

Synthesis and Characterization of Iron^{II}, Cobalt^{II}, Nickel^{II}, Copper^{II}, and Zinc^{II} Complexes Using Diphenylmethyl Xanthate Ligand

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Abstract—Potassium diphenylmethyl xanthate and its monomeric complexes were synthesized at room temperature under inert gas and stirring condition. The ligand and its complexes of the general formula [M(L)₂] (where, M = Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II}) were characterized by spectroscopic methods (IR, UV-Vis, ¹H-, ¹³C-, DEPT-, HMQC-, and COSY-NMR), elemental analysis, metal content, magnetic susceptibility measurement, and molar conductance. These studies revealed the formation of four-coordinate complexes.

Index Terms—Four-coordinate complexes, Potassium diphenylmethyl xanthate ligand, Structural study, Xanthate complexes.

I. INTRODUCTION

Xanthates are an important class of organic species that have shown a range of applications have attracted chemists. This based on their industry applications, analytical, and coordination chemistry. They have been used in industry as flotation agents for nonferrous metal sulfide ore (Coucouvani, 1979; Rao, 1971). Further, their role as additives lubricating oils is well documented (Rao, 1971). Based on their coordination behavior, xanthates as reagents have been used in analytical determination and separation of a large numbers of metal ions (Exarchos, et al., 2001; Cox, et al., 1996; and Vastag, et al., 1990). Some of xanthates species and their metal complexes are used as pharmaceuticals for HIV infections. Furthermore, xanthate-based gold^(I) complexes have played a key role in the design and fabrication of electronic and sensor devices. Recently, the preparation of monomeric five-coordinate Cu-xanthates adducts with pyridine derivatives have been

reported (Gurpreet, et al., 2013). The introduction of pyridyl moiety was to overcome the instability of the four-coordinate Cu-xanthates complexes (Kour, et al., 2013). In this paper, we describe the synthesis and physical characterization of potassium diphenylmethyl xanthate ligand and its monomeric metal complexes with some of divalent transition metal ions (Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II}).

II. EXPERIMENTAL

A. Materials

Chemical reagents were commercially available and used without purification (Diphenyl Benzophenone - Sigma-Aldrich 99%, Sodium Borohydrate - Merck 99%, Potassium hydroxide - Sigma-Aldrich 85%, Carbon Disulfide - Aldrich 99%, Metal chloride salt - Fluka 98%, and Methanol - Sigma-Aldrich 99%).

B. Physical measurements

Elemental analyses (C, H, N, and S) were carried out on a Heraeus instrument (vario EL). Melting points were obtained by a Buchi SMP-20 capillary melting point apparatus. IR spectra were recorded as ATR uses a smart diamond ATR attachment on a Thermo-Nicolet Fourier transform-infrared (FTIR) spectrometer (AVATAR 320) in the range of 4000–500/cm, and as CsI discs using a Shimadzu 8300 FTIR spectrophotometer in the range of 600–300/cm. Electronic spectra were measured between 200 and 1000 nm with 10⁻³ M solutions in dimethylsulfoxide (DMSO) spectroscopic grade solvent at 25°C using a Perkin-Elmer spectrophotometer Lambda. NMR spectra (¹H, ¹³C, DEPT, ¹H-¹H COSY, and ¹³C-¹H HMQC NMR) were acquired in DMSO-d₆ solutions using a Jeol Lambda 400 MHz spectrometer with tetramethylsilane for ¹H NMR. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Conductivity measurements were made with DMSO solutions using a Jenway 4071 digital conductivity meter, and room temperature magnetic moments were measured with a magnetic susceptibility balance (Johnson Matthey Catalytic System Division).

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III. SYNTHESIS

A. Preparation of diphenylmethanol (Al-Fahdawi and Al-Salihi, 2015)

The ligand has prepared by dissolving (1 g, 5.51 mmol) of diphenyl benzophenone (1.0417 g, 27.55 mmol) of sodium borohydride with continues stirring in 50 ml of methanol for 1 h and then the mixture was treated with microwave for 3 min. The solvent was removed under reduced pressure and the residue was purified using unplat silica gel chromatography with eluent (9.5:0.5 dichloromethane/methanol) at $R_f=0.8$. Yield: 1.28 g, (98.1%), m.p. 63–64°C. IR (ATR cm^{-1}) characterization was as follows: 3270 $\nu(\text{O-H-O})$, 3084 $\nu_{\text{ar}}(\text{C-H})$, 1493 and 1454 $\nu_{\text{ar}}(\text{C=C})$. NMR data (ppm), δ_{H} (400 MHz, chloroform-D): 7.39–7.25 (m, 10H), 5.83 (s, 1H, OH), 2.35 (s, 1H, C-H); δ_{C} (100.63 MHz, CDCl_3): 76.07, 126.36, 127.47, 128.46, 144.25. X-ray crystallography shows H-atoms were placed in calculated positions [O1-C1=1.4348(16), O1-H1=0.91(2), 1.4348(16), O1B-C1B=1.4352(15), and O1B-H1B=0.923(19)] and were included in the refinement in the riding model approximation. The yield was 1.28 g (98.1%) of m.p. 63–64°C.

B. Preparation of xanthate salt

Xanthate salt was prepared by a conventional method (Seleem, et al., 2011) as in the following: To a suspension of finely powdered (1.1 g, 20 mmol), potassium hydroxide was dissolved in 20 ml of dioxane and a solution (10 mmol) of diphenylmethanol and (1.8 g, 24 mmol) of carbon disulfide in 10 ml of dioxane was add. The mixture was stirred overnight at room temperature, then 7 ml from diethyl ether was added, and the mixture was stirred for an additional 1 h. A pale-yellow solid was collected by filtration, washed with ether, and dried under vacuum. Yield: 1.28 g, (98.1%) of m.p.= 93–94°C, IR (ATR cm^{-1}) characterization was as follows: 3049 $\nu_{\text{ar}}(\text{C-H})$, 1618–1488 $\nu_{\text{ar}}(\text{C=C})$. NMR data (ppm), δ_{H} (400 MHz, Chloroform-Dme): 7.79–7.47 (m, 10H), 1.62 (s, 1H, C-H); δ_{C} (100.63 MHz, CDCl_3): 116.33, 128.29, 129.97, 132.40, 137.65, 196.40.

C. General synthesis of the complexes

A general method was used to obtain the required metallic xanthate complexes as follows:

Metal chloride salt (1 mmole) was dissolved in 10 ml of ethanol and mixed with methanolic solution of the potassium xanthate ligand (2 mmol) in methanol (15 mL). The mixture was allowed to stir overnight at room temperature, then distilled water was added for precipitating the product. The resulted solid was filtered off, washed by methanol, and dried at room temperature to give the required xanthate complex. Elemental analysis data, colors, and yields for the complexes are given in Table I.

IV. RESULTS AND DISCUSSION

Free xanthate ligand was obtained from the reaction of diphenyl methanol with carbon disulfide in alkaline medium (KOH). The general synthetic method involves the reaction

of some transition metals with alkali metal salt of the corresponding thioacid (exothermic behavior) as shown in Fig. 1.

Xanthate ligand complexes with Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , and Cd^{II} ions were obtained in a moderate yields. The compounds were characterized by ^1H - and ^{13}C -NMR, elemental analysis, IR, UV-Vis, magnetic susceptibility, and conductivity measurements. Diphenylmethanol compound was characterized by IR, thin-layer chromatography (TLC), X-RD powder, ^1H - and ^{13}C -NMR spectra, elemental analysis, and X-ray single crystal diffraction analysis (Al-Fahdawi and Al-Salihi, 2015) (see experimental section).

IR (ATR) spectrum of the ligand shows characteristic bands due to the $\nu(\text{O-H})$ and $\nu(\text{C=C})$ at 3270 cm^{-1} and (1493, 1454) cm^{-1} , respectively, as functional groups (Seleem, et al., 2011). ^1H -NMR spectrum for the ligand shows characteristic single peak at $\delta = 5.83$ ppm, which attributed to O-H protons. The spectrum displays single resonances at $\delta = 2.35$ ppm assigned to methanolic group (C-H). These signals in diphenylmethanol compound are appeared at down filed when they are attached withdrawing groups CS_2 to the xanthate salt (Srinivasan, et al., 2012). Whereas IR (ATR) spectrum bands of the xanthate salt ligand show bands at 1618–1488 cm^{-1} due to $\nu(\text{C=C})$ assigned to the aromatic groups, also the spectrum shows band at 1073 cm^{-1} due to $\nu(\text{C=S})$. The disappearance of $\nu(\text{O-H})$ band due to the replacement of the hydrogen atom by CS_2 . The ^1H -NMR spectrum for xanthate salt appears as expected downfield at $\delta = 1.62$ ppm due to (C-H) methanolic group and 7.79–7.49, which assigned to aromatic protons (Al-Fahdawi, et al., 2013). The absence of O-H group signal assigned that the CS_2 is in attach with oxygen atom. ^{13}C -NMR shows important peaks at CS_2 which detected at 196.40 ppm, which is disappeared in DEPT ^{13}C -NMR, because it is quaternary carbon (Al-Fahdawi, et al., 2014; Beer, et al., 2003). That is the metal directed to the desired xanthate complexes. These new complexes were characterized by many techniques such as ATR. The infrared spectra ATR show characteristic bands of ligand and its complexes as shown in Table II.

The important bands of these complexes are ranged about 1230 ± 15 cm^{-1} and 1050 ± 10 cm^{-1} which are due to the $\nu(\text{C-O-C})$ and $\nu(\text{C=S})$ for Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , and Cd^{II} metal ion complexes, respectively (Al-Fahdawi and Al-Salihi, 2015). After complexation, the frequency of $\nu(\text{C-}$

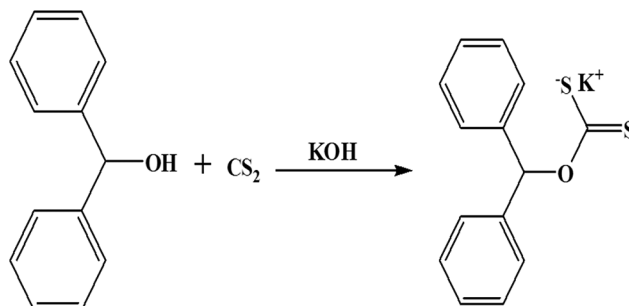


Fig. 1. The synthetic route for ligand and general structure for suggested complexes

TABLE I
COLORS, YIELDS, MELTING POINTS, (M, C, H, S) ANALYSIS, AND MOLAR CONDUCTANCE VALUES COMPLEXES

Molecular formula	M.Wt	Weight of yield g	Yield%	Color	m.pc°	Found (calc%)				$\Sigma M(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$
						M	C	H	S	
$C_{24}H_{22}O_2S_4Fe$	526.37	0.107	54	Red	169–171	10.56 -10.54	63.8 -63.83	4.2 -4.17	24.35 -24.31	11.3
$C_{24}H_{22}O_2S_4Co$	528.99	0,086	43	Dark blue	232–234	11.14 -11.05	63.53 -63.51	4.19 -4.15	24.17 -24.19	18.8
$C_{24}H_{22}O_2S_4Ni$	529.21	0,126	63	Green	160–161	11.17 -11.09	63.52 -63.49	4.17 -4.15	24.21 -24.18	10.9
$C_{24}H_{22}O_2S_4Cu$	533.72	0.114	59	Dark green	135–137	12.38 -12.36	62.99 -62.95	4.13 -4.12	23.95 -23.98	16.2
$C_{24}H_{22}O_2S_4Zn$	535.91	0.083	41	White	151–152	12.27 -12.2	62.65 -62.69	4.16 -4.1	23.91 -23.88	13.5
$C_{24}H_{22}O_2S_4Cd$	582.93	0,114	52	White	193–195	19.25 -19.23	57.68 -57.63	3.8 -3.77	21.99 -21.95	17.8

TABLE II
FTIR BANDS FOR XANTHATE COMPLEXES

Compound	$\nu(X-O-X)$	$\nu(X-O)$	$\nu(X=\Sigma)$	$\nu(M-\Sigma)$
Xanthate	1235	1156	1073	
[Fe-Xanthate]	1223	1192	1032	370
[Co-Xanthate]	1237	1185	1038	360
[Ni-Xanthate]	1220	1191	1050	365
[Cu-Xanthate]	1233	1176	1068	350
[Zn-Xanthate]	1231	1181	1059	355
[Cd-Xanthate]	1240	1201	1061	360

FTIR=Fourier transform-infrared

O-C) and $\nu(C=S)$ bands was shifted to higher and lower frequencies, respectively, for Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , and Cd^{II} metal ion complexes indicating that the complexation was carried out through sulfur, which has been confirmed by the frequency of $\nu(M-S)$ $360 \pm 10 \text{ cm}^{-1}$ (Al-Fahdawi, et al., 2014; Beer, et al., 2003). The analytical data as shown in Table I agree with the suggested formulae $C_{14}H_{11}KOS_2$ (Fig. 1). Molar conductance of the complexes in DMSO solutions is indicative of their nonelectrolytic nature (Yu, et al., 2009). UV-Vis spectra of the Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , and Cd^{II} complexes exhibited different extents of red shift of bands related to the ligand field $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, bands in the range of 321–450 nm are related to the charge transfer transition (C.T) (Griffith, et al., 2011; Ma et al., 2011) (Table III).

Magnetic moment value of the Fe^{II} complex is in accordance of tetrahedral geometry (Aly, et al., 1985). This has been confirmed by its UV-Vis in DMSO, which displays band in the $d-d$ region at 626 nm, due to ${}^5T_2 \rightarrow {}^5E$, indicating a tetrahedral structure (Batten and Robson, 1998). The cocomplex displays additional bands in the $d-d$ region at 474 and 670 nm, related to ${}^4A_2^{(F)} \rightarrow {}^4T_2^{(F)}$ and ${}^4T_1^{(F)} \rightarrow {}^4T_2^{(F)}$, characteristic for tetrahedral geometry around Co^{II} atom (Aly, et al., 1985). Magnetic moment of this complex is typical for tetrahedral structure (Carlucci, et al., 2003). The spectrum of the Ni^{II} complex displays band in the $d-d$ region, which is characteristic of square planar complexes. The magnetic moment value of the Ni^{II} complex, as well as the other analytical data, is in agreement with its square planar

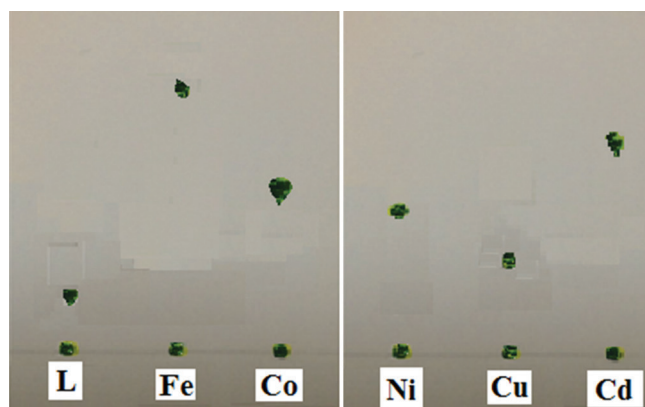


Fig. 2. The thin-layer chromatography measurements for the [L] Ligand and its Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , and Cd^{II} metal ion

structures (Batten, 2001; Zelenak and Gyoryov, 2002). The Cu^{II} complex exhibited electronic spectrum and magnetic moment confirming tetrahedral structure. The electronic spectra of the Zn^{II} and Cd^{II} complexes exhibited bands related to ligand field and ($L \rightarrow M$) charge transfer (Lever, 1984). These complexes are diamagnetic as expected (d^{10} system) and normally prefer tetrahedral coordination. TLC measurement for the derivative ligands [L] and its complexes were performed with Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , and Cd^{II} are showed in Fig. 2.

The appearance of new spots with different R_f of Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , and Cd^{II} indicated the formation of the complexes by comparison with the R_f of the ligand (Table IV).

X-ray powder diffraction (XRD) pattern of Co^{II} complex shows well-defined crystalline peaks indicating that the sample is 20% crystalline in nature (Dokken, et al., 2009), and the XRD powder diffraction pattern of copper complex has been given in Fig. 3.

In Fig. 3, The XRD of Co^{II} metal complex of different scale particles is well coincident with each other, and it means that different forms of complexes have the same structure (Guillemet-Fritsch, et al., 2006). The sample has been dried and then scanned in the 2θ range of 10–80° confirming four coordination around Co ion complex (Kavitha and Lakshmi, 2017; Zheng, et al., 2017).

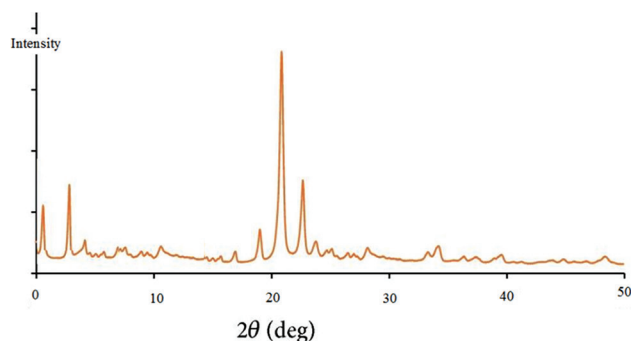
TABLE III
 UV-VIS MEASUREMENTS AND MAGNETIC MOMENT FOR XANTHATE COMPLEXES

Compound	Band	Wave number	ϵ_{\max}	Assignment	Magnetic moment (B.M)
	Position λ_{nm}	(cm^{-1})	($\text{dm}^{-1} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)		
[Xanthate]	261	38314	1680	$\pi \rightarrow \pi^*$	
	365	27395	36		
[Fe-Xanthate]	270	37037	983	Intra ligand	4.5
	315	31746	381	C.T	
	436	22936	283	C.T	
	626	15974	21	$^5T_2 \rightarrow ^5E$	
[Co-Xanthate]	257	38911	1339	$\pi \rightarrow \pi^*$	4.2
	474	21097	57	$^4A_2^{(F)} \rightarrow ^4T_1^{(P)}$	
	670	14925	18	$^4T_1^{(F)} \rightarrow ^4T_2^{(F)}$	
[Ni-Xanthate]	266	37594	880	$\pi \rightarrow \pi^*$	Diemagnetic
	450	22222	165	$^3A_2g \rightarrow ^1T_1g^{(P)}$	
	632	15823	47	$^3A_2g \rightarrow ^3T_1g^{(F)}$	
[Cu-Xanthate]	259	38616	1739	$\pi \rightarrow \pi^*$	1.6
	505	19802	300	$^2T_2 \rightarrow ^2E$	
[Zn-Xanthate]	263	38023	1127	$\pi \rightarrow \pi^*$	Diemagnetic
[Cd-Xanthate]	259	38616	1659	$\pi \rightarrow \pi^*$	Diemagnetic

TABLE IV

 THE TLC MEASUREMENTS FOR THE [L] LIGAND AND ITS Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , AND Cd^{II} COMPLEXES

Compound	Range of Rf (mm)
Xanthate	1.2
[Fe-Xanthate]	4.5
[Co-Xanthate]	3.1
[Ni-Xanthate]	2.4
[Cu-Xanthate]	1.7
[Cd-Xanthate]	4.0

Fig. 3. The X-ray powder diffraction of Co^{II} metal complex

V. CONCLUSION

In recent years, considerable attention has been devoted to the formation of stable four-coordinate xanthate complexes that consist with CS_2 group which have numerous important applications. The reaction of diphenyl methanol with CS_2 in alkaline solution gives the required xanthate ligand. It is observed from research data in this study existence of four-coordinated complexes with Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , and Cd^{II} metal ions.

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