

Spectral and Thermal Studies on Some New Anionic Mixed Alkyldithiocarbonato-Oxinate Transition Metal Complexes

Aref A. M. Aly* and Asma I. El-Said

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

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Alkyldithiocarbonates, Transition Metal Complexes

The preparation and characterization of some anionic mixed ligand complexes of Co(II), Ni(II) and Cu(II) containing the two anionic ligands alkyldithiocarbonate and oxinate are reported. The ionic nature of the complexes was inferred from the conductivity data. Alkyldithiocarbonates act in these complexes as bidentate ligands. Based on the spectroscopic and magnetic data the complexes appear to possess pseudo-octahedral metal coordination.

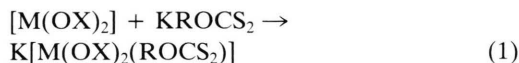
Introduction

In recent years there has been an increasing interest in the chemistry of alkyldithiocarbonates, due mainly to their analytical and industrial applications [1]. Although some simple anionic dithiocarbonato complexes *e.g.* $[M(ROCS_2)_3]^-$ ($M = Fe(II), Ni(II)$ or $Pt(II)$; $R =$ alkyl groups) [2–4] are reported in the literature, to the best of our knowledge no reports are known regarding the preparation of anionic mixed ligand complexes of alkyldithiocarbonates, except for some intermediates, which are formed during some reactions of dithiocarbonato complexes [5]. Therefore, and as an extension of our studies on alkyldithiocarbonates [6–8] we are examining the interaction of Co(II), Ni(II) and Cu(II) oxinates with potassium alkyldithiocarbonates.

Results and Discussion

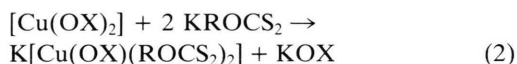
The isolated complexes are listed in Table I together with their analytical data, colour, molar conductance and magnetic moment. The results agree with the formulation of the complexes shown in Table I.

Potassium alkyldithiocarbonates react with Co(II), Ni(II) oxinates according to the following reaction:

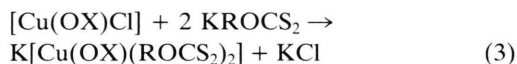


$M = Co(II), Ni(II)$; $OX =$ oxinate; $ROCS_2^- =$ alkyldithiocarbonate, $R = Me-, Et-, Pr-, Bu-,$ or $Chl.$

The reaction with Cu(II) oxinate proceeds, however, in a somewhat different way and obeys the following reaction:



However, another reaction mechanism can be suggested, which may include the initial formation of the complex $[Cu(OX)Cl]$ [9], which in turn interacts with two molecules of potassium alkyldithiocarbonates (eq. (3)), as the reaction of $CuCl_2 \cdot 2H_2O$, oxine and $KROCS_2$ was made *in situ* (see the experimental part).



The complexes in DMF display conductivity values in the range $63-75 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ characteristic of 1:1 electrolytes [10]; an ionic formulation is thus suggested for the complexes. The IR spectra of the complexes are tabulated in Table II.

The dithiocarbonate moiety presents two characteristic bands in the regions $1210-1250$ and $1030-1070 \text{ cm}^{-1}$, which are attributed to $\nu C-O-C$ and $\nu C=S$, respectively [11]. These bands are sensitive to the change in environment and are coupled to a great extent; *e.g.* the band at 1250 cm^{-1} in bis(ethyldithiocarbonato)Ni(II) was found to contain an appreciable contribution from $C-O-R$ stretch and some contribution from $C=S$ stretch, and the band around 1060 cm^{-1} had a major contribution from $C=S$ [12].

The vibrational mode $\nu C=S$ is of particular importance, because it indicates whether the dithiocarbonate behaves in a monodentate or bidentate fashion. In our complexes the presence of only one band in

* Reprint requests to Dr. A. A. M. Aly.

Table I. Analytical results, colour, molar conductance and magnetic moment data of the complexes.

No.	Compound	Colour	C [%] (calcd)	H [%] (calcd)	N [%] (calcd)	S [%] (calcd)	Λ^a [Ohm ⁻¹ cm ² mol ⁻¹]	μ_{eff} [B. M.]
1	K[Co(OX) ₂ (MeOCS ₂)]	yellowish green	(48.67) 49.09	(3.06) 3.15	(5.67) 5.82	(12.99) 12.54	68	4.34
2	K[Co(OX) ₂ (EtOCS ₂)]	green	(49.69) 50.11	(3.37) 3.08	(5.51) 5.57	(12.63) 12.40	65	4.29
3	K[Co(OX) ₂ (PrOCS ₂)]	dark green	(50.66) 51.12	(3.67) 4.06	(5.37) 5.55	(12.29) 12.36	63	4.33
4	K[Co(OX) ₂ (BuOCS ₂)]	dark green	(51.57) 51.18	(3.95) 4.16	(5.23) 5.85	(11.97) 11.28	partially soluble	4.31
5	K[Ni(OX) ₂ (MeOCS ₂)]	light green	(48.69) 48.52	(3.06) 3.67	(5.67) 6.01	(13.00) 12.89	64	3.42
6	K[Ni(OX) ₂ (EtOCS ₂)]	light green	(49.71) 50.22	(3.37) 3.89	(5.52) 5.74	(12.64) 12.17	63	3.44
7	K[Ni(OX) ₂ (PrOCS ₂)]	green	(50.68) 50.28	(3.67) 4.01	(5.37) 5.05	(12.30) 12.82	67	3.39
8	K[Ni(OX) ₂ (BuOCS ₂)]	yellowish green	(51.60) 51.53	(3.95) 4.16	(5.23) 5.48	(11.97) 12.00	partially soluble	3.31
9	K[Ni(OX) ₂ (ChlOCS ₂)]	yellowish green	(53.48) 52.87	(4.12) 4.70	(4.98) 4.72	(11.42) 12.01	65	3.41
10	K[Cu(OX)(MeOCS ₂) ₂]	dark green	(33.85) 32.48	(2.62) 2.30	(3.03) 3.08	(27.81) 26.98	insoluble	1.83
11	K[Cu(OX)(EtOCS ₂) ₂]	green	(36.82) 35.91	(3.29) 3.01	(2.86) 3.06	(26.21) 26.03	70	1.81
12	K[Cu(OX)(PrOCS ₂) ₂]	yellowish green	(39.47) 38.88	(3.89) 3.36	(2.70) 2.54	(24.79) 24.19	partially soluble	1.81
13	K[Cu(OX)(BuOCS ₂) ₂]	light green	(41.84) 41.59	(4.43) 4.59	(2.56) 2.18	(23.51) 22.75	75	1.80
14	K[Cu(OX)(ChlOCS ₂) ₂]	light green	(46.62) 45.94	(4.72) 4.21	(2.34) 2.72	(21.46) 20.96	72	1.83

^a In DMF.

Table II. Important IR bands of the complexes.

Compound	Dithiocarbonate		8-Hydroxyquinoline	
	$\nu\text{C}-\text{O}-\text{C}$	$\nu\text{C}=\text{S}$	$\nu\text{C}-\text{O}$	$\nu\text{C}=\text{N}$
K[Co(OX) ₂ (MeOCS ₂)]	1250	1050	1110	1580
K[Co(OX) ₂ (EtOCS ₂)]	1250	1030	1110	1570
K[Co(OX) ₂ (PrOCS ₂)]	1240	1060	1120	1590
K[Co(OX) ₂ (BuOCS ₂)]	1250	1060	1115	1570
K[Ni(OX) ₂ (MeOCS ₂)]	1220	1060	1110	1590
K[Ni(OX) ₂ (EtOCS ₂)]	1220	1060	1120	1595
K[Ni(OX) ₂ (PrOCS ₂)]	1240	1060	1110	1590
K[Ni(OX) ₂ (BuOCS ₂)]	1220	1070	1120	1590
K[Ni(OX) ₂ (ChlOCS ₂)]	1250	1040	1120	1590
K[Cu(OX)(MeOCS ₂) ₂]	1220	1050	1120	1590
K[Cu(OX)(EtOCS ₂) ₂]	1235	1030	1110	1580
K[Cu(OX)(PrOCS ₂) ₂]	1220	1060	1120	1590
K[Cu(OX)(BuOCS ₂) ₂]	1210	1050	1120	1590
K[Cu(OX)(ChlOCS ₂) ₂]	1210	1040	1110	1580

the region 1030–1070 cm⁻¹ strongly supports the bidentate coordination of the dithiocarbonate moiety [13]. For the oxinate part, $\nu\text{C}-\text{O}$ band is found in the range 1110–1120 cm⁻¹, typical of oxinate com-

plexes of metals [14]; $\nu\text{C}=\text{N}$ occurs in the region 1570–1595 cm⁻¹.

The electronic spectral data of the complexes are recorded in Table III; the spectra of the complexes

Table III. Electronic spectral data of the complexes (cm^{-1}).

Compound	d–d	Charge transfer	Intraligand transitions
K[Co(OX) ₂ (MeOCS ₂)]	16.666	23.315	–
K[Co(OX) ₂ (EtOCS ₂)]	16.129	20.408	28.571 35.714
K[Co(OX) ₂ (PrOCS ₂)]	16.393	23.255	27.777 34.482
K[Co(OX) ₂ (BuOCS ₂)]	16.231	20.833	28.571 32.258 35.714
K[Ni(OX) ₂ (MeOCS ₂)]	16.393	21.739	27.027 31.250
K[Ni(OX) ₂ (EtOCS ₂)]	16.666	21.739	27.027 31.250
K[Ni(OX) ₂ (PrOCS ₂)]	16.666	21.739	27.027 24.390 31.250
K[Ni(OX) ₂ (BuOCS ₂)]	16.666	21.739	27.027 24.390 31.250
K[Ni(OX) ₂ (ChlOCS ₂)]	15.625	21.276	26.315 24.390 31.250
K[Cu(OX)(MeOCS ₂) ₂]	15.151	24.390	29.850 31.440 37.710
K[Cu(OX)(EtOCS ₂) ₂]	15.384	24.691	29.411 31.250 37.735
K[Cu(OX)(PrOCS ₂) ₂]	15.251	24.380	29.850 31.250 37.729
K[Cu(OX)(BuOCS ₂) ₂]	15.625	24.390	29.411 31.250
K[Cu(OX)(ChlOCS ₂) ₂]	15.625	21.276 24.390	26.315 31.250

were measured in chloroform solution. The spectra of the Co(II) complexes display a d–d band in the region 16,126–16,666 cm^{-1} . The appearance of this band ($^4\text{T}_{1g}(\text{P}) \leftarrow ^4\text{T}_{1g}$) is typical of octahedrally coordinated Co(II). For the Ni(II) complexes the band, which appears at 15,625–16,666 cm^{-1} is ascribed to a d–d transition ($^3\text{T}_{1g} \leftarrow ^3\text{A}_{2g}$) characteristic of octahedral Ni(II) complexes. The Cu(II) complexes exhibit the d–d transitions as a broad band at 15,151–15,625 cm^{-1} .

On the basis of their high intensity, bands occurring in the region 20,408–24,390 cm^{-1} for Co(II) and Ni(II) complexes are ascribed to charge transfer transitions (most probably $\text{L} \rightarrow \text{M}$). For the Cu(II) complexes, these bands are shown in the range 21,276–24,691 cm^{-1} .

The absorption bands, which are located in the region 26,315–29,850 cm^{-1} for Co(II), Ni(II) and Cu(II) complexes, are tentatively assigned to the

coordinated oxinate. The replacement of the band at 21,739 cm^{-1} by a band at 26,109 cm^{-1} was reported [15] for the chloroform solution of Ni(II) oxinate to which methanol was added. This behaviour was explained by the transformation of the metal oxinate from the tetrahedral structure into the distorted octahedral structure of the methanolic adduct [15].

Further, the bands appearing at $\sim 31,000$ – $37,000$ cm^{-1} are evidently internal transitions in the dithiocarbonate moiety [16]. The magnetic moments measured at room temperature were found to fall in the ranges 4.31–4.34, 3.31–3.44, 1.80–1.83 B.M. corresponding to Co(II), Ni(II) and Cu(II) complexes, respectively. These ranges are expected for octahedral complexes.

From the consideration of the d values and intensities of the X-ray powder diffraction data of the complexes it could be concluded that they are nearly isostructural.

The thermal decomposition of some compounds was studied in the temperature range 100–400 °C using a thermal balance. These compounds are: K[Co(OX)₂(PrOCS₂)], K[Co(OX)₂(BuOCS₂)], K[Ni(OX)₂(MeOCS₂)], K[Ni(OX)₂(PrOCS₂)], K[Cu(OX)(EtOCS₂)₂] and K[Cu(OX)(ChlOCS₂)₂]. The general feature of the TGA thermograms of the complexes is that three decomposition steps are observed; for the compound K[Cu(OX)(ChlOCS₂)₂], however, only one step was recorded. In Table IV the temperature of each step in the respective thermogram is listed. There are, however, no obvious trends in the temperatures of these decomposition steps, but two facts are apparent. First, the first decomposition steps in the compounds K[Co(OX)₂(BuOCS₂)] (225 °C), K[Ni(OX)₂(MeOCS₂)] (220 °C) and K[Cu(OX)(EtOCS₂)₂] (230 °C) correspond to the decomposition of the oxinate moiety. Second, the first steps in the TGA curves of K[Co(OX)₂(PrOCS₂)] (180 °C) and K[Ni(OX)₂(PrOCS₂)] (170 °C) are

Table IV. Thermal data of some of the complexes.

Complex	Decomposition steps (°C)
K[Co(OX) ₂ (PrOCS ₂)]	180, 270, 420
K[Co(OX) ₂ (BuOCS ₂)]	225, 290, 405
K[Ni(OX) ₂ (MeOCS ₂)]	220, 385, 435
K[Ni(OX) ₂ (PrOCS ₂)]	170, 292, 390
K[Cu(OX)(EtOCS ₂) ₂]	230, 270, 340
K[Cu(OX)(ChlOCS ₂) ₂]	270

consistent with the loss of one propylene molecule, a behaviour which is similar to the mass spectral fragmentation patterns of some isopropylthiocarbonato complexes [17], where a sequential loss of the alkene from the dithiocarbonato group was noticed.

Experimental

The chemicals in this research were of analytical grade. Potassium alkyldithiocarbonates were prepared according to previously published methods [18].

In general, the complexes were prepared by adding an ethanolic solution of oxine (4.2 mmol) to a stirred ethanolic solution of the metal chlorides (2.1 mmol). After 15 min an aqueous ethanolic solution of alkyldithiocarbonates (4.2 mmol) was added dropwise whereupon the products of the metal complexes separated, which were filtered off, washed with alcohol and dried over P_4O_{10} .

Physical measurements

IR spectra of the complexes were recorded on a Perkin-Elmer 599B spectrophotometer as KBr discs. Electronic spectra were scanned on a Shimadzu 200S spectrophotometer. Conductivity measurements were obtained using a LF Digi 550 conductance bridge in DMF solutions at 10^{-4} M concentration. Magnetic measurements were carried out with the Gouy balance using $Hg[Co(NCS)_4]$ as calibrant. Diamagnetic corrections were made using Pascal's constants. X-ray powder diffraction patterns were recorded on a Philips (powder diffraction) 1710 diffractometer. Thermogravimetric analyses were determined on a thermobalance of the type Sartorius 2003 MP. The temperature was measured using a Chromal-Alumal thermocouple attached to a digital multimeter type Weston model 6100, the heating rate was adjusted to be $7^\circ C/min$.

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