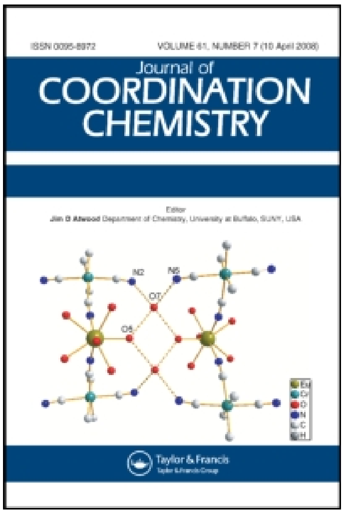

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Synthesis and characterization of a new pyrrolidine containing sulfur ligand and the transition metal complexes of Co(II), Ni(II) and Cu(I)

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

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Potassium 1,3-dipyrrolidinopropan-2-*O*-xanthate (**LK**), and its complexes with Co(II), Ni(II) and Cu(I) have been prepared and characterized as $[CoL_2(H_2O)_2]\cdot 2H_2O$, $[NiL_2(H_2O)_2]$ 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); Cu(I) complexes; Xanthate

1. Introduction

Metal-xanthates can be bidentate chelates or monodentate or network solids, showing a wide range of coordination behavior. The ligands themselves 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]. Many complexes have been prepared and studied during the last several decades [2].

Metal xanthates are most 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 large numbers 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 of Co(II), Ni(II) and Cu(I) are semiconductors [5]. Xanthates also are biologically active [3, 6, 7]. Xanthate complexes of cobalt [8–12], nickel [12, 13–24], copper [4, 12, 25, 26], iron [27], platinum, palladium, 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-dipyrrolidinopropan-2-*O*-xanthate. Their structures were determined by elemental analysis, magnetic susceptibility, thermogravimetric analysis, FT-IR, ^1H and ^{13}C NMR spectroscopies.

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2. Experimental

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

2.1. *Physical measurments*

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 plates. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 High Performance Digital FT-NMR spectrometer operating at 400.13, 100.63 MHz, respectively. Data were recorded for solutions in $CDCl_3$ for **LH**, and in DMSO for **LK**. The ^{1}H 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 content of the complexes was determined on a Ati Unicam (Model 929) Atomic Absorption Spectrophotometer, with solutions prepared by decomposing compounds in concentrated acid [$HCl : HNO_3$ (3 : 1)] and diluted with pure water. Thermogravimetric curves were recorded on a Shimadzu TG-50 thermobalance under nitrogen.

2.2. *Synthesis of 1,3-dipyrrolidinopropan-2-ol (LH)*

A solution of 1,3-dichloropropan-2-ol (12.9 g, 100 mmol) in toluene (10 mL) was added to a solution of pyrrolidine (14.22 g, 200 mmol) and triethylamine (20.24 g, 200 mmol) in toluene (100 mL). The mixture was stirred and refluxed for 6 h. After completing the reaction, the mixture was left overnight. Triethylamine salt was separated by filtration and toluene was removed under vacuum. The liquid product was distilled at 122°C and 2 mm-Hg. Characteristic IR bands (NaCl cell, cm^{-1}) and ^{1}H NMR bands (DMSO-d_6, δ ppm) are listed in tables 2 and 5. Characteristic ^{13}C NMR bands are (DMSO-d_6, δ ppm, 100.63 MHz): 23.73 (C_1), 54.65 (C_2), 61.01 (C_3), 67.58 (C_4).

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

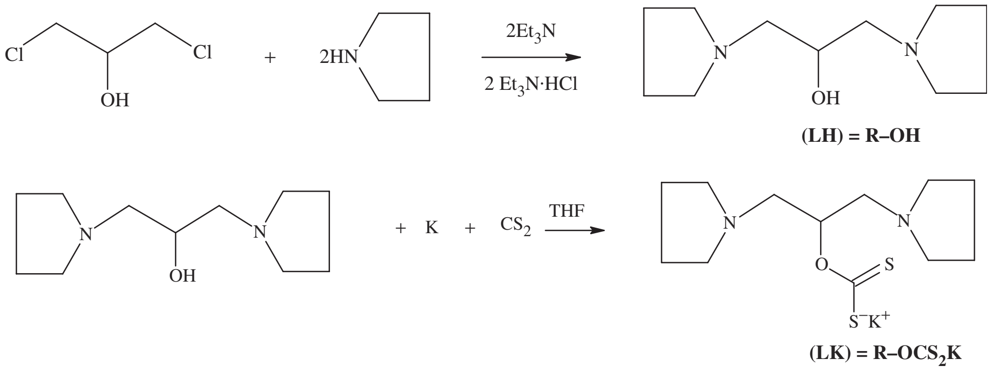
Metallic potassium (0.782 g, 20 mmol) was added to a solution of 1,3-dipyrrolidinopropan-2-ol (3.97 g, 20 mmol) in THF (150 mL) at 50–60°C and the reaction continued until metallic potassium reacted completely. Then the solution was cooled to -20°C and CS_2 (1.52 g, 20 mmol) in THF (10 mL) was added dropwise to the mixture and allowed to react for 4 h under argon. Potassium xanthate (**LK**) was filtered off, washed with THF, diethyl ether, and petroleum ether to obtain white crystals. Product was crystallized from acetonitrile. Compound (**LK**) was dried under vacuum over P_2O_5. Characteristic IR bands (KBr pellets, cm^{-1}) and ^{1}H NMR bands (DMSO-d_6, δ ppm) are in tables 2 and 5. Characteristic ^{13}C NMR bands are (DMSO-d_6, δ ppm, 100.63 MHz): 24.03 (C_1), 55.02 (C_2), 58.25 (C_3), 78.65 (C_4), 230.26 (C_5).

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

A solution of xanthate (**LK**) (0.200 g, 0.587 mmol) in water (30 mL) was added to a solution of metal salt (0.320 mmol) [$CoCl_2 \cdot 6H_2O$ (0.0761 g), $CuSO_4 \cdot 5H_2O$ (0.0798 g), $NiCl_2 \cdot 6H_2O$ (0.0760 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 P_2O_5. They are soluble in ethanol, methanol, acetone, DMSO, DMF and chloroform, and insoluble in water, diethyl ether, petroleum ether and hexane.

3. Results and discussion

The new ligand, potassium 1,3-dipyrrolidinopropan-2-*O*-xanthate **(LK)** was prepared in a two-stage process as shown in scheme 1. The structural characterization data of **LH** and **LK** are given in the experimental section and tables 1–5. The characterization of the



Scheme 1. Preparation of potassium 1,3-dipyrrolidinopropan-2-*O*-xanthate ligand.

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

Compounds	F.W. ($g\,mol^{-1}$)	Color	M.P. (dec) (°C)	Yield (%)	μ_{eff} (B.M.)
R–OH (**LH**) $C_{11}H_{22}N_2O$	198.38	Colorless		82	–
R–OCS_2K (**LK**) $C_{12}H_{21}KN_2OS_2$	312.59	White	209	93	–
$[CoL_2(H_2O)_2] \cdot 2H_2O$ $C_{24}H_{50}O_6S_4N_4Co$	677.99	Green	321	79	3.88
$[NiL_2(H_2O)_2]$ $C_{24}H_{46}O_4S_4N_4Ni$	641.71	Green	331	80	2.81
$CuL \cdot 2H_2O$ $C_{12}H_{25}O_3S_2N_2Cu$	373.07	Dark red	295	69	dia

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

Compounds	$\nu(H_2O)$	$\nu(OH)$	$\nu(C–H)$	$\nu(C–N)$	$\nu(C{=}S)$ and $\nu(C–O)_{asym}$	$\nu(CO)_{sym}$	$\nu(C–S)$
LH	–	3404	2972–2638	1479–1420	1114	1076	–
LK	–	–	2968–2638	1481–1400	1151–1080	1059	1013
$[CoL_2(H_2O)_2]$	3443	–	2968–2638	1483–1395	1167–1111	1059	1022
$[NiL_2(H_2O)_2]$	3424	–	2968–2638	1482–1438	1196–1109	1059	1023
$CuL \cdot 2H_2O$	3438	–	2968–2638	1482–1438	1163–1103	1059	1023

Table 3. TGA data of the ligand and complexes.

Compounds	Stability (°C)	Weight loss (%)	Residue
LK	20–200	65	K_2S
$[CoL_2(H_2O)_2] \cdot 2H_2O$	20–190	87	CoS
$[NiL_2(H_2O)_2]$	20–195	86	NiS
$CuL \cdot 2H_2O$	20–173	74	CuS

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

Compounds	Elemental analyses % calculated (found)			
	C	H	N	S
LK	46.10 (45.75)	6.78 (7.22)	8.96 (8.57)	20.52 (19.85)
$[CoL_2(H_2O)_2] \cdot 2H_2O$	42.51 (41.46)	7.44 (7.26)	8.23 (7.98)	18.92 (18.29)
$[NiL_2(H_2O)_2]$	44.92 (44.45)	7.24 (7.15)	8.73 (8.13)	19.99 (18.66)
$CuL \cdot 2H_2O$	38.63 (39.54)	6.76 (6.64)	7.51 (8.16)	17.19 (16.98)

Table 5. ^1H NMR spectral data **LH** and **LK**.

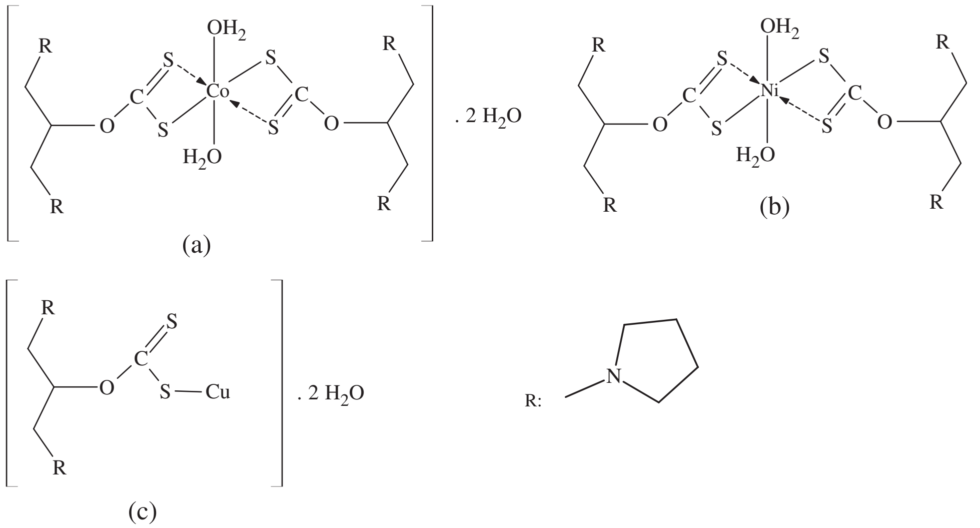
Compounds	R–OH (**LH**)	$R–OCS_2K$ (**LK**)
$–C–CH_2$	1.58 (8H, H_1)^{p}	1,70 (8H, H_1)^{p}
$–NCH_{2\ \mathrm{pyrrolidine}}$	2.20 (8H, H_2)^{t}	2.55 (8H, H_2)^{t}
$–NCH_{2\ \mathrm{aliphatic}}$	2.42 (4H, H_3)^{d}	2.65 (4H, H_3)^{d}
–CH	3.60 (1H, H_4)^{p}	5.75 (1H, H_4)^{p}
–OH	3.76 (1H, H_5)^{s}	–

^{s}singlet; ^{d}doublet; ^{t}triplet; ^{p}pentet, for numbering see figure 1.

ligand **LK** was carried out by elemental analyses, IR, ^1H and ^{13}C NMR, thermogravimetric analyses (TGA).

After deprotonation of 1,3-dipyrrolidinopropan-2-ol with metallic potassium, the addition of carbon disulfide readily affords the dithiocarboxylated potassium salt of 1,3-dipyrrolidinopropan-2-*O*-xanthate (**LK**) in good yield. The analytical data of **LK** and of the complexes are given in table 4. The structure of compounds **LH**, **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.

The characteristic stretching peaks in the IR spectra of the compounds (**LH**, **LK** and complexes) have been assigned in table 2. The IR spectrum of **LH** showed four different strong and sharp peaks at 3404 cm^{-1} for OH, 2972–2638 cm^{-1} for aliphatic C–H,



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

1479–1420 cm^{-1} for C–N and 1076 cm^{-1} for C–O stretching vibrations. The C–N stretching bands for **LK** are wider than compound **LH** because of additional C–N binding.

The xanthates and complexes exhibit bands in the 1280–996 cm^{-1} region, which are related to the vibrations of S_2COR group [23, 30]. Those at approximately 1151 cm^{-1} are attributable to the asymmetric stretching vibrations of the C–O–C and C=S groups, while the bands around 1013 cm^{-1} belong to the ν(C–S) vibration. The C–O–C symmetric vibrations are observed around 1059 cm^{-1}.

The band observed at 1013 cm^{-1} for **LK** is characteristic for the C–S bonds of the xanthates [31, 32], which is shifted to higher frequencies, indicating that the (C$\overset{\cdot\cdot}{-}$S) groups take part in complexation in the complexes [33]. IR absorption of aliphatic C–H for **LK** and its metal complexes appear at 2968–2638 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 1647, 1667 and 1656 cm^{-1} and stretching vibrations in the 3402, 3353 and 3438 cm^{-1}, respectively.

^{1}H NMR data of **LH** and **LK** are presented in table 5. The OH peak is observed at 3.76 ppm for **LH**. The methyne proton next to the oxygen atom is very well characterized by the ^{1}H NMR spectra that show a pentet at 5.75 ppm for **LK**, although it is observed at 3.60 ppm for **LH** (table 5). 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.

In order to identify structures of the xanthate ligand, ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d$_6$. When compared to **LH**, the methyne protons of **LK** are shifted to lower field, the signal of the methyne carbon at **LK** also shifted downfield, and the ^{13}C NMR spectra of the xanthate ligand shows an additional peak at 230.26 ppm for **LK** (figure 1) supporting the authenticity of the potassium salt of the ligand **(LK)** [29]. **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

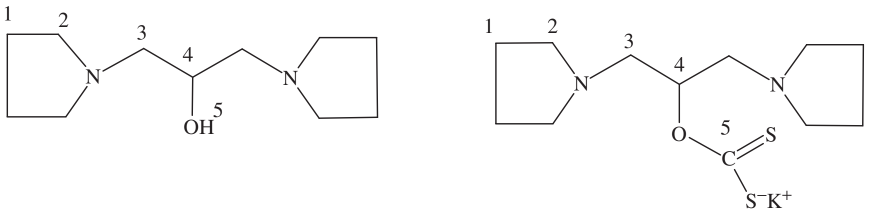


Figure 1. The structure of **LH** and the ligand **LK**.

has a linear structure (scheme 2) [2, 3]. Cupric sulfate reacts with potassium xanthate to give cupric xanthate; but cupric xanthate decomposes into cuprous xanthate and dixanthogen [3, 26, 34, 35].

To further characterize the structure of the complexes the magnetic moments were measured at room temperature. Co(II) and Ni(II) complexes are paramagnetic and their magnetic susceptibility values are 3.88 and 2.81 BM, respectively, suggesting octahedral geometry.

The TGA curves were recorded in the temperature range 25–900°C under nitrogen. The TGA values showed the Co(II) complex has four moles of H_2O. In TGA curves, two of these were separated from the complex in the range of 120–200°C, which are implied as hydration water. The other 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 take part as coordination water. The number of water molecules was calculated from the TGA curves. Found: 10.60 and 5.59%. Calcd: 10.62 and 5.61% respectively. Two moles of water in the Cu(I) complex also removed before 200°C (Found: 9,62%. Calcd: 9.65%). With increasing temperature, complexes lose weight slowly between 200–900°C and the lost weight is respectively 87, 88 and 76% for Co(II), Ni(II) and Cu(I) complexes (table 3). In all cases the final products are metal sulfides. These results are in good accordance with the composition of the complexes (table 1).

4. Conclusions

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

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