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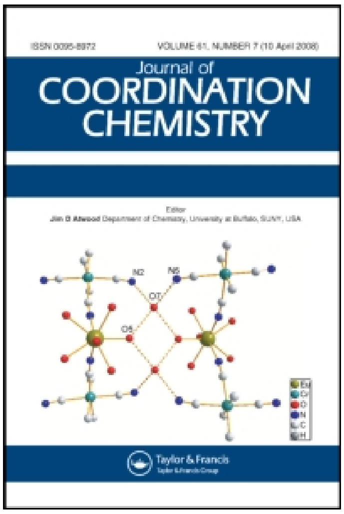

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Synthesis and characterization of a new morpholine-containing sulfur ligand and transition metal complexes of Co(II), Ni(II) and Cu(I)

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Synthesis and characterization of a new morpholine-containing sulfur ligand and transition metal complexes of Co(II), Ni(II) and Cu(I)

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Potassium 1,3-dimorpholinopropan-2-*O*-xanthate (**LK**) and its complexes with Co(II), Ni(II) and Cu(I) ions have been prepared and characterized as $[CoL_2(H_2O)_2]$, $[NiL_2(H_2O)_2]$ 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 of considerable interest as ligands because they can form bidentate chelates and monodentate or network solids, showing a wide range of coordination behavior. The ligands can be varied by modification of the alkyl chain to access a host of electronic and steric environments, as well as inducing changes in solubility and other physical attributes [1]. The chemistry of the xanthates has developed rapidly and many complexes have been prepared and studied during the past several decades [2].

Metal xanthates are well known as 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 [3]. Metal-xanthate complexes have low solubility products and high stability constants, and therefore xanthates exhibit high efficacy for the removal of metal ions [4]. Potassium 1,3-dipiperidin-1-ylpropan-2-*O*-xanthate and its complexes with Co(II), Ni(II) and Cu(I) are semiconductors [5]. Xanthates are also biologically active compounds [3, 6, 7]. Xanthate complexes of cobalt [8–12], nickel [12–24], copper [4, 12, 25, 26], iron [27], platinum, palladium,

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chromium and cobalt [10], zinc [28], iron, zinc, copper, lead and nickel [1] have been reported.

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

2. Experimental

1,3-Dimorpholinopropan-2-ol (**1**) and potassium 1,3-dimorpholinopropan-2-*O*-xanthate (**LK**) were prepared by a reported procedure [29]. All reagents were purchased from Merck, Acros and Fluka and are chemically pure. Solvents were dried by conventional methods.

2.1. *Physical measurements*

Elemental analyses (C, H, N and S) were determined on a LECO-932 CHNSO instrument. IR spectra were recorded on a Mattson 1000 FT-IR spectrometer as KBr pellets and as liquid between NaCl windows. ^{1}H 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 for solutions in $CDCl_3$ for **1**, and in DMSO for **LK**. ^{1}H and ^{13}C chemical shifts were measured using $SiMe_4$ as 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 on an Ati Unicam (Model 929) atomic absorption spectrophotometer; solutions were prepared by dissolving compounds in concentrated acid mixture [$HCl : HNO_3$ (3 : 1)] and diluting with pure water. Thermogravimetric curves were recorded on a Shimadzu TG-50 thermobalance under nitrogen.

2.2. *Synthesis of 1,3-dimorpholinopropan-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 morpholine (17.42 g, 200 mmol) and triethylamine (20.24 g, 200 mmol) in toluene (100 mL). The mixture was stirred and refluxed for 8 h, and then left overnight at room temperature. Triethylamine salt was removed by filtration and toluene was removed under vacuum. The liquid product was distilled at 122°C and 2 mmHg in vacuum. Characteristic IR bands (NaCl cell, cm^{-1}) and ^{1}H NMR bands (DMSO-d_6, δ ppm) are shown in tables 2 and 5. Characteristic ^{13}C NMR bands (DMSO-d_6, δ ppm, 100.63 MHz): 64.23 (C_1), 54.35 (C_2), 63.37 (C_3), 67.27 (C_4).

2.3. *Synthesis of potassium 1,3-dimorpholinopropan-2-O-xanthate (LK)*

Metallic potassium (0.782 g, 20 mmol) was added to a solution of 1,3-dimorpholinopropan-2-ol (4.60 g, 20 mmol) in THF (150 mL) at 50–60°C; reaction was continued until metallic potassium reacted completely. 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. The reaction was carried out for 4 h under argon. Potassium xanthate (**LK**) was filtered off, washed with THF, diethylether and petroleum ether, yielding white crystals. The product was crystallized from acetonitrile. **LK** was dried under vacuum over P_2O_5. Characteristic IR bands (KBr pellets, cm^{-1}) and ^1H NMR bands (DMSO-d_6, δ ppm) are shown in tables 2 and 5. Characteristic ^{13}C NMR bands (DMSO-d_6, δ ppm, 100.63 MHz): 67.15 (C_1), 54.78 (C_2), 60.88 (C_3), 76.00 (C_4), 229.80 (C_5).

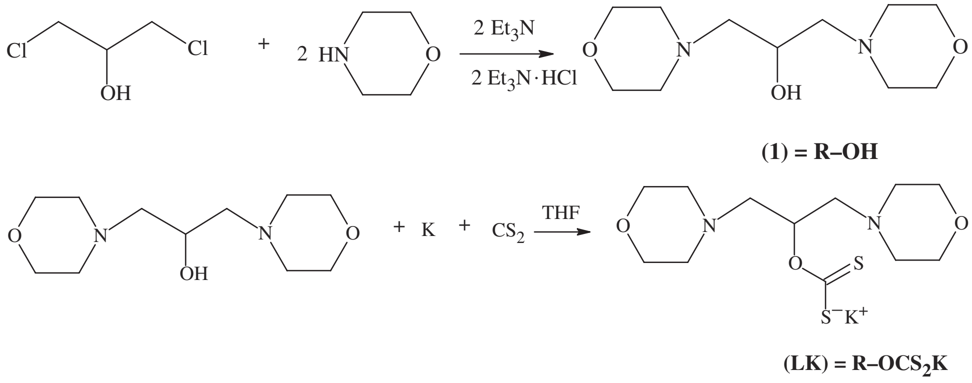
2.4. *Synthesis of the Ni(II), Co(II) and Cu(I) complexes*

A solution of **LK** (0.200 g, 0.580 mmol) in water (50 mL) was added to a solution of a metal salt (0.290 mmol) [$CoCl_2 \cdot 6H_2O$ (0.0690 g), $NiCl_2 \cdot 6H_2O$ (0.0690 g) or $CuSO_4 \cdot 5H_2O$ (0.0462 g)] in water (10 mL) and the mixture stirred at ambient temperature for 15 min. The precipitated complexes were filtered off through a sintered funnel, washed with water, diethylether and petroleum ether several times and dried under vacuum over P_2O_5. The complexes are soluble in ethanol, methanol, acetone, DMSO, DMF and chloroform, and insoluble in water, diethylether, petroleum ether and hexane.

3. Results and discussion

The new ligand, **LK**, was prepared by a two-stage process as shown in scheme 1. Structural characterization data for **1** and **LK** are given in the experimental section and in tables 1–5. Characterization of the ligand **LK** was carried out by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopies and thermogravimetric analysis (TGA).

After deprotonation of 1,3-dimorpholinopropan-2-ol with metallic potassium, the addition of carbon disulfide readily affords the dithiocarboxylated potassium salt of **LK** in good yield. Analytical data for **LK** and the complexes are given in table 4. Structures of **1**, **LK** and complexes of Co(II), Ni(II) and Cu(I) are shown in scheme 2. Carbon and hydrogen atoms were numbered for ^1H and ^{13}C NMR.



Scheme 1. The reaction pathway of xanthate (**LK**).

Table 1. The colors, formulas, formula weights, melting points, magnetic susceptibilities and yields of the ligand and the complexes.

Compound	Formula	FW (g mol^{-1})	Color	m.p. (dec.) (°C)	Yield (%)	μ_{eff} (BM)
R–OH (**1**)	$C_{11}H_{22}N_2O_3$	230.30	Colorless	–	82	–
R–OCS$_2$K (**LK**)	$C_{12}H_{21}KN_2O_3S_2$	344.59	White	236	94	–
[CoL$_2$(H$_2$O)$_2$]	$C_{24}H_{46}O_8S_4N_4Co$	705.95	Green	284	77	3.95
[NiL$_2$(H$_2$O)$_2$]	$C_{24}H_{46}O_8S_4N_4Ni$	705.73	Green	198	71	2.81
CuL · 2H$_2$O	$C_{12}H_{25}O_5S_2N_2Cu$	405.07	Dark red	207	68	diamagnetic

Table 2. Characteristic IR bands (cm^{-1}) of **1**, the ligand (**LK**) and complexes.

Compound	ν(H$_2$O)	ν(OH)	ν(C–H)	ν(C–N)	ν(C=S) and ν(C–O)$_{asym}$	ν(CO)$_{sym}$	ν(C–S)
1	–	3447	2967–2803	1460–1420	1116	1071	–
LK	–	–	2990–2817	1457–1441	1145–1081	1056	1018
[CoL$_2$(H$_2$O)$_2$]	3443	–	2990–2824	1459–1440	1144–1070	1055	1034
[NiL$_2$(H$_2$O)$_2$]	3424	–	2990–2847	1455–1429	1153–1071	1055	1035
CuL · 2H$_2$O	3438	–	2990–2797	1457–1441	1133–1071	1055	1035

Table 3. TGA data for the ligand and the complex.

Compound	Stability (°C)	Weight loss (%)	Residue
LK	20–204	68	K$_2$S
[CoL$_2$(H$_2$O)$_2$]	20–192	87	CoS
[NiL$_2$(H$_2$O)$_2$]	20–191	88	NiS
CuL · 2H$_2$O	20–170	76	CuS

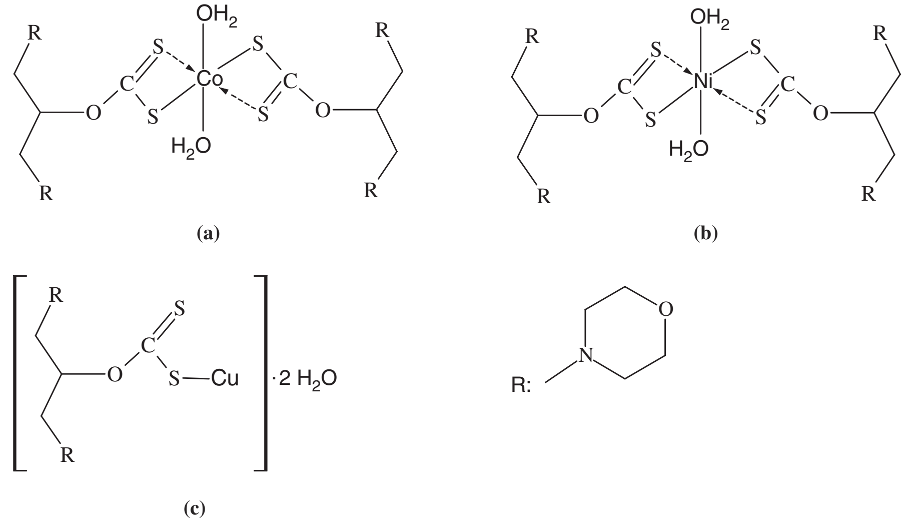
Table 4. Elemental analyses of the ligand and the complexes.

	% Calculated (found)			
Compound	C	H	N	S
LK	41.83 (41.89)	6.55 (5.69)	8.13 (8.01)	18.61 (18.43)
[CoL$_2$(H$_2$O)$_2$]	40.83 (40.76)	6.58 (5.69)	7.93 (8.00)	18.17 (17.45)
[NiL$_2$(H$_2$O)$_2$]	40.84 (40.53)	6.58 (6.35)	7.94 (7.86)	18.77 (17.76)
CuL · 2H$_2$O	35.58 (35.36)	6.23 (5.97)	6.92 (6.75)	15.84 (15.26)

Table 5. ^{1}H NMR spectral data for the starting substances **1** and **LK**.

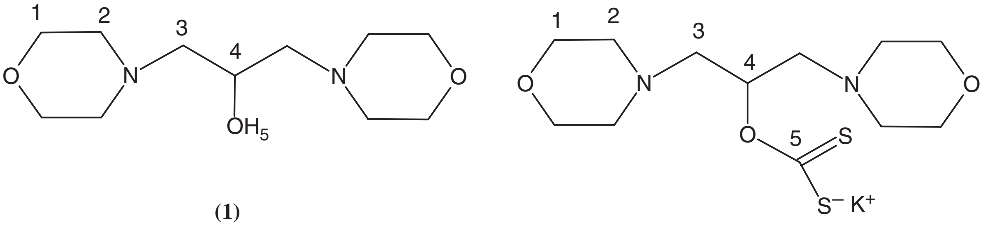
	R–OH (**1**)	R–OCS$_2$K (**LK**)
–OCH$_2$	3.64 (8H, H_1)[t]	3.59 (8H, H_1)[t]
–NCH$_{2\ morph}$	2.50 (8H, H_2)[t]	2.56 (8H, H_2)[t]
–NCH$_{2\ aliphatic}$	2.28 (4H, H_3)[d]	2.52 (4H, H_3)[d]
–CH	3.83 (1H, H_4)[p]	5.83 (1H, H_4)[p]
–OH	3.50 (1H, H_5)[s]	–

[s] singlet; [d] duplet; [t] triplet; [p] pentet.
For numbering see figure 1.



(a) **(b)** **(c)**

Scheme 2. Suggested structures for the complex of the ligand **LK**.



(1) **(LK)**

Figure 1. The structure of **1** and the ligand **LK**.

Characteristic stretching peaks in the IR spectra of the compounds (**1**, **LK** and complexes) were assigned as in table 2. The IR spectrum of **1** showed four different strong and sharp peaks at 3444 cm^{-1} for OH, 2967–2803 cm^{-1} for aliphatic C–H, 1460–1420 cm^{-1} for C–N and 1071 cm^{-1} for C–O stretching vibrations. The C–N stretching bands for **LK** are broader than for **1** because of additional C–N bindings.

The xanthates and complexes exhibit bands in the 1280–996 cm^{-1} region that are related to the vibrations of S_2COR [23, 30]. Those at ca 1144 cm^{-1} are attributable to the asymmetric stretching vibrations of the C–O–C and C=S groups, while the bands at ca 1018 cm^{-1} belong to the ν(C–S) vibration. The C–O–C symmetric vibrations are observed at ca 1055 cm^{-1}.

The band observed at 1018 cm^{-1} for **LK** is characteristic for the C–S bonds of the xanthates [31, 32]; it is shifted to higher frequencies, indicating that the C–S groups take part in complexation in the complexes [33]. IR absorption of aliphatic C–H for **LK** and its metal complexes appears at 2968–2790 cm^{-1}. The presence of water in the complexes of Co(II), Ni(II) and Cu(I) is supported by the existence of bending vibrations at 1647, 1667 and 1656 cm^{-1} and stretching vibrations at 3443, 3424 and 3438 cm^{-1}, respectively [12].

^{1}H NMR data for **1** and **LK** are presented in table 5. The methyne proton next to the oxygen atom is well characterized by the ^{1}H NMR spectra, which show a downfield multiple peak at 3.64 ppm. The OH proton peak is observed at 3.50 ppm (figure 1). Although the Cu(I) complex is diamagnetic, its ^{1}H and ^{13}C NMR spectra could not be measured as the complex is insoluble in common solvents.

To identify the structure of the xanthate ligand, ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d$_6$. Compared to **1**, the methyne proton of **LK** is shifted to lower field, the signal of the methyne carbon for **LK** is also shifted downfield, and the ^{13}C NMR spectrum of the xanthate ligand shows an additional peak at 229.80 ppm for **LK** (figure 1). This supports the authenticity of the potassium salt of the ligand (**LK)** [29]. 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 the xanthate ligand and has a linear structure (scheme 2) [2, 3]. 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 [3, 26].

Magnetic susceptibility measurements provide information to characterize the structure of the complexes, and magnetic moments of the complexes were measured at room temperature. The Co(II) and Ni(II) complexes were paramagnetic and their magnetic susceptibility values are 3.95 and 2.81 BM, respectively. These values suggest octahedral geometry for the Co(II) and Ni(II) complexes of **LK**.

To examine the thermal stability of the ligand and complexes, TGA was carried out at 20–900°C in nitrogen. The TGA values showed that Co(II) and Ni(II) complexes have two moles of H_2O. In the TGA curves, two moles of water in the Co(II) and Ni(II) complexes separated from the complexes above 200°C, which implies, in each case, that these are coordinated water. The loss of water was determined from the TGA curves and then the number of water molecules was calculated [for Co(II) and Ni(II): found 5.00%, 4.98%; calcd 5.10%, 5.10%, respectively]. Two moles of water in the Cu(I) complex were also removed below 200°C (found 8.5%; calcd 8.8%). The complexes lose weight slowly as the temperature increases from 200 to 900°C and the weight loss is, respectively, 87%, 88%, 76% (table 3). In all cases the final products are the metal sulfides. These results are in accord with the composition of the complexes (table 1).

4. Conclusions

Potassium 1,3-dimorpholinopropan-2-*O*-xanthate was synthesized from 1,3-dimorpholinopropan-2-ol, metallic potassium and carbon disulfide. The complexes of Co(II), Ni(II) and Cu(I) ions with potassium 1,3-dimorpholinopropan-2-*O*-xanthate were prepared and characterized by FT-IR, ^{1}H and ^{13}C NMR spectroscopies, elemental analyses, magnetic susceptibility and TGA techniques. Copper(I) xanthate is diamagnetic, whereas the cobalt(II) and nickel(II) complexes are paramagnetic. The cobalt(II) and nickel(II) dithiocarbonate complexes have octahedral geometry, whereas the copper(I) dithiocarbonate complex is linear. The C–S band, which is one of the characteristic IR peaks for xanthates, is shifted to higher frequencies at the IR spectra of the complexes. The stoichiometries of the complexes were $[CoL_2(H_2O)_2]$, $[NiL_2(H_2O)_2]$ and $CuL \cdot 2H_2O$.

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