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THERMOGRAVIMETRIC STUDY OF SOME DIVALENT METAL CHELATE POLYMERS OF DITHIOOXAMIDE*

R. S. Bottei and C. P. McEachern**

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana, USA

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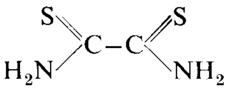
The thermal properties of polymeric chelates of dithiooxamide with divalent copper, cobalt, zinc and nickel have been investigated. The order of thermal stability is Ni > Co ~ Zn > Cu, which is the same as that observed for previously studied naphthazarin and rhodizonic acid chelates. The procedural decomposition temperatures indicate that the dithiooxamide chelates, which are not aromatic, are about as stable as the aromatic naphthazarin and rhodizonic acid chelates. Several unsuccessful attempts were made to prepare beryllium and manganese (II) chelates.

Previous studies in this laboratory on the thermal stabilities of chelate polymers [1–6] have centered on bisdioxa systems, where the metal is surrounded by four oxygen atoms. Since it seemed desirable to study chelate polymers in which atoms other than oxygen were involved in chelation, a study was undertaken of dithiooxamide (rubeanic acid) chelates in which two nitrogens and two sulfur atoms are bonded to the central metal atom. It is also one of the simplest molecules to produce chelate polymers.



Dithiooxamide

The copper(II), cobalt(II) and nickel(II) chelates of dithiooxamide were prepared by Ray and Ray [7]. The chelates had a metal-to-ligand ratio of 1 : 1. Ray and Bahr [8] found the nickel chelate to be diamagnetic. Jensen [9] by analogy with nickel(II) mercaptide, which was diamagnetic and known to be polymeric, assigned a cis-polymeric structure to nickel(II) dithiooxamide. From some infrared data in the 4000–2000 cm^{-1} region, Barcelo [10] thought that both the ligand and the metal chelates might possibly exist in a transplanar keto form. Kanda, Ito and Nogaito [11] studied the magnetic, electrical and infrared spectral properties of rubeanato copper(II) co-ordination polymer and proposed a cupric-acetate-type chain structure for the chelate.

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** Present address: E. I. duPont de Nemours & Co., Photoproducts Division, Parlin, N. J.

Experimental

Preparation of dithiooxamide chelates: The procedure was similar to that of Ray and Ray [7] except that it was not necessary to neutralize with base to precipitate the nickel and cobalt chelates. Dithiooxamide, obtained from Mallinckrodt Chemical Works, was purified by extraction in a Soxhlet extractor with 95% ethanol for 24 hours. Ten millimoles (1.20 g) of dithiooxamide was dissolved in 250 ml 95% ethanol. To the solution was added 50 ml of aqueous metal solutions, containing 11 – 21 mmoles (2.6 – 3.0 g) of nickel hexahydrate, cobaltous acetate tetrahydrate, zinc acetate dihydrate, or cupric sulfate pentahydrate. There was immediate precipitation. The precipitates were allowed to settle overnight, centrifuged, washed several times with distilled water, 95% ethanol, and acetone. They were filtered on a medium porosity sintered glass crucible and dried overnight. Yields were about 1.5 g.

Interfacial polymerization method: This method was also used to prepare the cobalt and copper chelates of dithiooxamide. About 25 mmoles of cobaltous acetate tetrahydrate or cupric sulfate pentahydrate (6.2 g) in 50 ml distilled water were added to a suspension of 25 mmoles (3.1 g) of dithiooxamide in 300 ml benzene in a Waring Blender. The mixture was agitated for 20 minutes and then filtered on a sintered glass crucible. The precipitate was washed extensively with 95% ethanol until the washing became clear. It was then dried overnight in an evacuated desiccator. Yields were 1.2 and 4.0 g, respectively.

Reaction of dithiooxamide with beryllium and manganese: Addition of aqueous solutions of beryllium sulfate tetrahydrate or manganous sulfate monohydrate to alcoholic dithiooxamide failed to yield chelates even after addition of aqueous sodium hydroxide. The alcoholic ligand solution did not change color.

Analysis of chelates. Carbon and hydrogen analyses were performed by Midwest Microlab, Indianapolis, Indiana, and by Schwarzkopf Analytical Laboratory Woodside, New York. Metals were analyzed by dissolving 0.05 – 0.15 g of the metal chelate in 1 : 1 nitric-sulfuric acid. Copper and cobalt were determined electrogravimetrically, zinc as mercurithiocyanate and nickel as the dimethylglyoxime complex.

Thermogravimetric measurements. The construction and method of operation [12] of the manually operated thermobalance used in this investigation have been previously described. The TG curves for all the samples were obtained by using approximately 50 mg samples of air-dried material, in a nitrogen atmosphere. The heating was fairly constant for all runs, approximately 5°/min. The instrument was checked using calcium oxalate.

Results and discussion

Physical properties: The copper and nickel chelates are brittle solids, whereas the zinc and cobalt chelates are powders. The colors of the chelates are given in Table 1. All chelates are insoluble in a wide variety of polar and nonpolar organic solvents including: ethanol, methanol, acetone, dimethylformamide, 1,4-dioxane, carbon tetrachloride, chloroform, benzene, ethyl ether, and n-pentane. Only the zinc chelate showed a very slight solubility in 1,2-dimethoxyethane, and the nickel chelate a very slight solubility in dimethylsulfoxide. None of the chelates sublimed on heating.

Composition: The chelates were dried for an hour at 110° before analysis. The results are given in Table 1. Composition analyses indicate that the copper and zinc chelates are anhydrous, whereas the nickel chelate is a monohydrate, and the cobalt chelate is a dihydrate. Ray and Ray [7] reported that the copper and nickel chelates were anhydrous and the cobalt chelate was a dihydrate. More recently in a review, Ray and Xavier [13] stated that the elemental composition of the copper chelate corresponded more closely to a hemihydrate than an anhydrous chelate.

A correction was made for adsorbed water for the copper chelate. It was assumed that the difference between the calculated and experimental percent hydrogen was due to adsorbed water when results were high for hydrogen and correspondingly low for carbon and copper. The calculated values are based on 1 : 1 chelates,

Table 1

Elemental analysis of the dithiooxamide chelates

Chelate	Color	Element	%, calculated	%, experimental	%, corrected	Carbon : metal ratio
CuL	green-black	C	13.22	11.45	11.91	2 : 1.08
		H	1.11	1.54	1.11	
		N	15.42	13.88	14.11	
		S	35.29	32.66	33.96	
		Cu	34.97	32.79	34.10	
CoL · $2H_2O$	orange-brown	C	11.27	11.74		2 : 0.85
		H	2.84	2.09		
		N	13.14	13.89		
		S	30.09	28.88		
		Co	27.65	24.58		
ZnL	light yellow	C	13.09	13.27		2 : 0.97
		H	1.10	1.33		
		N	15.26	15.30		
		S	34.94	34.75		
		Zn	35.62	34.49		
NiL · H_2O	blue-violet	C	12.39	12.71		2 : 0.99
		H	2.08	1.87		
		N	14.45	15.18		
		S	33.07	33.10		
		Ni	30.12	29.96		

which would correspond to polymers of infinite length. Elemental analyses of the chelates show that they approach a 1 : 1 metal to ligand ratio.

The copper and cobalt chelates, prepared by interfacial polymerization contain less metal than those for alcohol-water solution. The percent copper is 30.97, while that for cobalt is 22.38. This is probably due to the occlusion of free dithiooxamide in the chelate itself which could not be removed by washing.

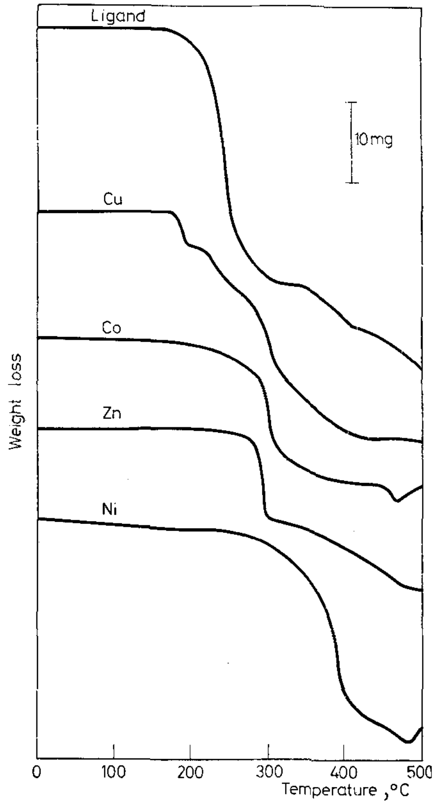

Fig. 1. TG curves of dithiooxamide and its chelates

Thermal properties: Figure 1 presents typical TG curves of the dithiooxamide chelates. The procedural decomposition temperatures are given in Table 2. These temperatures were obtained by extending the linear portions of the weight-loss curves in the region of accelerated weight loss. The point of intersection of the two lines was taken as the decomposition temperature.

The order of decreasing thermal stability is: Ni > Co ~ Zn > Cu. The cobalt and nickel chelates show no loss of water before the onset of decomposition. There

Table 2

Procedural decomposition temperatures of the dithiooxamide chelates

Chelate	Temperature, °C
Ligand	213
Copper	197
Zinc	293
Cobalt	296
Nickel	367

is no distinguishable plateau that can be attributed to an anhydrous chelate. Water loss must occur simultaneously with thermal decomposition.

The shapes of the weight-loss curves of the cobalt and copper chelates, prepared by interfacial polymerization were similar to those prepared from alcohol-water solution, but the procedural decomposition temperatures differed. The decomposition temperature of the copper chelate was approximately 20° greater (217°),

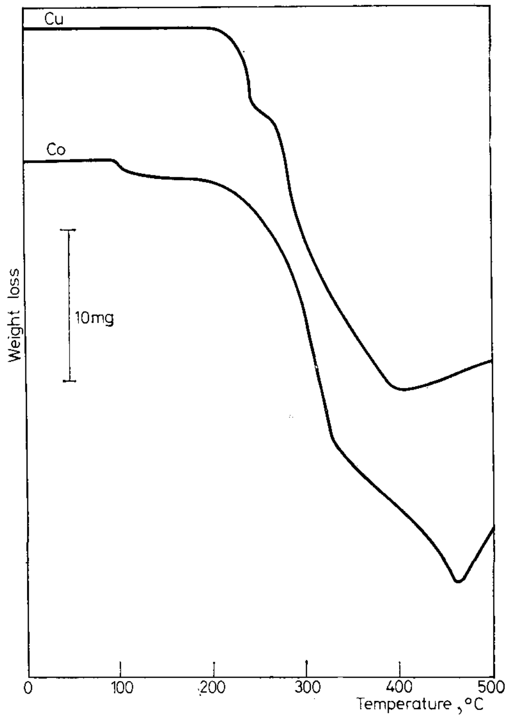

Fig. 2. TG curves of copper and cobalt chelates of dithiooxamide prepared by interfacial polymerization

whereas the temperature of the cobalt chelate was approximately 15° less (280°). TG curves are shown in Figure 2.

The order of thermal stability of the dithiooxamide chelates is the same as that observed by Bottei and Gerace [1] for the naphthazarin chelates, and by Bottei and Greene [4] for the rhodizonic acid chelates. The procedural decomposition temperatures (°C) of the naphthazarin chelates are: Cu 260, Co 272, Zn 318, and Ni 327, and for rhodizonic acid chelates: Cu 183, Co 345, Zn 355, and Ni 386.

It was believed that aromatic systems would have enhanced thermal stability. By comparing the three systems, it is seen that the dithiooxamide chelates, which are not aromatic, are about as stable as the aromatic naphthazarin and rhodizonic acid chelates.

Residues: Table 3 shows the observed weight of residue for the dithiooxamide chelates and the calculated percentage weight remaining for the various metal sulfides. Since the thermal analysis was performed in an inert atmosphere, it was believed that the residues would probably be sulfides.

Table 3

Residue percentages

Chelate	Residue	Calculated	Observed
Copper	Cu_2S	45.1	44.7
Cobalt	Co_2S_3	50.0	54.2
Zinc	ZnS	53.1	57.9
Nickel	NiS	46.5	44.7

An attempt was made to correlate the relative thermal stabilities of the chelates with the free energy of formation of their respective sulfides [14]: Cu_2S −20.6, ZnS −43.2, Co_2S_3 −47.6 and NiS −18.8. However, no relationship could be made, since the order of decreasing thermal stability of the metal dithiooxamides did not correspond with the order of increasing thermodynamic stability of the metal sulfides.

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RÉSUMÉ — On a étudié les propriétés thermiques des chélates polymères du dithiooxamide avec le cuivre, le cobalt, le zinc et le nickel. Leur stabilité thermique suit le même ordre que celui observé pour les chélates de la naphtazarine et de l'acide rhodizonique, étudiés préalablement (Ni $>$ Co $\sim$ Zn $>$ Cu). Les températures de décomposition qui ont été trouvées indiquent que les chélates non aromatiques du dithiooxamide ont à peu près la même stabilité que les chélates aromatiques de la naphtazarine et de l'acide rhodizonique. A plusieurs reprises, on a tenté sans succès de préparer des chélates avec le béryllium et le manganèse.

ZUSAMMENFASSUNG — Die thermischen Eigenschaften polymerer Chelate von Dithiooxamid mit zweiwertigem Kupfer, Kobalt, Zink und Nickel wurden untersucht. Die Reihenfolge der thermischen Stabilität von Ni $>$ Co $\sim$ Zn $>$ Cu ist dieselbe, welche für die vorhergehend untersuchten Naphthazarin- und Rhodizonsäure-Chelate beobachtet wurde. Die Zersetzungstemperaturen der Vorgänge deuten darauf hin, daß die nicht aromatischen Dithiooxamid-Chelate etwa die gleiche Stabilität besitzen, wie die aromatischen Naphthazarin- und Rhodizonsäure-Chelate. Mehrere erfolglose Versuche wurden zur Herstellung von Beryllium- und Mangan(II)-Chelaten durchgeführt.

Резюме — Исследованы термические свойства полимерных хелатов дитиооксамида с двухвалентными медью, кобальтом, цинком и никелем. Установленный ряд термостабильности: Ni $>$ Co $\sim$ Zn $>$ Cu тот же, что и для ранее исследованных хелатов нафтазариной и родизоновой кислот. Температуры распада показывают, что дитиооксамидные хелаты, не являющиеся ароматическими, почти так же стабильны, как ароматические хелаты нафтазариной и родизоновой кислот. Удачны отдельные попытки с целью приготовления хелатов с берилием и марганцем (II).