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 $[\text{M}(L)_2]$ (where, $\text{M} = \text{Fe}^{II}$, $\text{Co}^{II}$, $\text{Ni}^{II}$, $\text{Cu}^{II}$, $\text{Zn}^{II}$, and $\text{Cd}^{II}$) were characterized by spectroscopic methods (IR, UV-Vis, $^1$H-, $^{13}$C-, DEPT-, HQMC-, 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 (Coucouvanis, 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$^{(III)}$ 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 ($\text{Fe}^{II}$, $\text{Co}^{II}$, $\text{Ni}^{II}$, $\text{Cu}^{II}$, 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 micro-nano 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 ($^1$H, $^{13}$C, DEPT, $^1$H-$^1$H COSY, and $^{13}$C-$^1$H HMQC NMR) were acquired in DMSO-d6 solutions using a Jeol Lambda 400 MHz spectrometer with tetramethylsilane for $^1$H 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).
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 unplait silica gel chromatography with eluent (9.5:0.5 dichloromethane/methanol) at Rf = 0.8. Yield: 1.28 g, (98.1%), m.p. 63–64°C.

IR (ATR cm⁻¹) characterization was as follows: 3270 ν(O-H-O), 3084 ν(C-H), 1493 and1454 ν(C=C). NMR data (ppm), δH (400 MHz, chloroform-D): 7.39–7.47 (m, 10H), 1.62 (s, 3H, C-H); δC (100.63 MHz, CDCl₃): 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 added. 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 ν(C-H), 1618–1488 ν(C=C). NMR data (ppm), δH (400 MHz, Chloroform-Dme): 7.79–7.47 (m, 10H), 1.62 (s, 1H, C-H); δC (100.63 MHz, CDCl₃): 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.

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 thiocarboxylic acid (exothermic behavior) as shown in Fig. 1.

Xanthate ligand complexes with FeIII, CoII, NiII, CuII, ZnII, and CdII ions were obtained in a moderate yields. The compounds were characterized by ¹H- and ¹³C-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 ¹³C-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 ν(O-H) and ν(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 δ = 5.83 ppm, which attributed to O-H protons. The spectrum displays single resonances at δ = 3.35 ppm assigned to methanolic group (C-H). These signals in diphenylmethanol compound are appeared at down filed when they are attached withdrawing groups CS₂ 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 ν(C=C) assigned to the aromatic groups, also the spectrum shows band at 1073 cm⁻¹ due to ν (C-S). The disappearance of ν(O-H) band due to the replacement of the hydrogen atom by CS₂. The ¹H-NMR spectrum for xanthate salt appears as expected downfield at δ = 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 CS₂ is in attach with oxygen atom. ¹³C-NMR shows important peaks at CS₂, which detected at 196.40 ppm, which is disappeared in DEPT ¹³C-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 u(C-O-C) and u(C=S) for FeIII, CoII, NiII, CuII, ZnII, and CdII metal ion complexes, respectively (Al-Fahdawi and Al-Salihi, 2015). After complexation, the frequency of u(C-
TABLE I
Colors, yields, melting points, (M, C, H, S) analysis, and molar conductance values complexes

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>M.Wt</th>
<th>Weight of yield g</th>
<th>Yield%</th>
<th>Color</th>
<th>m.p°C</th>
<th>Found (calc%)</th>
<th>ηM(Ω ⁻¹ cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{24}H_{52}O_{12}S_{4}Fe</td>
<td>526.37</td>
<td>0.107</td>
<td>54</td>
<td>Red</td>
<td>169–171</td>
<td>10.56</td>
<td>63.8</td>
</tr>
<tr>
<td>C_{24}H_{52}O_{12}S_{4}Co</td>
<td>528.99</td>
<td>0.086</td>
<td>43</td>
<td>Dark blue</td>
<td>232–234</td>
<td>11.14</td>
<td>63.53</td>
</tr>
<tr>
<td>C_{24}H_{52}O_{12}S_{4}Ni</td>
<td>529.21</td>
<td>0.126</td>
<td>63</td>
<td>Green</td>
<td>160–161</td>
<td>11.17</td>
<td>63.52</td>
</tr>
<tr>
<td>C_{24}H_{52}O_{12}S_{4}Cu</td>
<td>533.72</td>
<td>0.114</td>
<td>59</td>
<td>Dark green</td>
<td>135–137</td>
<td>13.28</td>
<td>62.99</td>
</tr>
<tr>
<td>C_{24}H_{52}O_{12}S_{4}Zn</td>
<td>535.91</td>
<td>0.083</td>
<td>41</td>
<td>White</td>
<td>151–152</td>
<td>12.27</td>
<td>62.65</td>
</tr>
<tr>
<td>C_{24}H_{52}O_{12}S_{4}Cd</td>
<td>582.93</td>
<td>0.114</td>
<td>52</td>
<td>White</td>
<td>193–195</td>
<td>19.25</td>
<td>57.68</td>
</tr>
</tbody>
</table>

Fig. 2. The thin-layer chromatography measurements for the [L] Ligand and its Fe, Co, Ni, Cu, and Cd metal ion structures (Batten, 2001; Zelenak and Gyoryov, 2002). The Cu complex exhibited electronic spectrum and magnetic moment confirming tetrahedral structure. The electronic spectra of the Zn and Cd complexes exhibited bands related to ligand field and (L→M) charge transfer (Lever, 1984). These complexes are diamagnetic as expected (d® system) and normally prefer tetrahedral coordination. TLC measurement for the derivative ligands [L] and its complexes were performed with Fe, Co, Ni, Cu, and Cd are showed in Fig. 2.

The appearance of new spots with different R_f of Fe, Co, Ni, Cu, and Cd 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 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 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 20 range of 10–80° confirming four coordination around Co ion complex (Kavitha and Lakshm, 2017; Zheng, et al., 2017).

O=C) and v(C=S) bands were shifted to higher and lower frequencies, respectively, for Fe, Co, Ni, Cu, Zn, and Cd metal ion complexes indicating that the complexation was carried out through sulfur, which has been confirmed by the frequency of v(M=S) 360 ± 10 cm⁻¹ (Al-Fahdawi, et al., 2014; Beer, et al., 2003). The analytical data as shown in Table I agree with the suggested formulae $C_{14}H_{25}KOS_2$(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, Co, Ni, Cu, Zn, and Cd complexes exhibited different extents of red shift of bands related to the ligand field π → π* and n → π* 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 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 $T_1^g → E$ 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 $A_2^g → T_2^g$ and $T_2^g → T_1^g$, characteristic for tetrahedral geometry around Co atom (Aly, et al., 1985). Magnetic moment of this complex is typical for tetrahedral structure (Carlucci, et al., 2003). The spectrum of the Ni complex displays band in the d-d region, which is characteristic of square planar complexes. The magnetic moment value of the Ni complex, as well as the other analytical data, is in agreement with its square planar structures (Batten, 2001; Zelenak and Gyoryov, 2002). The Cu complex exhibited electronic spectrum and magnetic moment confirming tetrahedral structure. The electronic spectra of the Zn and Cd complexes exhibited bands related to ligand field and (L→M) charge transfer (Lever, 1984). These complexes are diamagnetic as expected (d® system) and normally prefer tetrahedral coordination. TLC measurement for the derivative ligands [L] and its complexes were performed with Fe, Co, Ni, Cu, and Cd are showed in Fig. 2.

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TABLE III
UV-Vis measurements and magnetic moment for xanthate complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Band Position $A_{\text{max}}$ (nm)</th>
<th>Wave number $\lambda_{\text{max}}$ (cm$^{-1}$)</th>
<th>$e_{\text{max}}$</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>Assignment</th>
<th>Magnetic moment (B.M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Xanthate]</td>
<td>261</td>
<td>38314</td>
<td>1680</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>Intra ligand</td>
<td>4.5</td>
</tr>
<tr>
<td>[Fe-Xanthate]</td>
<td>270</td>
<td>37037</td>
<td>983</td>
<td>C.T</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>[Co-Xanthate]</td>
<td>315</td>
<td>31746</td>
<td>381</td>
<td>C.T</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>[Ni-Xanthate]</td>
<td>436</td>
<td>22936</td>
<td>283</td>
<td>C.T</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>[Cu-Xanthate]</td>
<td>626</td>
<td>15974</td>
<td>21</td>
<td>$^3T_g \rightarrow E$</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>[Zn-Xanthate]</td>
<td>257</td>
<td>38911</td>
<td>1339</td>
<td>$^1A_g \rightarrow ^1T_g$</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>[Cd-Xanthate]</td>
<td>474</td>
<td>21097</td>
<td>57</td>
<td>$^1A_g \rightarrow ^1T_g$</td>
<td>4.5</td>
<td></td>
</tr>
</tbody>
</table>

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 CS2 group which have numerous important applications. The reaction of diphenyl methanol with CS2 in alkaline solution gives the required xanthate ligand. It is observed from research data in this study existence of four-coordinated complexes with Fe$^{III}$, Co$^{II}$, Ni$^{II}$, Cu$^{II}$, Zn$^{II}$, and Cd$^{II}$ metal ions.

REFERENCES


