



ISSN:1306-3111

e-Journal of New World Sciences Academy
2010, Volume: 5, Number: 2, Article Number: 3A0022

PHYSICAL SCIENCES

Received: December 2009

Accepted: March 2010

Series : 3A

ISSN : 1308-7304

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**THE SYNTHESIS, CHARACTERIZATION OF A NOVEL XANTHATE COMPLEXES OF
COBALT NICKEL AND COPPER**

ABSTRACT

1,3-di(4-methylpiperidino)propan-2-ol (ROH) was synthesized from the reaction of 1,3-dichloropropan-2-ol with 4-methylpiperidine. Potassium 1,3-di(4-methylpiperidino)propan-2-O-xanthate (ROCSSK) was obtained from the reaction of 1,3-di(4-methylpiperidino)propan-2-ol (ROH) with carbon disulfide and metallic potassium. All products were generally obtained in high yields. Xanthate complexes of Co(II), Ni(II) and Cu(I) was synthesized in the medium water as $[CoL_2(H_2O)_2]$, $[NiL_2(H_2O)_2].2H_2O$ and $[CuL].2H_2O$. The novel xanthate ligand and its complexes were defined by FTIR, 1H and ^{13}C NMR spectroscopies, elemental analyses, magnetic susceptibility and TGA techniques.

Keywords: Co(II), Ni(II) and Cu(I) Complexes, Xanthate, NMR, Synthetic Procedures

**YENİ BİR KSANTATIN SENTEZİ VE KOBALT, NİKEL, BAKIR KOMPLEKSLERİNİN
KARAKTERİZASYONU**

ÖZET

1,3-di(4-metilpiperidino) propan-2-ol (ROH) 1,3- dikloropropan-2-ol ile 4-metilpiperidinin reaksiyonundan sentezlendi. Potasyum 1,3-di (4-metilpiperidino) propan-2-O-ksantat (ROCSSK) 1,3-di (4-metilpiperidino) propan-2-ol (ROH) ile karbon disülfür ve metalik potasyumun reaksiyona sokulmasıyla elde edildi. Bütün ürünler genel olarak yüksek verimle elde edildi. Co(II), Ni(II) ve Cu(I) ksantat kompleksleri su ortamında, $[CoL_2(H_2O)_2]$, $[NiL_2(H_2O)_2].2H_2O$ ve $[CuL].2H_2O$ olarak sentezlendi. Yeni ksantat ligandı ve kompleksleri, FT-IR, 1H ve ^{13}C NMR spektroskopisi, elementel analiz, magnetik süsseptibilite ve TGA teknikleri ile yapıları aydınlatıldı.

Anahtar Kelimeler: Co(II), Ni(II) and Cu(I) Kompleksleri, Ksantat, NMR, Sentetik Prosedür

1. INTRODUCTION (GİRİŞ)

Metallic xanthates are important from several viewpoints. They are used as reagents for the removal of the metal ions from solutions such as waste waters, and in the flotation of minerals that have been studied extensively [1, 2, 3, 4, and 5]. There are many publications about the complexes of the xanthates. The xanthate complexes of cobalt [6, 7, 8, 9, and 10], nickel [10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21 and 22], copper [5, 10, 23, and 24], iron [25], platinum, palladium, chromium and cobalt [8], zinc [26], iron, zinc, copper, lead and nickel [3] have been reported. The electrochemical behavior of xanthate complexes was widely investigated [14, 27, 28, and 29].

2. RESEARCH SIGNIFICANCE (ÇALIŞMANIN ÖNEMİ)

Here we report the preparation of the complexes of Co(II), Ni(II) and Cu(I) with 1,3-di(4-methylpiperidino)propan-2-O-xanthate. Their structures were determined by elemental analysis, magnetic susceptibility, thermogravimetric analyses, FT-IR, ¹H and ¹³C NMR spectroscopies.

3. EXPERIMENTAL (DENEYSEL YÖNTEM)

3.1. Materials and Instrumental Techniques

(Materyaller ve Enstrümental Teknikler)

1,3-di(4-methylpiperidino)propan-2-ol (**1**) and potassium 1,3-di(4-methylpiperidino)propan-2-O-xanthate (**LK**) were prepared by a reported procedure [30]. All reagents were purchased from Merck, Acros, and Fluka companies and are chemically pure. Solvents were dried by conventional methods.

Elemental analyses (C, H, N, and S) were determined on a LECO-932 CHNSO auto elemental analysis apparatus. IR spectra were recorded on a Mattson 1000 FT-IR spectrometer as KBr pellets and NaCl window. ¹H and ¹³C NMR spectra were recorded on Bruker DPX-400 High Performance Digital FT-NMR spectrometer operating at 400.13, 100.63 MHz, respectively. Data were recorded for solutions in CDCl₃ for **1**, and in DMSO for **LK**. The ¹H and ¹³C chemical shifts were measured using SiMe₄ as an internal standard. Magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model MK1) at room temperature using Hg[Co(SCN)₄] as calibrant; diamagnetic corrections were calculated from Pascal's constants. Melting points were determined on a Gallenkamp melting point apparatus. The metal contents of the complexes were determined by an Ati Unicam (Model 929) Atomic Absorption Spectrophotometer, which solutions were prepared by decomposing of compounds in concentrated acid mixture [HCl : HNO₃ (3:1)] and diluted with pure water. Thermogravimetric curves were recorded on a Shimadzu TG-50 thermobalance under nitrogen atmosphere.

3.2. Synthetic Procedures (Sentetik Prosedür)

1,3-di(4-methylpiperidino)propan-2-ol, 1,3-di(4-methylpiperidino)propan-2-O-xanthate and their transition metal complexes were synthesized as follows:

3.3. Synthesis of 1,3-di(4-methylpiperidino)propan-2-ol, (**1**)

(1,3-di(4-metilpiperidino)propan-2-ol'ün Sentezi (**1**))

A solution of 1,3-dichloropropan-2-ol (12.9 g, 100 mmol) in toluene (10 mL) was added to a solution of 4-methylpiperidine (19,84 g, 200 mmol) and triethylamine (20.24 g, 200 mmol) in toluene (100 mL). The mixture was stirred and refluxed for 24 h. After completing the reaction, the mixture was left overnight. Triethylamine salt was separated by filtration and toluene was removed under vacuum. The

product was distilled under vacuum (158°C at 2 mm Hg) as colorless liquid (**1**). Yield: 15 g, 59%.

3.4. Synthesis of 1,3-di(4-methylpiperidino)propan-2-O-Xanthate, (LK) (1,3-di(4-metilpiperidino)propan-2-O-ksantatın Sentezi (LK))

Metallic potassium (0.782 g, 20 mmol) was added to a solution of 1,3-di(4-methylpiperidino)propan-2-ol (5.09 g, 20 mmol) in THF (150 mL) at 50-60°C. It was continued until metallic potassium was reacted completely. Then the solution was cooled to -20°C and the solution of CS₂ (1.52 g, 20 mmol) in THF (10 mL) was added dropwise to the mixture. It was reacted for 2 h. The reaction was carried out at argon atmosphere. Potassium xanthate (**LK**) was filtered off, washed with THF, diethyl ether, and petroleum ether to obtain as white crystals. Compound (**LK**) was dried under vacuum over P₂O₅. Yield 5.73 g, (78 %). Decompose 216 °C.

3.5. Synthesis of Transition Metal Complexes (Geçiş Metal Komplekslerinin Sentezi)

A solution of xanthate (**LK**) (0.200 g, 0.542 mmol) in water (100 mL) was added to a solution of metal salts (0.271 mmol) of [CoCl₂.6H₂O (0.0645 g), NiCl₂.6H₂O (0.0642 g), CuCl₂.2H₂O (0.0462 g)] in water (10 mL) by stirring at ambient temperature for 15 min. The precipitated complexes were filtered off by sintered funnel, washed with water diethyl ether and petroleum ether several times and dried under vacuum over P₂O₅. They are soluble in ethanol, methanol, acetone, DMSO, DMF and chloroform, and insoluble in water, diethyl ether, petroleum ether and hexane. [CoL₂(H₂O)₂] (green): Yield: 0,163 g (80%). Decompose 257 °C. [NiL₂(H₂O)₂].2H₂O (green): Yield: 0,165 g (77%). Decompose 204°C. CuL.2H₂O (brown): Yield: 0,080 g (69%). Decompose 262°C.

4. RESULTS AND DISCUSSION (BULGULAR VE TARTIŞMA)

After deprotonation of 1,3-di(4-methylpiperidino)propan-2-ol with metallic potassium, the addition of carbon disulfide readily affords the dithiocarboxylated potassium salt of 1,3-di(4-methylpiperidino)propan-2-O-xanthate (**LK**) in good yield (78%). The data of **LK** and of the complexes are given in Table 1, 2, and 3. The structure of compounds **1**, **LK** and complexes of Co(II), Ni(II) and Cu(I) are shown in Figure 1. Carbon and hydrogen atoms were numbered for ¹H and ¹³C NMR.

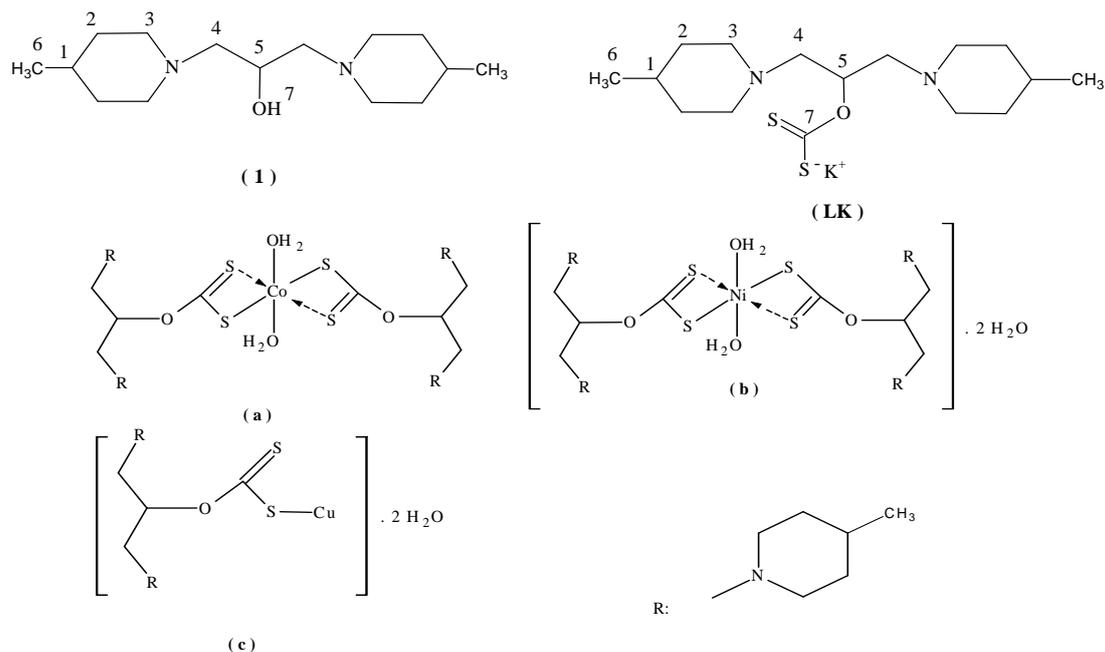


Figure 1. Structure of the compounds
(Şekil 1. Bileşiklerin yapıları)

The characteristic stretching peaks in the IR spectra of the compounds (**1**, **LK** and complexes) have been assigned as in Table 2. The IR spectrum of **1** showed four different strong and sharp peaks at 3204 cm^{-1} for OH, 2951-2794 cm^{-1} for aliphatic C-H, 1475-1425 cm^{-1} for C-N and 1073 cm^{-1} for C-O stretching vibrations. The C-N stretching bands for **LK** are wider than compound **1** because of new additional C-N bindings. The xanthates and complexes exhibit bands in the 1280-996 cm^{-1} region which are related to the vibrations of S_2COR group [20 and 27]. Those at approximately 1149-1088 cm^{-1} are attributable to the asymmetric stretching vibrations of the C-O-C and C=S groups, while the bands around 1019-1042 cm^{-1} belong to the $\nu(\text{C-S})$ vibration. The C-O-C symmetric vibrations are observed around 1065-1087 cm^{-1} .

The band observed at 1019 cm^{-1} for **LK** is characteristic for the C-S bonds of the xanthates [28 and 29], which is shifted to higher frequencies, indicating that the (C=S) groups take part in complexation in the complexes [30]. IR absorption of aliphatic C-H for **LK** and its metal complexes appear at 2951-2794 cm^{-1} . The presence of water molecule in the complexes of Co(II), Ni(II) and Cu(I) is supported by the existence of bending vibrations at 1651, 1602 and 1652 cm^{-1} and stretching vibrations in the 3447, 3428 and 3445 cm^{-1} , respectively [12].

Table 1. Analytical and physical data of the compounds
(Tablo 1. Bileşiklerin fiziksel ve analitik verileri)

	Formula	Color	Yield	(Decom.)	μ_{eff}	Calc. (Found) (%)			
	Weight		(%)	($^{\circ}\text{C}$)		(BM)	C	H	N
LK	368.64	White	78	216	-	51.83 (51.46)	8.45 (8.20)	7.55 (7.38)	17.30 (17.10)
$[\text{CoL}_2(\text{H}_2\text{O})_2]$	754.19	Green	80	257	3.87	50.96 (50.47)	8.30 (8.68)	7.43 (7.15)	17.01 (16.87)
$[\text{NiL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$	789.99	Green	77	204	2.77	48.65 (47.05)	8.44 (7.66)	7.09 (7.19)	16.24 (15.91)
$\text{CuL} \cdot 2\text{H}_2\text{O}$	429.19	Brown	69	262	Dia.	44.77 (43.76)	7.76 (6.86)	6.53 (6.26)	14.94 (14.30)

Table 2. Characteristic IR vibrations of the ligand and complexes
(Tablo 2. Ligand ve komplekslerin karakteristik IR titreşimleri)

	ν(H ₂ O)	ν(OH)	ν(C-H)	ν(C-N)	ν(C=S) and ν(C-O) _{asym}	ν(CO) _{sy} m	ν(C-S)
1	-	3204	2951- 2794	1475- 1425	1157- 1126	1073	-
LK	-	-	2928- 2794	1452- 1391	1153- 1088	1065	1019
[CoL ₂ (H ₂ O) ₂]	3447	-	2951- 2806	1456- 1375	1153- 1119	1080	1023
[NiL ₂ (H ₂ O) ₂].2H ₂ O	3428	-	2951- 2805	1456- 1375	1150- 1119	1087	1023
CuL.2H ₂ O	3445	-	2947- 2797	1456- 1376	1149- 1134	1084	1042

The NMR data of **1** and **LK** are presented in Table 3. Although Cu(I) complex is diamagnetic, its ¹H and ¹³C NMR spectra couldn't be taken since the complex is insoluble in common solvents. The methyne proton next to the oxygen atom is very well characterized by the ¹H NMR spectra that show peaks at the lowest down field as multiple peak at 3.93 ppm for **1**. The OH proton peak is not observed because of hydrogen binding and solvent effect for the same compounds.

In order to identify structures of the xanthate ligand, ¹H and ¹³C NMR spectra were recorded in DMSO-d₆. When compared to **1**, the methyne protons of **LK** is shifted to the lower down field, the signal of the methyne carbon at **LK** are also shifted to the lower down field (5.77 ppm), and the ¹³C NMR spectra of the xanthate ligand shows an additional peak at 230.09 ppm for **LK**, supporting the authenticity of the potassium salt of the ligand (**LK**) [26]. The Potassium salt of the ligand (**LK**), with Co(II), Ni(II) and Cu(II) salts yielded complexes corresponding to the formula ML₂, Cu(II) is reduced to Cu(I) by xanthate ligand and Cu(I) complex is called cuprous xanthate which has linear structure (Figure 1) [2 and 3].

Table 3. ¹H and ¹³C NMR spectral data of the starting substances 1 and LK

(Tablo 3. 1 ve LK Maddelerinin ¹H and ¹³C NMR Spektral Verileri)

Compounds	¹ H NMR	¹³ C NMR
1	1.25-1.42 (10H, H ¹ and H ²)	30.80 (C ¹)
	2.03 (8H, H ³)	34.64 (C ²)
	2.19 (4H, H ⁴)	53.71 (C ³)
	3.93 (1H, H ⁵)	63.45 (C ⁴)
	0.98 (6H, H ⁶)	64.60 (C ⁵)
		22.12 (C ⁶)
LK	1.31 (2H, H ¹)	31.15 (C ¹)
	2.01 (8H, H ²)	35.07 (C ²)
	2.48 (8H, H ³)	55.11 (C ³)
	1.55 (4H, H ⁴)	30.86 (C ⁴)
	5.75 (1H, H ⁵)	76.66 (C ⁵)
		22.80 (C ⁶)
	0.92 (6H, H ⁶)	230.09 (C ⁷)

For numbering see Figure 1.

Since magnetic susceptibility measurements provide sufficient information to characterize the structure of the complexes; the magnetic moments of the complexes were measured at room temperature.

Co(II) and Ni(II) complexes are paramagnetic and their magnetic susceptibility values are 3.87 BM, 2.77 BM, respectively. These values suggest octahedral geometry for the Co(II) and Ni(II) complexes of **LK**. The TGA curves were recorded in the temperature range 25-900°C under nitrogen atmosphere. The TGA values showed that Ni(II) complex has four mole of H₂O. In TGA curves, two of these were removed from the complex in the range of 120-200°C, which are implied as hydration water. The other two moles of water in the Ni(II) and Co(II) complexes separated from the complexes above 200°C, which implies, in each case, that these take part as coordination water in the Co(II) and Ni(II) complexes. Two moles of water in the Cu(I) complex also removed before 200°C. In all cases the final products are the metal sulfides. These results are in good accordance with the composition of the complexes (Table 1).

5. CONCLUSION AND RECOMMENDATIONS (SONUÇ VE ÖNERİLER)

The complexes of Co(II), Ni(II) and Cu(I) ions with potassium salt of 1,3-di(4-methylpiperidino)propan-2-O-xanthate have been prepared and characterized by FT-IR, ¹H and ¹³C NMR spectroscopies, elemental analyses, magnetic susceptibility and TGA techniques. The structures of the complexes were found as [CoL₂(H₂O)₂], [NiL₂(H₂O)₂].2H₂O and CuL.2H₂O.

ACKNOWLEDGEMENT (TEŞEKKÜR)

We gratefully acknowledge the financial support of Fırat University Research Fund (Project No: FÜNAF-487).

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