

Mixed Dithizonato-Alkylxanthato Complexes of Ni(II): Spectral, Magnetic, and Thermogravimetric Studies

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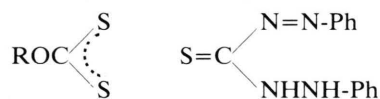
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Mixed Ligand Complexes, Dithizone, Thermogravimetric Studies

Mixed ligand complexes of the type $\text{Ni}(\text{ROCS}_2)_2(\text{HDz})$ have been prepared, where R = methyl, ethyl, propyl, butyl and cyclohexyl, and HDz = dithizonate anion. These complexes were identified on the basis of spectroscopic measurements (IR, UV-VIS and NMR), magnetic moment values, thermogravimetric analysis, and analytical data. The results permit assignment of a tetrahedral structure for these complexes.

Introduction

Dithizone is widely used in analytical chemistry for selective spectrophotometric determinations of various metals [1, 2]. Further, dithizone has excellent properties as a chelating agent [1], binding in its coordination with transition metal ions almost exclusively through the soft sulphur and the hard nitrogen atoms [3, 4]. Some mixed ligand complexes of transition metals including the dithizonate anion are reported in the literature [5, 6, 7]. In view of the current interest in dithiolato mixed ligand complexes [8–15] and in view of the importance of metal xanthates in many analytical and industrial applications [16] we have embarked on the study of a number of mixed dithizonato-alkylxanthato complexes of Ni(II).



Xanthate anion, xan Dithizone, H_2Dz

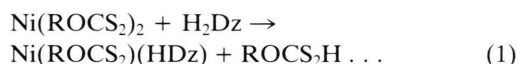
R = Methyl, Mexan; R = Ethyl, Etzan;

R = Propyl, Przan; R = Butyl, Buzan;

R = Cyclohexyl, Cyzan.

Results and Discussion

The complexes are obtained from the reaction between bis(alkylxanthato)nickel(II) and dithizone in the molar ratio 1:1. The reaction proceeds according to the following equation:



The complexes are soluble in chloroform and acetone, partially soluble in alcohol; the compounds are green or brown in colour. Analytical data, magnetic moments and colours of the complexes are listed in Table I.

The infrared spectra of the complexes present the characteristics of both the dithizonato and the xanthato ligands. Relevant vibrational frequencies of the complexes are reported in Table II. Dithizone acts towards metal ions as a monobasic or dibasic acid [4, 17], forming primary or secondary dithizonates [18]. The IR spectra of several primary and secondary dithizonates have been recorded in the literature [19].

The present complexes show $\nu(\text{NH})$ bands in the range $3240\text{--}3260\text{ cm}^{-1}$, in the same range expected for primary dithizonates [4]; δNH , however, appears in the range $1520\text{--}1530\text{ cm}^{-1}$ [20]. The strong band located at 1320 cm^{-1} is correlated with the $\nu(\text{N}\text{--}\text{C})$ mode of the $\text{N}\text{--}\text{C}_6\text{H}_5$ bond. Furthermore, the $\nu(\text{CS})$ frequency may be assigned to the band at 875 cm^{-1} . This band is shifted to a lower frequency, which is typical of sulphur coordination of a thioamide ligand [4].

The xanthate moiety shows $\nu(\text{CO})$ stretching vibrations in the range $1120\text{--}1150\text{ cm}^{-1}$, *i.e.* in the range expected for mixed ligand complexes of xanthato metal complexes [21, 22]. The stretching vibration of $\nu(\text{CS})$ is observed in the region $1030\text{--}1050\text{ cm}^{-1}$; this range is also typical for mixed ligand complexes of xanthates [14, 21], in which xanthate coordinates in a bidentate fashion.

The electronic spectra of the complexes were recorded in chloroform solutions; the spectral data of the complexes are summarized in Table III. The complexes exhibit a band in the region $17.7\text{--}17.8\text{ kK}$

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Table I. Analytical data and physical properties of the complexes.

Compound	Colour	C [%] (calcd)	H [%] (calcd)	N [%] (calcd)	S [%] (calcd)	Yield [%]	μ_{eff} (B.M.)
Ni(Mexan)(HDz)	dark brown	(42.77) 43.49	(3.35) 3.20	(13.29) 12.87	(22.83) 23.07	70	3.32
Ni(Etxan)(HDz)	dark brown	(44.16) 43.75	(3.70) 3.54	(12.87) 12.41	22.10 22.16	70	3.38
Ni(Prxan)(HDz)	dark green	(45.45) 45.59	(4.03) 4.00	(12.47) 12.43	(21.41) 20.14	75	3.36
Ni(Buxan)(HDz)	green	(46.66) 45.67	(4.34) 4.30	(12.09) 11.03	20.76 19.50	80	3.34
Ni(Cyxan)(HDz)	green	(49.09) 48.6	(4.53) 4.71	(11.44) 11.08	(19.65) 20.15	80	3.33

Compound	Dithizonate moiety				Xanthate moiety	
	$\nu(\text{NH})$	$\delta(\text{NH})$	$\nu(\text{N}-\text{C})$	$\nu(\text{CS})$	$\nu(\text{CO})$	$\nu(\text{CS})$
Ni(Mexan)(HDz)	3260	1520	1320	875	1130	1030
Ni(Etxan)(HDz)	3260	1530	1320	875	1120	1030
Ni(Prxan)(HDz)	3260	1520	1320	875	1130	1040
Ni(Buxan)(HDz)	3260	1520	1320	875	1130	1050
Ni(Cyxan)(HDz)	3240	1530	1320	875	1160	1050

Table II. Principal infrared bands of the complexes (cm^{-1}).

characteristic of dithizonato nickel(II) upon adduct formation [5]; this band is also shown by the dithizonate anion and by most metal dithizonates (Hg, Pb, Zn, *etc.*) [5, 23]. In addition, the complexes display a band at 20.0–20.6 kK, which can be assigned – due to its intensity and position – to the spin-forbidden transition $^1\text{T}_2 \leftarrow ^3\text{T}_1$ exhibited by tetrahedral Ni(II) complexes [24]. The transition $^3\text{A}_2 \leftarrow ^3\text{T}_1(\nu_2)$ probably lies out of the range of the used spectrophotometer. The transition $^3\text{T}_1(\text{P}) \leftarrow ^3\text{T}_1(\nu_3)$ may be obscured by the intraligand transition of the dithizonate moiety. The magnetic moment values (3.32–3.38 B.M.) are in agreement with

the above formulation of a tetrahedral structure of the complexes [26]. Bands appearing in the region 23.1–33.5 kK are attributed to charge transfer transitions, while those in the range 35.7–36.3 kK are due to intraligand transitions of the xanthate moiety [14, 25].

A spectrophotometric titration was carried out where dithizone was titrated into chloroform solutions (10^{-4} M) of alkylxanthato nickel(II). The spectra obtained from the successive additions of dithizone are characterized by three absorption bands at ~ 17.5 , ~ 20.8 , and ~ 23.8 kK. The first band increases in intensity relative to the second and third band suggesting that this band relates to the dithizonate part in the complexes.

The thermal behaviour of the complexes was studied over the temperature range 50–700 °C. The TGA thermograms indicate that there is no loss in weight up to ~ 150 °C. Beyond this temperature, decomposition starts with a maximum loss at ~ 180 , ~ 330 , and ~ 500 °C (obtained from the DTG curves). In the TGA thermogram of the compound Ni(cyxan)(HDz) the weight loss at 150–175 °C is consistent with the decomposition of the dithizonate moiety (Fig. 1). The decomposition of the complexes

Table III. Electronic spectral data of the complexes (kK).

Compound	Assignment		
	$^1\text{T}_2 \leftarrow ^3\text{T}_1$	Charge transfer	Intraligand transitions
Ni(Mexan)(HDz)	20.0	23.2 and 33.3	17.8 and 35.7
Ni(Etxan)(HDz)	20.4	23.3 and 33.5	17.7 and 35.8
Ni(Prxan)(HDz)	20.2	23.1 and 33.4	17.8 and 35.8
Ni(Buxan)(HDz)	20.2	23.3 and 32.2	17.7 and 36.3
Ni(Cyxan)(HDz)	20.6	23.5 and 31.7	17.7 and 35.7

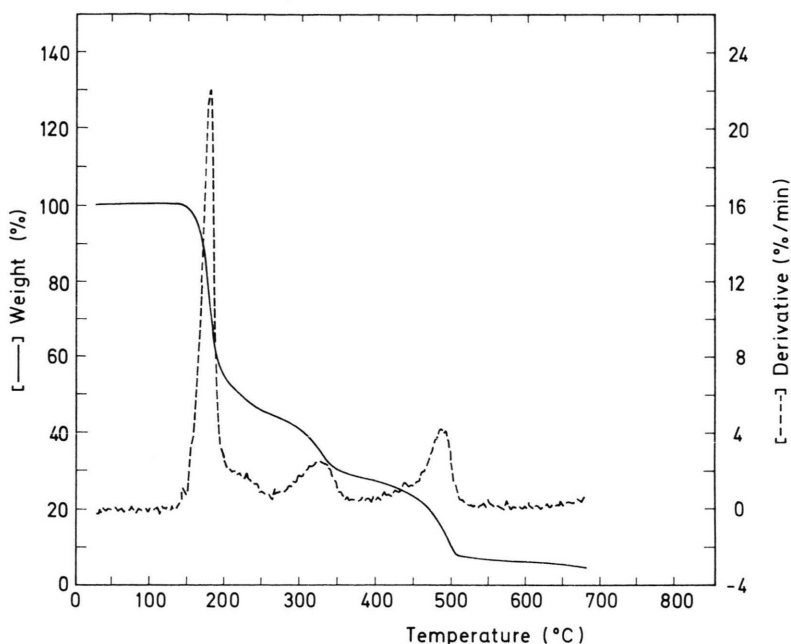


Fig. 1. TGA and DTG thermograms of Ni(Cyxn)(HDz).

continues on further heating up to 700 °C and the end product was identified as Ni₂O₃.

The ¹H NMR spectra (Table IV) of the complexes in deuterated chloroform show the characteristic resonances of both the dithizonates and the alkyl groups of xanthates. The aromatic protons of dithizonate appear in the region $\delta = 7.3\text{--}7.4$ ppm. The signal of the --NH proton of dithizonate is observed at $\delta = 8.9$ ppm.

Experimental

Physical measurements

The infrared spectra were obtained with KBr pellets on a Perkin Elmer 599 B recording spectrophotometer. Electronic spectra were obtained with a Shimadzu UV-200 S and matched 1 cm quartz cells. The magnetic measurements were obtained at

room temperature by the Gouy method using Hg[Co(NCS)₄] as the calibrant. Diamagnetic corrections were made using Pascal's constants. Thermal measurements were carried out on a 1090 Du Pont thermal analyser, with a furnace heating rate of 10 °C per minute. Proton nuclear magnetic resonance spectra were recorded on a Varian EM-390 NMR 90 MHz spectrometer. Tetramethylsilane (TMS) was employed as an external standard.

All starting materials and solvents used were of reagent grade. Dithizone (Merck) was used without purification. The Ni(ROCS₂)₂ precursors were prepared and purified following published procedures [27].

Preparation of the complexes

Since the preparation of the complexes followed essentially the same procedure, only the preparation

Complex	CH ₃	$\text{--CH}_2\text{--}$	--NH	Aromatic
Ni(Mexan)(HDz)	4.1 (s)	—	8.9 (s)	7.3 (m)
Ni(Etxan)(HDz)	1.4 (t)	4.5 (q)	8.9 (s)	7.3–7.4 (m)
Ni(Prxan)(HDz)	0.9 (t)	4.4 (t)	8.9 (s)	7.3–7.4 (m)
		1.8 (h)		
Ni(Buxan)(HDz)	0.9 (t)	1.2–1.9 (m)	8.9 (s)	7.3–7.4 (m)
		4.4 (t)		
Ni(Cyxn)(HDz)	—	1.2–2.0 (m)	8.9 (s)	7.3–7.4 (m)

Table IV. ¹H NMR chemical shifts (δ , ppm) of the complexes.

(s) = singlet, (q) = quartet, (t) = triplet, (m) = multiplet, (h) = hexet.

method for the complex (ethylxanthato)(dithizonato)nickel(II) will be described in detail as follows:

To a stirred chloroform solution (20 ml) of bis(ethylxanthato)nickel(II) (4 mmol) a chloroform solution (15 ml) of dithizone (4 mmol) was added

dropwise; the mixture was further stirred for about one hour. The reaction mixture was then evaporated to about one third the original volume where a dark brown product precipitated, which was collected, washed with cold chloroform, and dried *in vacuo* over P_4O_{10} .

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