050	418
29	[Zn(2-BuoEtXant) ₂]	---	1215	1061	430
30	[Zn(2-BuoEtXant) ₂ .(py) ₂]	---	1201	1068	418
31	[Zn(2-BuoEtXant) ₂ .(4-pic) ₂]	---	1173	1068	419
32	[Zn(2-BuoEtXant) ₂ .(iso-Q) ₂]	---	1201	1059	421
33	[Zn(2-BuoEtXant) ₂ .(3,5-lut) ₂]	---	1173	1068	420
34	[Zn(2-BuoEtXant) ₂ .(1,10-phen)]	---	1144	1070	418
35	[Zn(2-BuoEtXant) ₂ .(en)]	---	1144	1072	422



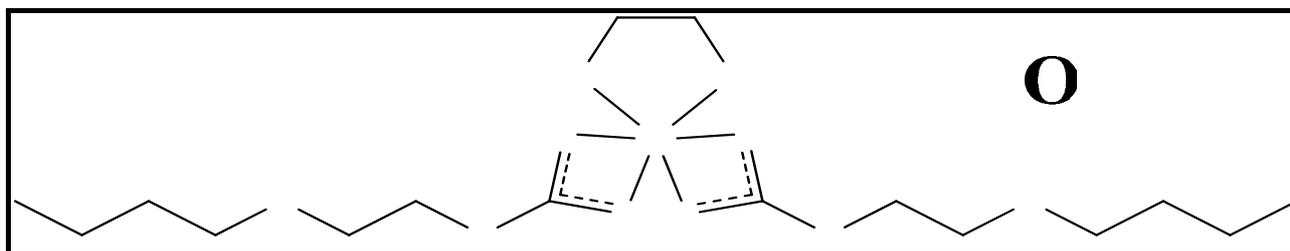
(a)



(b)



(c)



(d)

Fig. 1: Suggest structures (a) complexes [1, 8, 15, 22, 29], (b) complexes [2-5, 9-12, 16-19, 23-26, 30-33], (c) complexes [6, 13, 20, 27, 34] , (d) complexes[7, 14, 21, 28, 35]

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