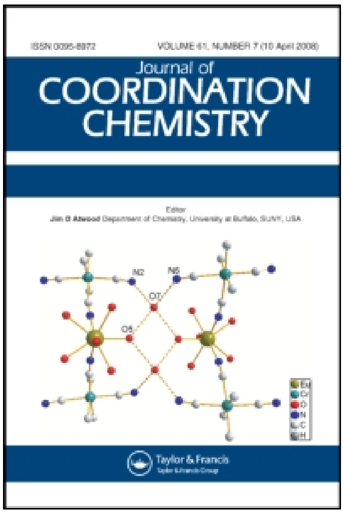

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Görgülü, Orhan A. , Arslan, Mustafa and Çıl, Erol(2006) 'Synthesis and characterization of potassium 1,3-bis(N-methylpiperazino)propan-2-*O*-xanthate and the complexes of Co(II), Ni(II) and Cu(I) ions', Journal of Coordination Chemistry, 59: 6, 637 — 642

To link to this Article: DOI: 10.1080/00958970500393356

URL: http://dx.doi.org/10.1080/00958970500393356

Journal of Coordination Chemistry
Vol. 59, No. 6, 15 April 2006, 637–642

Synthesis and characterization of potassium 1,3-bis(N-methylpiperazino)propan-2-*O*-xanthate and the complexes of Co(II), Ni(II) and Cu(I) ions

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(*Received 9 January 2005; in final form 15 April 2005*)

Potassium 1,3-bis(N-methyl piperazino)propan-2-*O*-xanthate (**LK**), and its complexes with Co(II), Ni(II) and Cu(I) ions have been prepared and characterized as $[CoL_2(H_2O)_2]$, $[NiL_2(H_2O)_2]\cdot 2H_2O$ and $CuL\cdot 2H_2O$ by FT-IR, ^1H and ^{13}C NMR spectroscopies, elemental analyses, magnetic susceptibility and TGA techniques.

Keywords: Co(II); Ni(II) and Cu(I) complexes; Xanthate

1. Introduction

Metal xanthates are extensively used as pharmaceuticals, fungicides, pesticides, rubber accelerators, corrosion inhibitors, agricultural reagents and, quite recently, in therapy for HIV infections [1–3]. These ligands usually form bidentate chelates, or monodentate discrete or network solids, showing a wide range of coordination behavior [4].

Metallic xanthates are well known reagents in the flotation of minerals of transition metals such as copper, zinc, cobalt and nickel, and in the separation and quantitative determination of a large number of cations [2]. Metal-xanthate complexes have low solubility products and high stability constants, and therefore xanthates exhibit high efficacy for removal of metal ions [2, 5]. Potassium 1,3-dipiperidin-1-ylpropan-2-*O*-xanthate and its complexes of Co(II), Ni(II) and Cu(I) are semiconductors [6]. There are many publications about complexes of xanthates; cobalt [7–11], nickel [11, 12–23], copper [5, 11, 24, 25], iron [26], platinum, palladium, chromium and cobalt [9], zinc [27], iron, zinc, copper, lead and nickel [4].

Here we report the preparation of complexes of Co(II), Ni(II) and Cu(I) with potassium 1,3-bis(N-methyl piperazino)propan-2-*O*-xanthate. Structures were determined by elemental analysis, magnetic susceptibility, thermogravimetric analyses, FT-IR, ^1H and ^{13}C NMR spectroscopies.

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500393356

2. Results and discussion

After deprotonation of 1,3-bis(N-methyl piperazino)propan-2-ol with metallic potassium, the addition of carbon disulfide readily affords the dithiocarboxylated potassium salt of 1,3-bis(N-methyl piperazino)propan-2-*O*-xanthate (**LK**) in good yield. Data for **LK** and its complexes are given in tables 1–3. The structures of compounds **1**, **LK** and complexes of Co(II), Ni(II) and Cu(I) are shown in scheme 1. Carbon and hydrogen atoms were numbered for ^{1}H and ^{13}C NMR.

The characteristic stretching peaks in the IR spectra have been assigned as in table 2. The IR spectrum of **1** showed four strong and sharp peaks at 3384 cm^{-1} for OH, 2942–2681 cm^{-1} for aliphatic C–H, 1475–1420 cm^{-1} for C–N, and 1085 cm^{-1} for C–O stretching vibrations. The C–N stretching bands for **LK** are broader than for compound **1** because of additional C–N bindings.

The xanthates and complexes exhibit bands from 1280–996 cm^{-1} that are related to the vibrations of S_2COR [22, 28]. Those at approximately 1170 cm^{-1} are attributable

Table 1. Analytical and physical data of the compounds.

	Formula weight	Color	Yield (%)	(Decom) (°C)	μ_{eff} (BM)	Calcd (Found) (%)			
						C	H	N	S
LK	370.69	Yellowish	88	198	–	45.36	7.36	15.11	17.30
						(45.11)	(7.20)	(15.05)	(16.98)
$[CoL_2(H_2O)_2]$	762.19	Brown	75	269	3.78	44.12	8.22	14.71	16.83
						(44.67)	(7.66)	(14.75)	(16.37)
$[NiL_2(H_2O)_2]\cdot 2H_2O$	797.99	Green	75	276	2.90	42.14	8.35	14.05	16.02
						(41.83)	(7.66)	(13.86)	(15.86)
$CuL\cdot 2H_2O$	431.17	Brown	70	273	Dia.	38.99	7.26	12.99	14.88
						(38.61)	(6.12)	(12.82)	(14.18)

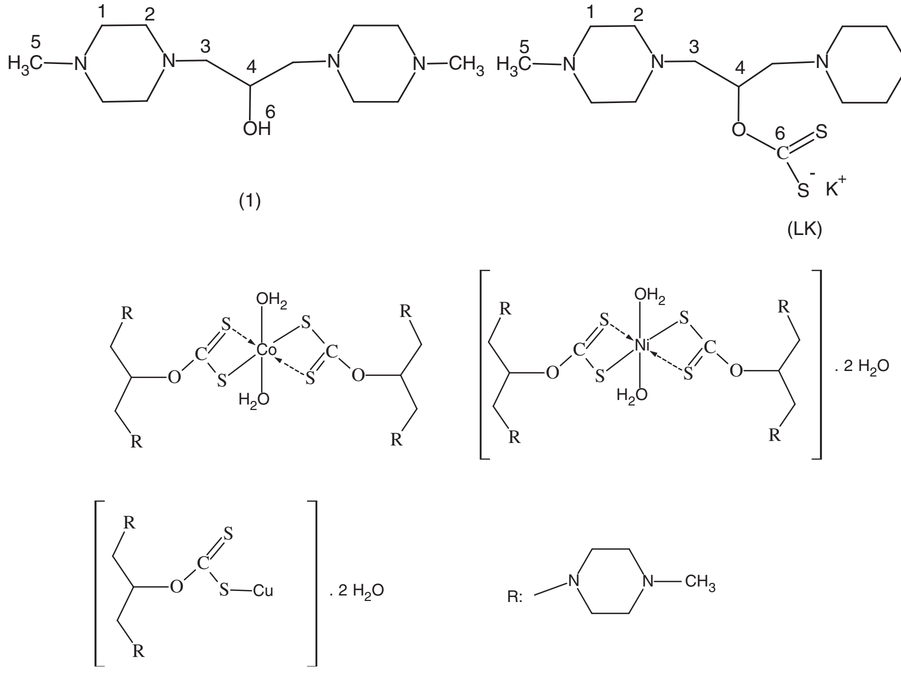
Table 2. Characteristic IR vibrations of the ligand and complexes.

	$\nu(H_2O)$	ν(OH)	ν(C–H)	ν(C–N)	ν(C=S) and $\nu(C\text{–}O)_{asym}$	$\nu(CO)_{sym}$	ν(C–S)
1	–	3384	2942–2681	1475–1420	–	1085	–
LK	–	–	2952–2690	1460–1423	1170–1092	1056	1008
$[CoL_2(H_2O)_2]$	3453	–	2960–2881	1468–1436	1185–1040	1056	1028
$[NiL_2(H_2O)_2]\cdot 2H_2O$	3430	–	2965–2833	1462–1427	1188–1084	1056	1024
$CuL\cdot 2H_2O$		–	2965–2857	1469–1435	1191–1102	1056	1019

Table 3. ^{1}H and ^{13}C NMR spectral data of **1** and **LK**.

Compounds	^{1}H NMR	^{13}C NMR
1	2.51 (8H, H_1); 2.39 (8H, H_2); 2.60 (4H, H_3); 3.93 (1H, H_4); 2.27 (6H, H_5)	54.25 (C_1); 52.50 (C_2); 61.68 (C_3); 63.90 (C_4); 45.50 (C_5)
LK	2.40 (8H, H_1); 2.37 (8H, H_2); 2.52 (4H, H_3); 5.75 (1H, H_4); 2.25 (6H, H_5)	54.73 (C_1), 52.94 (C_2), 59.23 (C_3), 75.56 (C_4), 45.56 (C_5), 230.10 (C_6)

For numbering see scheme 1.



Scheme 1. Structures of the compounds.

to the asymmetric stretching vibrations of the C–O–C and C=S groups, while bands around 1008 cm^{-1} belong to the υ(C–S) vibration. The C–O–C symmetric vibrations are observed around 1056 cm^{-1}.

The band observed at 1008 cm^{-1} for **LK** is characteristic for the C–S bonds of xanthates [29, 30], shifted to higher frequencies indicating that (C$\overset{\cdots}{-}$S) groups take part in complexation in the complexes [31]. IR absorptions of aliphatic C–H for **LK** and its metal complexes appear between 2952 and 2797 cm^{-1}. The presence of water in the complexes is supported by a bending vibration at 1691–1625 cm^{-1} and stretching vibrations in the 3430–3353 cm^{-1} region [12].

The NMR data of **1** and **LK** are presented in table 3. In the ^{1}H NMR of **1**, methyl, methylene (in the piperazine ring), methylene (out of ring) and methyne protons appear at 2.27 (H_5), 2.51 (H_1) and 2.39 (H_2), 2.60 (H_3), 3.93 (H_4), respectively. In the ^{13}C NMR of **1**, CH_3, CH_2 (in the piperazine ring), CH_2 (aliphatic) and CH are observed at 45.50 (C_5), 54.25 (C_1) and 52.50 (C_2), 61.68 (C_3), 63.90 (C_4), respectively. Although the Cu(I) complex is diamagnetic, its ^{1}H and ^{13}C NMR spectra could not be taken since the complex is insoluble in common solvents. The methyne proton next to the oxygen atom is very well characterized by the ^{1}H NMR spectra as a multiplet peak at 3.93 ppm. The OH proton was not observed for **1**. The ^{1}H NMR spectrum of **1** was unchanged in D_2O. The DMSO-d_6 may obscure the proton of OH place under the proton peak of H_2O in DMSO (near 3.53 ppm).

In order to identify the xanthate ligand, ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6. When compared to **1**, all protons especially the methyne protons of **LK** are shifted downfield (at 5.75 ppm); the signals of all carbons in **LK** are also shifted downfield except for C_3, and the ^{13}C NMR spectrum of the xanthate ligand shows an additional peak at 230.10 ppm for **LK**, supporting the authenticity of the potassium salt of the ligand (**LK**) [31]. The potassium salt of the ligand (**LK**), with Co(II), Ni(II) and Cu(II) salts yielded complexes corresponding to the formula ML_2, Cu(II) is reduced to Cu(I) by xanthate ligand and Cu(I) complex, cuprous xanthate, has a linear structure (scheme 1) [1, 2]. The copper salt also behaves as the reducing agent cupric sulfate first reacts with potassium xanthate to give cupric xanthate. Cupric xanthate being unstable, decomposes into cuprous xanthate and dixanthogen [2, 25, 33].

The magnetic moments of the complexes were measured at room temperature to provide further information on the structures. Co(II) and Ni(II) complexes are paramagnetic with magnetic susceptibility values of 3.78 BM and 2.90 BM, respectively, suggesting octahedral geometry for Co(II) and Ni(II) complexes.

TGA curves were recorded in the temperature range 25–900°C under nitrogen. The TGA values showed the Ni(II) complex to have four moles of H_2O. Two were removed from the complex between 120 and 200°C, which implies hydration water. The other two moles of water in the Co(II) and Ni(II) complexes were removed above 200°C, implying that these are coordinated. Two moles of water in the Cu(I) complex are removed before 200°C. In all cases the final products are the metal sulfides. These results are in good accord with the composition of the complexes (table 1).

3. Conclusions

The complexes of Co(II), Ni(II) and Cu(I) with potassium 1,3-bis(N-methyl piperazino)propan-2-*O*-xanthate have been prepared and characterized by FT-IR, ^1H and ^{13}C NMR spectroscopies, elemental analyses, magnetic susceptibility and TGA techniques. The structures of the complexes were found as $[CoL_2(H_2O)_2]$, $[NiL_2(H_2O)_2]\cdot 2H_2O$ and $CuL\cdot 2H_2O$.

4. Experimental

4.1. *General remarks*

1,3-bis(N-methylpiperazino)propan-2-ol (**1**) and potassium 1,3-bis(N-methyl piperazino)propan-2-*O*-xanthate (**LK**) were prepared by a reported procedure [32]. All reagents were purchased from Merck, Acros, and Fluka 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 mulls. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 High Performance Digital FT-NMR spectrometer operating at 400.13, and 100.63 MHz, respectively. Data were recorded in DMSO-d_6 solution for **1** and **LK**. The ^1H and ^{13}C chemical shifts were measured using $SiMe_4$ 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, with solutions prepared by decomposing compounds in concentrated acid mixture [HCl : HNO_3 (3 : 1)] and diluted with pure water. Thermogravimetric curves were recorded on a Shimadzu TG-50 thermobalance under nitrogen atmosphere.

4.2. *Synthetic procedures*

1,3-bis(N-methyl piperazino)propan-2-ol, 1,3-bis(N-methyl piperazino)propan-2-*O*-xanthate and their transition metal complexes were synthesized as follows:

4.2.1. Synthesis of 1,3-bis(N-methyl piperazino)propan-2-ol, 1. A solution of 1,3-dichloropropan-2-ol (12.9 g, 100 mmol) in toluene (10 mL) was added to a solution of piperazine (20.03 g, 200 mmol) and triethylamine (20.24 g, 200 mmol) in toluene (100 mL). The mixture was stirred and refluxed for 16 h. After completing the reaction, the mixture was left overnight. Triethylammonium 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: 16.0 g, 62.40%.

4.2.2. Synthesis of 1,3-bis(N-methyl piperazino)propan-2-*O*-xanthate, LK. Metallic potassium (0.782 g, 20 mmol) was added to a solution of 1,3-bis(N-methyl piperazino) propan-2-ol (5.28 g, 20 mmol) in THF (150 mL) at ambient temperature and reaction continued until metallic potassium was reacted completely. Then the solution was cooled to −20°C and a solution of CS_2 (1.52 g, 20 mmol) in THF (10 mL) was added dropwise to the mixture. Reaction was continued for 4 h under argon. Potassium xanthate (**LK**) was filtered off, washed with THF, diethyl ether, and petroleum ether to give white crystals. Product was crystallized from acetonitrile, and dried under vacuum over P_2O_5. Yield 6.5 g (87.67%). Decomposition, 198°C.

4.2.3. Synthesis of transition metal complexes. A solution of xanthate (**LK**) (0.200 g, 0.540 mmol) in water (50 mL) was added to a solution of $CoCl_2 \cdot 6H_2O$ (0.0761 g, 0.270 mmol) in water (10 mL) by stirring at ambient temperature for 15 min. The precipitated complex was filtered off by sintered funnel, washed with water, diethyl ether and petroleum ether several times and dried under vacuum over P_2O_5. It is soluble in ethanol, methanol, acetone, DMSO, DMF and chloroform and insoluble in water, diethyl ether, petroleum ether and hexane. $[CoL_2(H_2O)_2]$ (green): Yield: 0.154 g (75%). Decomposition 269°C.

The complexes of Ni(II) and Cu(I) were prepared by a different experimental method because they are soluble in water. Xanthate (**LK**) (0.200 g, 0.540 mmol) and metal salts (0.270 mmol) of [$CuCl_2 \cdot 2H_2O$ (0.0460 g), $NiCl_2 \cdot 6H_2O$ (0.0760 g)] were dissolved in a minimum of water. Then the mixture was stirred at ambient temperature for 15 min. Water was removed at 40°C for 48 h. The complexes were washed with petroleum ether and diethyl ether. $[NiL_2(H_2O)_2] \cdot 2H_2O$ (green): Yield: 0.162 g, (75%). Decomposition 276°C. $CuL \cdot 2H_2O$ (brown): Yield: 0.081 g (70%). Decomposition 273°C.

Acknowledgement

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

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