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THERMAL AND SPECTRAL STUDIES OF SOME DIVALENT METAL CHELATES OF QUINIZARIN *

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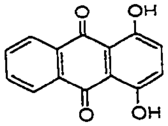
ABSTRACT

The thermal and spectral properties of the chelates of quinizarin with copper, cobalt and nickel have been investigated. The decreasing order of thermal stability for the chelates is Ni > Co > Cu. The chelates are compared with the corresponding chelates of naphthazarin The effect on the thermal stability of the addition of a benzene ring to naphthazarin is compared with a previous study on 2,4-dinitrosoresorcinol and 2,4-dinitroso-1,3-naphthalenediol. Several unsuccessful attempts were made to prepare a zinc chelate of this ligand.

INTRODUCTION

Quinizarin, 1,4-dihydroxy-9,10-anthraquinone, has been used as a fungicide to control mildew on cranberry and bean seedlings [1], and as a pesticide against the subterranean termite, Reticulitermes [2].



Quinizarin

In its role as a dyeing agent, quinizarin can be found in polyester materials [3,4] and in nylon non-absorbable surgical sutures used in general surgery [5]. Protected by many patents, the use of quinizarin as an initiator for photopolymerization and as an ultraviolet holdback material in non-silver photocopying compounds is well documented [6—8]. It has been used as an additive in synthetic ester-based lubricating oils to help prevent oxidation and corrosion in gas turbines, jet aircraft engines, automobile racing car transmissions, and pneumatic tools [9—18]. It was just this kind of application, that of being used as an additive in oil formulation, that stirred interest in metal chelate polymers in the late nineteen-forties.

Quinizarin is capable of being tetrafunctional and should form linear poly-

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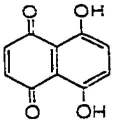
mers when reacted with suitable metal ions. Metal chelate polymers of quinizarin have been reported by Korshak et al. [19]. They prepared the chelates by reacting equimolar mixtures of quinizarin and the acetylacetonate of the metal in a condensation tube at 220° C under nitrogen, and studied the decompensation of the chelates in air (static) by following visually the degree of degradation of the compounds in melting point tubes. In a study by Jackson and Leonard [20] on some divalent chelates of quinizarin, solvent molecules were thought to be present in the coordination sphere of the metal but the polymer formulations proposed violated the law of charge balance.

O'Connell [21] prepared some divalent metal chelates of quinizarin for use as additives to polyacrylonitrile co-polymers. They were found to increase the weather resistance of the colored co-polymers. While temperatures of decomposition for the metal chelates were given, no mention of thermal technique or experimental atmosphere were given.

The preparation and characterization of some divalent metal chelates of quinizarin were undertaken for two reasons. First, the effect on thermal stability by adding a benzene ring to 2,4-dinitrosoresorcinol has been investigated by Bottei and Lusardi [22]. Bottei and Gerace [23] had also prepared and studied the thermal properties of some divalent metal chelates of naphthazarin.



Naphthazarin

It would be of interest, therefore, to study the chelates of quinizarin to see if the addition of a benzene ring on to naphthazarin had the same effect as in the 2,4-dinitroso-1,3-naphthalenediol chelates [22]. Secondly, since a variety of factors such as conditions of preparation and methods of determining thermal stability can affect procedural decomposition temperatures, it was deemed necessary to prepare the quinizarin chelates under the same experimental conditions used by Bottei and Gerace [23] for the naphthazarin chelates.

EXPERIMENTAL

Preparation of chelates

All chemicals used in this work were reagent grade. Common organic solvents, commercially available, were used without further purification. Crude quinizarin (Eastman Organic Chemicals) was purified by Soxhlet extraction using toluene as the solvent. Analysis: Calcd. for $C_{14}H_8O_4$: %C, 70.00; %H, 3.33. Found: %C, 69.98, %H, 3.35.

To 1 g of quinizarin (0.004 moles) in 1000 ml of 95% alcohol was added with stirring 0.004 moles of either cupric acetate tetrahydrate, cobalt acetate tetrahydrate or nickel acetate tetrahydrate in 500 ml of water. The solution was then refluxed overnight and then allowed to cool to room temperature. The precipitate was collected by centrifugation, transferred to a medium porosity glass-fritted funnel and washed well with water, acetone, and ether. Since the acetone wash solutions were still colored with quinizarin after repeated washings, the products were purified by extraction with 100 ml of acetone for several hours in a Soxhlet extractor. Yields ranged from 0.8 to 1.0 g.

Attempts to prepare the zinc chelate by the same method failed. Even when two equivalents of base were added to the reaction solution, no precipitate formed.

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; and nickel, 232.0 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 Infragraph 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 were 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 $10^\circ C\ min^{-1}$. A temperature correction table was used to correct for the non-linearity of the chromel—alumel junction with temperature.

Differential thermal analysis

A Fischer series 200A differential thermalyzer was used in conjunction with a Texas Instruments servo-writer II recorder. The furnace temperature was controlled by using a Fischer platinel thermocouple, while measurement of sample temperatures was made by a Fischer 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 were placed 100 mg of alumina (α-Al_2O_3) 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.

RESULTS AND DISCUSSION

Physical properties

All of the chelates of quinizarin were dark purple powders which were insoluble in common organic solvents.

Composition

Metal analyses for each of the anhydrous chelates are given in Table 1. It was assumed that the difference between the calculated and experimental values for the metal was due to absorbed water. Adsorbed water was confirmed by thermogravimetric data. All of the chelates of quinizarin have a 1 : 1 metal to ligand ratio.

TABLE 1

Composition of the metal chelates of quinizarin

Chelate	Element	Calcd	Exp.	Corrected	Adsorbed H_2O (%)
CuL	Cu	21.06	19.87	21.39	7.1
CoL	Co	19.83	16.35	18.86	13.3
NiL	Ni	19.77	16.31	19.42	16.0

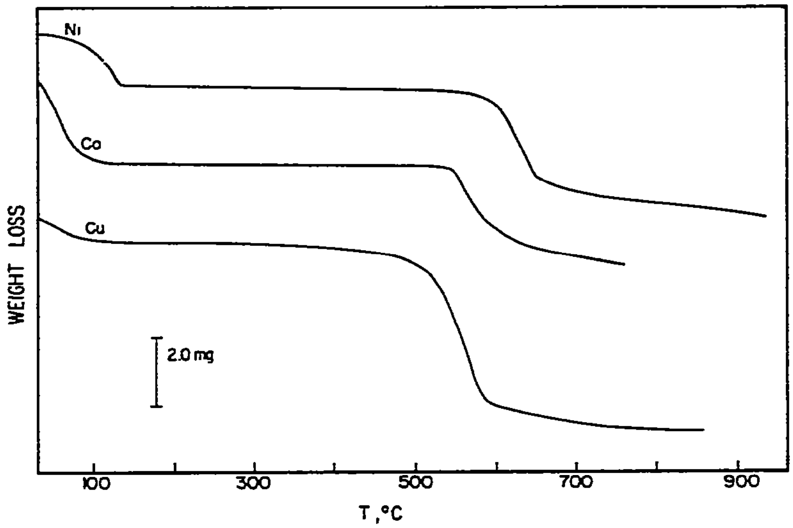


Fig. 1. Thermogravimetric analysis curves of the metal chelates of quinizarin.

Thermal stability

Thermogravimetric analysis curves for the metal chelates of quinizarin are presented in Fig. 1. Differential thermal analysis curves are given in Fig. 2. The procedural decomposition temperatures obtained from these curves are given in Table 2. For comparison, the procedural decomposition temperatures of the naphthazarin chelates are also listed. The decreasing order of

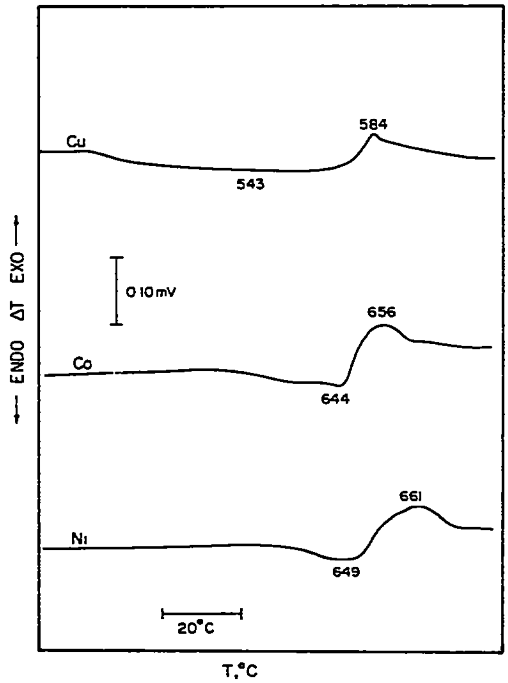


Fig. 2. Differential thermal analysis curves for the metal chelates of quinizarin.

TABLE 2

TGA and DTA procedural decomposition temperatures (°C) for quinizarin chelates; TGA procedural decomposition temperatures (°C) for the naphthazarin chelates (nitrogen atmosphere)

Chelate	Quinizarin		Naphthazarin
	TGA	DTA	TGA
Copper	506	584	260
Cobalt	547	656	272
Nickel	574	661	327

thermal stability for decomposition of the quinizarin chelates by TGA is Ni > Co > Cu. The same order is maintained from DTA studies. This is the same thermal stability order observed for the naphthazarin chelates. Also the addition of a benzene ring to the naphthazarin system has resulted in the increased thermal stability of the metal chelate polymers of quinizarin over those of naphthazarin. The somewhat surprising result is that the quinizarin chelates are, however, about 246°C more thermally stable than the corresponding naphthazarin chelates. This great increase was unexpected since the metal chelates of 2,4-dinitroso-1,3-naphthalenediol [22] are only 10—19°C more stable than the 2,4-dinitrosoresorcinol chelates studied by Bottei and McEachern [24]. It seems, therefore, that the increase in thermal stability in going from a benzene ring system to a naphthalene ring system is not as great as going from a naphthalene ring system to an anthracene ring system. This, however, will have to be checked by further study.

A possible explanation for the large increase in thermal stability of the quinizarin chelates over the naphthazarin chelates might be that the quinizarin polymer chains are longer and allow for more intermolecular interactions (and hence thermal stability) than do the naphthazarin chelates.

In the DTA curves from Fig. 2, it can be seen that all of the chelates exhibited an endothermic peak just before the exothermic decomposition peak. These endothermic peaks could be due to fusion of the polymer chelate just before final decomposition.

An attempt to determine energy parameters from DTA curves employing the method of Borchardt and Daniels [25] failed. The values for E_a produced no reasonable trend, probably due to the broadness and poor definition of the peaks.

Residue analysis

On decomposition all of the metal chelates of quinizarin sublimed. An orange colored substance which quickly condensed on the pyrolysis tube walls in the TGA cell was identified by IR spectroscopy to have the same spectrum as that of the parent ligand, quinizarin. A black residue was produced by each chelate and was identified by X-ray powder diffraction analysis. For the copper and cobalt chelates the residues were found to contain

TABLE 3

Residue analysis of the quinizarin chelates

Chelate	Final product by X-ray	Residue weight (mg)	
		Calcd.	Obs.
Copper	CuO	2.40	4.0
Cobalt	CoO	2.47	>6.7 [a]
Nickel	Ni	1.66	4.8

[a] Continued to decrease at 650°C.

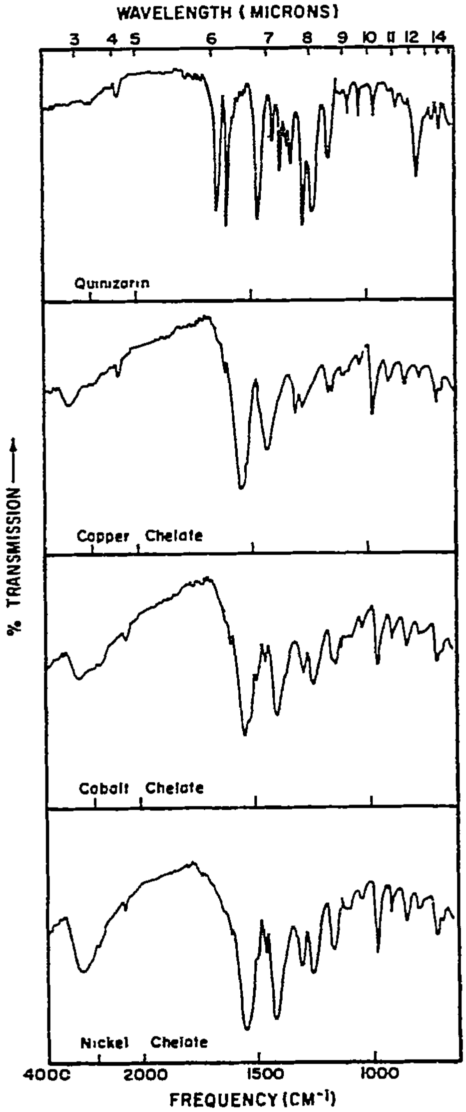


Fig. 3. IR absorption spectra of quinizarin and its chelates.

TABLE 4

ν(C=O) stretching frequencies (cm^{-1}) for quinizarin and its metal chelates

Compound	ν(C=O)	$\Delta\nu$(C=O)
Ligand	1640	
Copper	1540	100
Cobalt	1552	88
Nickel	1550	90

the metal oxide (MO), while the nickel chelate residue was nickel metal. Table 3 presents the residue data. In all cases the observed weight of the residue is greater than the calculated weight for the metal or metal oxide. Treating the residues with acid left a black powder, evidently carbon.

IR studies

The IR spectrum for the parent ligand and the cobalt, copper and nickel chelates of quinizarin are presented in Fig. 3. Spectroscopic bands in the 1700—1400 cm^{-1} region were the most interesting for these compounds. The parent ligand shows a band at 1640 cm^{-1} attributed to the carbonyl group that is adjacent to a hydroxyl group. Bands at 1600 cm^{-1} and 1460 cm^{-1} are associated with vibrations in the aromatic ring system. Upon chelation with a metal the hydrogen bonded carbonyl absorption undergoes a shift to approximately 1550 cm^{-1} due to involvement of both carbonyl groups in the metal bonding. A new and strong band can clearly be seen at approximately 1420 cm^{-1}. This band can be attributed to carbon—carbon bonds within the new chelate ring system produced.

Table 4 lists the ν(C=O) stretching frequencies for the ligand and its metal chelates. It can be seen that the shift in carbonyl frequencies does not follow the relative thermal stability order of the metal chelates. This suggests that indeed, intermolecular interactions and the thermal stability of the ligand are important determining factors in the thermal stability of the quinizarin chelate polymers and not the breaking of the intramolecular M—O bond. This same conclusion was drawn from the IR spectroscopic studies of the metal chelate polymers of 2,6-diaminopimelic acid and 4,4′-diamino-3,3′-dicarboxybiphenyl [26].

In all of the metal chelates there is a shoulder at 1640 cm^{-1}. This band, which is due to a hydrogen-bonded carbonyl entity and is very strong at 1640 cm^{-1} in the parent ligand, seems to indicate that the quinizarin molecule is acting as an end group in the polymers.

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