

THERMAL AND SPECTRAL STUDIES OF SOME DIVALENT METAL CHELATES OF 2,4-DINITROSO-1,3-NAPHTHALENEDIOL

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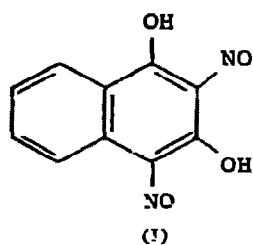
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ABSTRACT

The thermal and spectral properties of the chelates of 2,4-dinitroso-1,3-naphthalenediol with copper, cobalt, nickel, and zinc have been investigated. The decreasing order of thermal stability for the metal chelates is $Ni > Co \approx Zn > Cu$. With the exception of the copper chelate, which exploded, the chelates decomposed slowly. They are compared to the corresponding chelates of 2,4-dinitrosoresorcinol.

INTRODUCTION

Little work has appeared in the literature concerning 2,4-dinitroso-1,3-naphthalenediol (I). The possible use of this compound as an adhesion pro-



moter in the binding of urethane and butyl rubber has been investigated by the Firestone Tire and Rubber Co. [1]. It was observed by Mäkitie and Toivanen [2] that 2,4-dinitroso-1,3-naphthalenediol formed precipitates with copper, cobalt, nickel, iron and palladium. With the exception of a spectrophotometric study of the copper chelate, no further characterizations were made.

Previous thermal studies in this laboratory by Bottei and McEachern [3] have dealt with some divalent metal chelates of 2,4-dinitrosoresorcinol. This compound is similar to 2,4-dinitroso-1,3-naphthalenediol except that it has one less benzene ring than the naphthalenediol system. It would therefore be of interest to prepare some divalent metal chelates of 2,4-dinitroso-1,3-naphthalenediol and compare their thermal stabilities to those of the metal chelates of 2,4-dinitrosoresorcinol. It would then be possible to determine the effect of increased resonance on the thermal stability of the 2,4-dinitroso-1,3-naphthalenediol chelates.

EXPERIMENTAL

Preparation of chelates

One gram (0.0046 moles) of 2,4-dinitroso-1,3-naphthalenediol (Eastman Chemical Co.) was added to 500 ml of 95% alcohol and refluxed for 1 h. The solution was then filtered through a medium porosity glass-fritted funnel to free the solution of any undissolved particles. To this filtrate was added, with stirring, 0.0046 moles of either cupric acetate monohydrate, cobalt acetate tetrahydrate, nickel acetate tetrahydrate or zinc acetate dihydrate dissolved in 50 ml of distilled water. This solution was then refluxed for 2 h and the precipitate collected by centrifugation. The metal chelates were washed with distilled water, 95% ethanol and ether, and dried in a vacuum oven at 40°C overnight. Yields ranged from 0.8–1.1 g.

The disodium salt was prepared by adding 2 equivalents of sodium ethoxide to a 95% alcoholic solution of the ligand. The precipitate was washed with ether.

Analysis of metal chelates

Metal analyses were performed by atomic absorption spectrophotometry using a Varian Techtron atomic absorption spectrophotometer, model 1200. The metal chelates were dissolved in a 3 : 1 nitric–sulfuric acid mixture and diluted with water to the appropriate concentration for analysis. Wavelengths used were: copper, 324.7 nm; cobalt, 240.7 nm; nickel, 232.0 nm; and zinc, 213.9 nm.

Absorption spectra

IR absorption spectra were obtained on a Perkin–Elmer Infracord 137-B, a Perkin–Elmer 457 grating spectrophotometer, or a Hilger–Watts Infra-graph H1200, using the potassium bromide disk method. Samples were prepared by mixing about 1 mg of sample with 200 mg of potassium bromide. The potassium bromide was dried at 160°C.

Thermogravimetry

Thermograms were obtained on a DuPont 900 differential thermal analyzer equipped with a DuPont 950 thermogravimetric analyzer. The temperature calibration was checked with calcium oxalate monohydrate. The cold junction chromel–alumel thermocouple was immersed in ice-water, which served as the reference temperature.

Thermogravimetric determinations were made on 10–12 mg of sample which was placed in a platinum boat. Lamp nitrogen (obtained from Cleveland Wire Works) flowed over the sample at the rate of 2 std. ft.³ h⁻¹. The nominal heating rate was 10°C min⁻¹. A temperature correction table was used to correct for the non-linearity of the chromel–alumel junction with temperature.

Differential thermal analysis

A Fisher series 200A differential thermal analyzer was used in conjunction with a Texas Instruments servo-writer II recorder. The furnace temperature was controlled by using a Fisher platinum thermocouple, while measurement of sample temperatures was made by a Fisher chromel—alumel thermocouple. Benzoic acid was used as standard to check the temperature programmer. The cold junction reference was an ice-water bath at 0°C.

A stream of lamp nitrogen (Cleveland Wire Works) was passed continuously over the sample during the run at 2 std. ft.³ h⁻¹. In each of seven quartz reference crucibles was placed 100 mg of alumina (α -Al₂O₃) which was previously fired at 1200°C. In the eighth quartz crucible was placed about 100 mg of sample. The sample was packed in the crucible by dropping the crucible 10 times from a height of about 60 cm inside a 5 mm diameter glass tube.

X-Ray powder patterns

Powder diffraction patterns of the TGA residues were obtained on a Norelco X-ray diffraction unit (Phillips Electronic Instruments, New York). Samples were ground in an agate mortar and loaded into 0.3 mm glass capillary tubes obtained from the Charles Supper Co., Massachusetts. Sample tubes were mounted in a 114.6 mm Debye—Scherer powder camera and irradiated with CuK α radiation for 1–4 h. The *d* spacings were calculated after the film measurements had been corrected for shrinkage. The ASTM (Hanawalt) tables were consulted to obtain the identity of the TGA residues.

Calculation of energy parameters from DTA

The method of Borchardt and Daniels [4] was employed. A compensating polar planimeter was used to obtain the areas under the DTA curves.

RESULTS AND DISCUSSION

Physical properties

All the metal chelates are powders which are insoluble in acetone, ethanol, and water. The colors of the chelates are given in Table 1.

Composition

Metal analyses for freshly dried (vacuum, 40°C) metal chelates are given in Table 1. The chelates were stored in a desiccator because they had a tendency to absorb moisture. Unlike the dinitrosoresorcinol chelates, these chelates were all anhydrous.

The copper, nickel, and zinc chelates of 2,4-dinitroso-1,3-naphthalenediol have a 1 : 1 metal—ligand ratio; the cobalt chelate approaches a 1 : 2 metal—

TABLE 1

Color and composition of the metal chelates of 2,4-dinitroso-1,3-naphthalenediol

Chelate	Color	Metal	Calc.	Obs.
CuL	Dark brown	Cu	23.59	22.93
NiL	Dark brown	Ni	21.37	20.76
ZnL	Light brown	Zn	23.23	22.59
CoL ₂	Brown	Co	12.00	13.46

ligand ratio. These are the same metal—ligand compositions observed for the metal chelates of 2,4-dinitrosoresorcinol.

Thermal stability

Typical weight loss curves for the metal chelates of 2,4-dinitroso-1,3-naphthalenediol are given in Fig. 1. DTA curves are given in Fig. 2. Procedural decomposition temperatures (°C) obtained from TGA studies are: copper, 204; zinc, 244; cobalt, 249; and nickel, 261. Procedural decomposition temperatures (°C) obtained from DTA studies are: copper, 207 (exploded); zinc, 251; cobalt, 258; and nickel, 278. The relative thermal stability order of the 1 : 1 metal—ligand chelates of 2,4-dinitroso-1,3-naphthalenediol as deter-

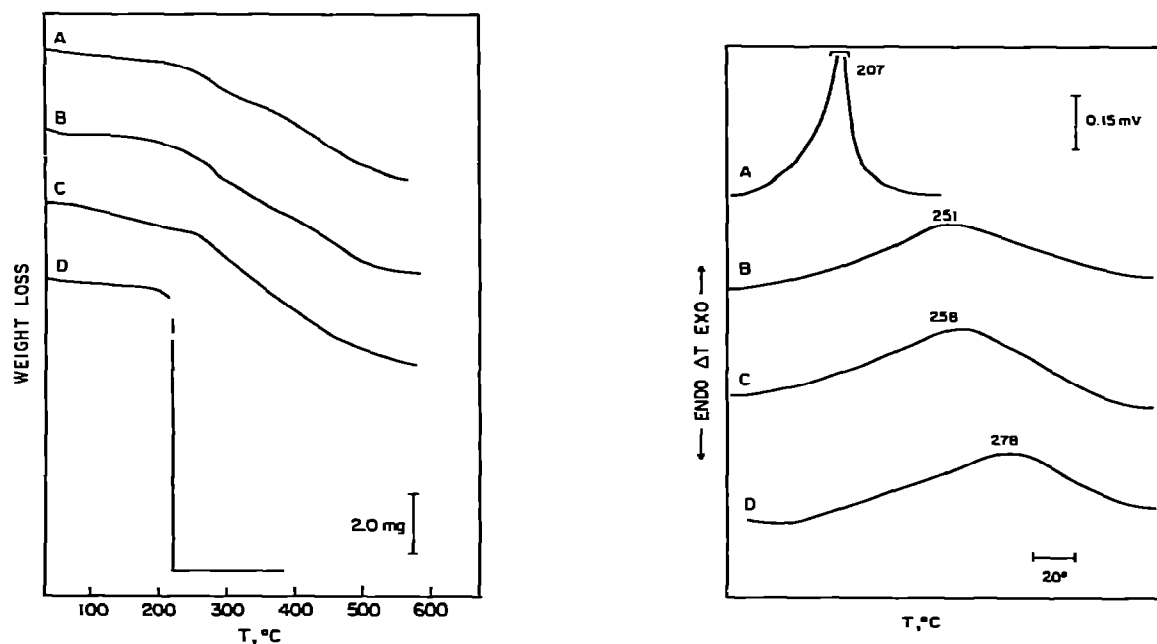
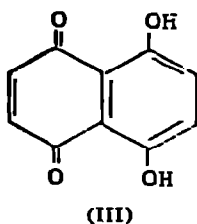
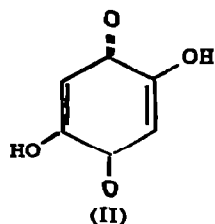


Fig. 1. Thermogravimetric analysis curves for the metal chelates of 2,4-dinitroso-1,3-naphthalenediol: A, zinc; B, cobalt; C, nickel; D, copper.

Fig. 2. Differential thermal analysis curves for the metal chelates of 2,4-dinitroso-1,3-naphthalenediol: A, copper; B, zinc; C, cobalt; D, nickel.

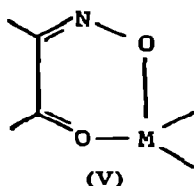
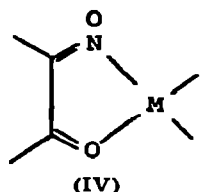
mined by TGA and DTA studies is: $\text{Ni} > \text{Zn} > \text{Cu}$. This is the same thermal stability order as observed for the metal chelates of 2,4-dinitrosoresorcinol studied by Bottei and McEachern [3]. In their study, all the metal chelates of 2,4-dinitrosoresorcinol exploded. In this study, only the copper 2,4-dinitroso-1,3-naphthalenediol chelate exploded. A bang could be heard in the furnace when the explosion occurred. The cobalt, nickel, and zinc chelates did not explode but rather decomposed slowly. Apparently, the addition of more resonance stabilization in the nitrosonaphthalene system than in the nitrosophenol system allows for a slower, non-detonating decomposition in these chelates. The copper chelate explodes at a much lower temperature, perhaps because of its catalytic nature in thermal degradation processes. For comparison, the exploding temperatures ($^{\circ}\text{C}$) of the dinitrosoresorcinol chelates as determined from TGA studies [3] are: copper, 189; zinc, 225; cobalt, 230; and nickel, 251. The addition of one more benzene ring has slightly increased ($10\text{--}19^{\circ}\text{C}$) the thermal stability of the dinitroso-naphthalenediol chelates over the corresponding metal chelates of dinitrosoresorcinol. There have been other studies where the effect of the addition of more benzene rings on the thermal stability of metal chelates has been investigated. Bottei and Fangman [5] prepared metal chelates of 2,4-dihydroxy-*p*-benzoquinone (II) and compared their thermal stabilities with those of the metal chelates of naphthazarin (III) prepared by Bottei and Gerace [6]. With the additional ring in the naphthazarin chelates, their thermal stabilities were increased an average of 20°C over the corresponding metal chelates of 2,5-dihydroxy-*p*-benzoquinone.



An attempt to determine energy parameters from DTA curves employing the method of Borchardt and Daniels [4] failed. The values for E_a produced no reasonable trend, probably due to the broadness and poor definition of the peaks.

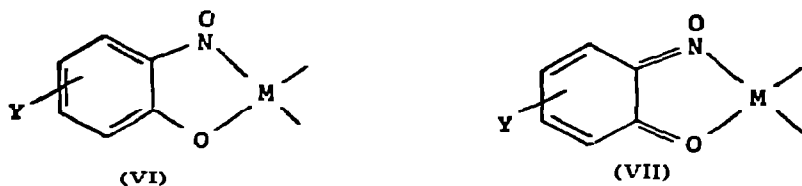
Bonding

o-Quinone mono-oximes are tautomeric with *o*-nitrosophenols [7]. In these compounds the oxime group can coordinate either through the nitrogen atom (IV) or through the oxygen atom (V) to the metal. By



analogy with an X-ray crystal structure determination of an *o*-nitroso-

phenol copper complex [8], it is believed that the dinitrosonaphthalenediol metal complexes can be represented in valence bond terms involving resonance between structures (VI) and (VII). Mass-spectral evidence from some copper and nickel *o*-nitrosophenol complexes [9] also supports the



formation of the complexes with nitrogen-coordinated five-membered chelate rings.

Residue analysis

The residues from TGA studies were analyzed using X-ray powder diffraction. All residues were determined to be the metal oxides: CuO, CoO, ZnO,

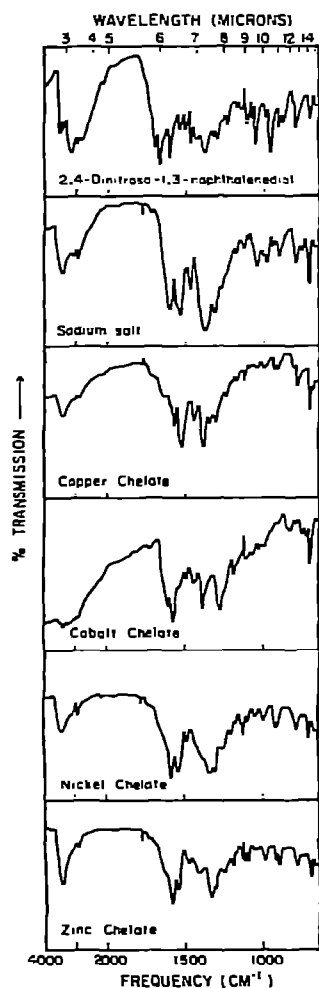


Fig. 3. IR absorption spectra of 2,4-dinitroso-1,3-naphthalenediol and its chelates.

and NiO. Dissolution of the residues in acid left a trace of black powder, evidently carbon.

IR studies

The IR spectra of 2,4-dinitroso-1,3-naphthalenediol, its disodium salt, and the metal chelates are given in Fig. 3. The sharp peaks in the spectrum of the ligand at 3500–3000 cm^{-1} disappeared upon chelation. These peaks lie in the range expected for the O–H stretching mode of an oxime, and for a phenolic OH involved in hydrogen bonding.

All the metal chelates show a broad absorption at 3460 cm^{-1} . This is probably due to absorbed water, which was present in all the chelates, as confirmed by TGA studies.

IR spectroscopic studies have shown that 2-nitroso-1-naphthol has the benzoquinone-oxime structure in the solid state [7]. In this state it has a strong band at 1668 cm^{-1} which has been assigned by Hadzi [7] to the $\nu(\text{C}=\text{O})$ stretching vibrations. The spectrum of 2,4-dinitroso-1,3-naphthalenediol also has a strong band at 1668 cm^{-1} . This is probably due to the $\nu(\text{C}=\text{O})$ stretching vibration. The $\nu(\text{C}=\text{O})$ vibrations for the ligand and metal chelates of 2,4-dinitroso-1,3-naphthalenediol are given in Table 2. It can be seen that changes due to coordination (i.e. shifting of the $\nu(\text{C}=\text{O})$ to lower frequencies) indicate a significant contribution from the quinone structure (VII) in the complex.

Below 1200 cm^{-1} , the IR spectra of the chelates does not resemble that of the ligand. The sharp, strong absorptions characteristic of the ligand are not present in the spectra of the chelates. No further assignments of the spectra were made.

It should be noted that a detailed assignment of the spectra of coordination compounds of 2-nitroso-1-naphthol were performed by Guerrieri and Siracusa [10]. From this IR study they concluded that coordination took place through the nitrosyl oxygen, giving a six-membered chelate ring (V). The crystal structure data of McPartlin [8] and *o*-nitrosophenols leads us to suppose that this is probably in error.

TABLE 2

$\nu(\text{C}=\text{O})$ stretching vibrations in the chelates of 2,4-dinitroso-1,3-naphthalenediol

Chelate	$\nu(\text{C}=\text{O}) \text{ cm}^{-1}$
Ligand	1668
Na	1605
Cu	1580
Ni	1592
Zn	1588
Co	1574

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