Journal of Thermal Analysis, Vol. 13 (1978) 231–239

THERMAL STUDIES OF SOME DIVALENT METAL CHELATES OF 8-MERCAPTOQUINOLINE

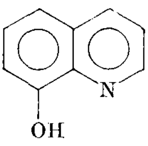
P. W. Bohn and R. S. Bottei

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana, U.S.A.

(Received May 24, 1977)

Divalent metal chelates of 8-mercaptoquinoline (8-MQ) were prepared with copper, nickel, cobalt, zinc, lead, iron, cadmium, and mercury. The thermogravimetry and differential thermal analysis of each of the chelates were studied and a thermal stability order of Cd > Co > Ni > Zn > Pb > Hg > Fe > Cu was obtained. This order is compared with the order obtained with 8-hydroxyquinoline (8-HQ) chelates and the relative thermal stability temperatures of the chelate series are discussed in terms of ligand differences.

Extensive work has been done on the properties of the divalent metal chelates of 8-hydroxyquinoline (8-HQ) (I).



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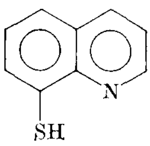

II

Thermal analyses have been done in air [1, 2], *in vacuo* [3], and in argon [4–6]. Following this previous investigators from this laboratory studied chelates of the saturated analog of 8-HQ, 1,2,3,4-tetrahydro-8-hydroxyquinoline [7].

Studies have been conducted into the possible use of the structurally similar ligand 8-mercaptoquinoline (8-MQ) (II) as a specific reagent for certain divalent metal cations [8]. Other studies include the determination of the heats and entropies of formation of the 1 : 1 complexes in aqueous dioxane solution [9] and a study of certain metal sensitive bands in the infrared spectra of the divalent chelates [10]. In view of these studies and the well characterized nature of the 8-HQ chelates it was deemed desirable to study the thermal properties of the divalent metal chelates of 8-MQ.

Experimental

Chemicals. All chemicals used were reagent grade. Commercially available organic solvents were used without further purification. 8-Mercaptoquinoline hydrochloride was obtained from the Sigma Chemical Corp., St. Louis, Missouri.

The hydrochloride was stored under N_2 in a dessicator in a dark bottle which was stored in a refrigerator. The compound was not noticeably decomposed one year after opening.

Preparation of chelates. Approximately 300 mg of the 8-mercaptoquinoline hydrochloride was dissolved in 300 ml of 95% ethanol by refluxing for about 15 minutes. Immediately upon contact with the ethanol the bright yellow hydrochloride turned a deep red color probably due to the formation of the dihydrate [11]. For the various preparations, the salts used (see Table 1) were dissolved in 50 ml of distilled water and added slowly to the refluxing ligand solution through the top of the reflux condenser. The salt solutions were made such that the ligand to metal ratio in solution would be approximately 2 : 1 with a slight excess of metal. Immediate precipitation occurred with the copper, nickel, zinc, lead, cobalt and iron solutions. Several drops of 0.1 *N* NaOH were added to the cadmium and mercury solutions because no precipitation was evident upon addition of the metal solutions. In all cases the solutions were refluxed for about one hour to insure complete reaction. The resulting solutions were filtered through medium porosity 60-ml glass sintered crucibles and the residues were washed with copious amounts of hot distilled water and 95% ethanol. The residues were dried at 40° in vacuum and stored under N_2 in dessicators. Data on the preparation of the chelates are presented in Table 1.

Table 1

Preparation of metal chelates

Chelate	Salt used	Color	Yield, %
$Cu(C_9H_6NS)_2$	$Cu(C_2H_3O_2)_2 \cdot H_2O$	light brown	80.5
$Ni(C_9H_6NS)_2$	$Ni(C_2H_3O_2)_2 \cdot 4H_2O$	dark purple	87.0
$Co(C_9H_6NS)_2$	$Co(C_2H_3O_2)_2 \cdot 4H_2O$	dark brown	80.0
$Zn(C_9H_6NS)_2$	$Zn(C_2H_3O_2)_2 \cdot 2H_2O$	yellow	86.5
$Pb(C_9H_6NS)_2$	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	gold	85.3
$Cd(C_9H_6NS)_2$	$Cd(C_2H_3O_2)_2 \cdot 2H_2O$	yellow	83.2
$Hg(C_9H_6NS)_2$	$HgCl_2$	beige	96.7
$Fe(C_9H_6NS)_2$	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	dark brown	85.5

Infrared spectra. Infrared absorption spectra were taken on a Perkin-Elmer 457 grating spectrophotometer using the KBr disc method. The sample discs were prepared from 1 mg metal chelate and 200 mg KBr.

Thermal analyses. The thermogravimetry work was done with a DuPont 950 thermogravimetric analyzer in conjunction with a DuPont 900 differential thermal analysis recorder. Samples were prepared by air drying the chelate at 110°, grinding 10 to 12 mg of the chelate to a fine powder and loading the platinum boat. The differential thermal analysis work was done with a Fisher 260F oven, a Fisher 360 linear temperature programmer, and a Fisher recorder. Samples were prepared by air drying the chelate at 110° and grinding to a fine powder. Then about 70 mg of the powder was loaded into quartz DTA crucibles and packed by dropping through a 50 cm long pyrex tube after each addition of chelate. All thermal measurements were carried out at a heating rate of 10°/min and under N_2.

X-ray powder patterns. X-ray powder diffraction patterns of the DTA residues were taken with a Norelco diffractometer employing Cu Kα radiation with a nickel filter. Samples were prepared by grinding the cooled DTA residues and loading them into capillaries.

Analyses of chelates. Data on the metal analyses are shown in Table 2. The nickel, copper, cobalt, zinc, lead, and cadmium chelates were analyzed by atomic absorption spectrophotometry using a Varian 1200 spectrometer. Samples were prepared by dissolving enough metal chelate to give a concentration in the middle of the range of standard solutions in 10 ml HNO_3, heating to fumes, and diluting to 1 liter with distilled water.

Table 2

Analysis of metal chelates

Chelate	Theoretical % metal	Actual % metal
Cu $(C_9H_6NS)_2$	16.55	16.39±.14
Ni $(C_9H_6NS)_2$	15.48	15.21±.58
Co $(C_9H_6NS)_2$	15.51	15.39±.34
Zn $(C_9H_6NS)_2$	16.91	17.00±.42
Pb $(C_9H_6NS)_2$	39.27	39.25±.92
Cd $(C_9H_6NS)_2$	25.97	26.05±.94
Hg $(C_9H_6NS)_2$	38.50	41.42±.08
Fe $(C_9H_6NS)_2$	14.84	14.88±.25

Iron was determined by titration with potassium dichromate after pre-reduction with a Jones reductor. Mercury was determined gravimetrically by a method adapted from Hillebrand and Lundell [12] in which the mercury is weighed as $Hg_5(IO_6)_2$.

Results and discussion

Preparations. All chelates were colored powders and nearly quantitative yields were obtained although no special effort was made to obtain them in quantitative yield. All metal analyses were close to the theoretical value calculated for anhydrous complexes. Further support for the anhydrous nature of the chelates lies in the lack of weight loss around 100° in the thermogravimetric curves for all chelates.

Infrared absorption spectra were taken and excellent agreement with the spectra of Mido and Sekido [10] was obtained for the chelates of copper, nickel, cobalt, lead, zinc, and cadmium.

Thermal analyses. All thermogravimetric curves are shown in Fig. 1. The protonated ligand 8-MQ · HCl was run on the thermobalance for reference purposes. Rapid decay was observed beginning around 100° and ending around 190° which left a residue weighing 11.5% of the weight of the original compound. The black residue was probably carbonaceous in nature. Of the thermogravimetric curves of the metal chelates the curves for the nickel, cobalt, zinc, cadmium, and mercury chelates showed only a single break while the chelates of copper, iron and lead showed more complex behavior.

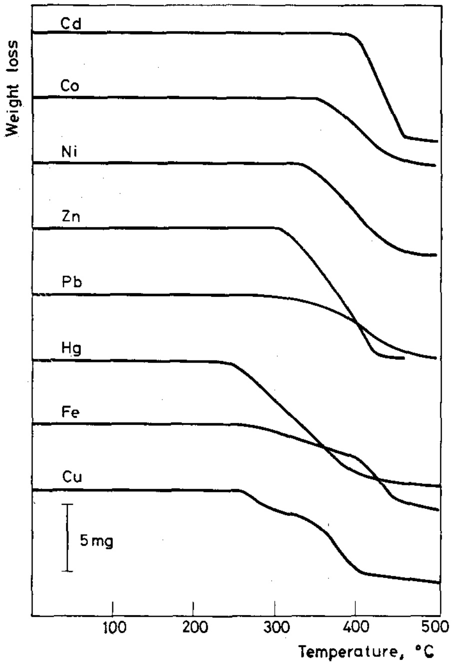

Fig. 1. Thermogravimetric curves of divalent metal chelates of 8-mercaptoquinoline

$Cu(MQ)_2$ gave a thermal stability temperature of 263° but in the region from 294 to 353° the rate of decomposition decreased. Above 353° the decomposition again became more rapid. $Pb(MQ)_2$ gave a thermal stability temperature of 295° but an inflection point occurred at 377° which led to more rapid decomposition. $Fe(MQ)_2$ had the first inflection point at 274° and subsequently accelerated its decomposition at 408°.

The differential thermal analysis curves are shown in Fig. 2. The nickel, zinc, lead, cobalt, and cadmium chelates gave a single endotherm at a somewhat lower temperature than the thermal stability temperature obtained by extrapolating the fairly linear portions of the thermogravimetric curve before and after the initial inflection point. The mercury chelate did not show an endotherm in the vicinity of the thermal stability temperature but did show a single endotherm at 158°. The iron and copper chelates gave two endotherms. In both cases the first endotherm corresponded to the onset of weight loss in the thermogravimetric measurements and the higher temperature endotherm corresponds to the onset of the slope change in the thermogravimetric curve. Thermal data are summarized in Table 3.

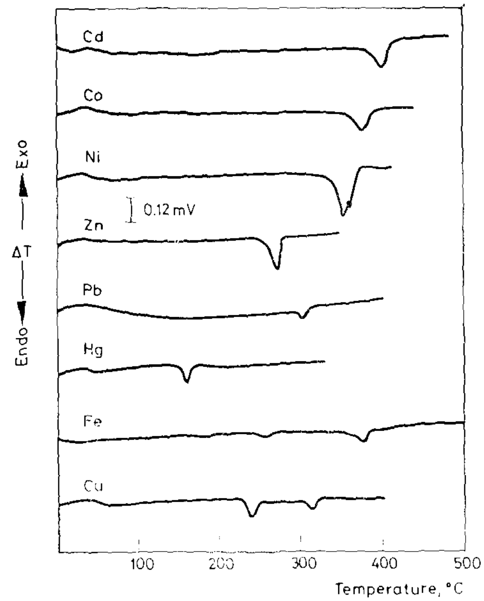

Fig. 2. DTA plots of divalent metal chelates of 8-mercaptoquinoline

Table 3

Thermal analyses

Chelate	Thermal stability temperature, °C	Inflection temperature, °C	Endotherms, °C
Cu $(MQ)_2$	263	353	241 318
Fe $(MQ)_2$	274	408	257 378
Hg $(MQ)_2$	283		158
Pb $(MQ)_2$	295	377	299
Zn $(MQ)_2$	359		277
Ni $(MQ)_2$	371		352
Co $(MQ)_2$	380		369
Cd $(MQ)_2$	402		404

Theoretical weight loss calculations were made on the basis of the conversion of all the metal thio-oxinate to the divalent metal sulfide. The results are shown in Table 4. The actual and theoretical weight loss figures agree fairly well for the chelates of copper, nickel, lead and cadmium. The zinc and mercury chelates lost more weight than was calculated while the iron and cobalt chelates lost less than the theoretical amount.

Table 4

Weight loss calculations

Chelate	Theoretical weight loss, %	Actual weight loss, %
Cu $(MQ)_2$	75.1	66.0
Ni $(MQ)_2$	76.1	68.0
*Co $(MQ)_2$	78.1	46.0
Zn $(MQ)_2$	74.7	97.7
Pb $(MQ)_2$	54.7	47.0
Cd $(MQ)_2$	66.6	79.5
Hg $(MQ)_2$	55.3	84.5
Fe $(MQ)_2$	76.6	57.7

* Calculated from 4 Co $(MQ)_2$ — Co_4S_3

Powder diffraction patterns indicate that the divalent metal sulfide is the major decomposition product present in the DTA residue for all chelates except cobalt. Co_4S_3 is the product of the decomposition of the cobalt chelate. All of the powder diffraction patterns indicate other components besides the metal sulfides, however, due to the complexity of the patterns, they could not be analyzed for all components.

The combined evidence indicates that the thermal stability temperatures obtained from the thermogravimetric curves cannot be absolutely assigned to the onset of thermal decomposition. In all cases the possibilities of sublimation, volatilization, and decomposition exist. Presumably volatilization may occur for any of the chelates and it is not distinguishable by the methods employed. The presence of two breaks in the thermogravimetric curves of the copper, lead, and iron chelates suggests the processes of sublimation and decomposition begin at different temperatures in these chelates. For the copper and iron chelates the presence of DTA endotherms at temperatures just below each of the thermogravimetric inflection points confirms the separate beginnings. For the mercury, zinc, nickel, cobalt, and cadmium chelates it is impossible to tell from the experimental data whether the initial weight loss is due to decomposition, sublimation, or a combination of both. The fairly good agreement between the theoretical and actual weight losses for the cadmium and nickel chelates indicates decomposition is the major process while the large experimental weight losses for the zinc and mercury chelates suggest that sublimation plays a major role for these. The weight loss behavior of the cobalt chelate indicates more complex processes and is not explained. The X-ray powder diffraction pattern of the cobalt chelate DTA residue indicates, among other products, Co_4S_3 which substantiates this notion. In view of these facts the term thermal stability temperature has been used instead of procedural decomposition temperature for these complexes.

The decreasing order of thermal stability as determined from the thermal stability temperatures of the divalent metal chelates of 8-MQ is Cd > Co > Ni > Zn > Pb > Hg > Fe > Cu. In comparison Charles, Perrotto, and Dolan obtained exactly the same order for the divalent metal chelates of 8-HQ with the exception of the mercury and iron chelates which they did not study [6]. In contrast the thermal stability order for the 8-MQ chelates is opposite the order of K_f values for the formation of 1 : 1 complexes in 50% v/v aqueous dioxane by Gutnikov and Freiser [9]. Their order was Cu > Pb > Ni = Zn > Co. This serves to point out the differences encountered working with complexes in solution and metal chelates in the solid state.

Although the same general order of stability is observed for divalent metal chelates of 8-MQ and 8-HQ, the chelates of 8-HQ have thermal stability temperatures which are higher than their 8-MQ analogs by 50 to 90° (Table 5). It is important to note that the study conducted by Charles was done in an Ar atmosphere. However, the relative magnitudes of the temperature differences, not the order, would be the only expected difference. Since the ligands are similar some factors affecting the thermal stability can be isolated and analyzed.

Table 5

Thermal stability temperatures

Metal	Temperature (8–MQ), °C	Temperature (8–HQ)*, °C
Cd	402	480
Co	380	455
Ni	371	420
Zn	359	410
Pb	295	360
Hg	283	
Fe	274	
Cu	263	355

* Values obtained by extrapolating published curves [6].

There are two factors which would tend to make the 8-MQ chelates more thermally stable than their 8-HQ counterparts. In the 8-MQ chelate there are two metal–sulfur bonds whereas in the 8-HQ chelates there are two metal–oxygen bonds. The metal–sulfur bonds would be expected to have a greater covalency than the metal–oxygen bonds. Also, the availability of empty 3d orbitals of the appropriate symmetry on sulfur would result in a greater pi bonding interaction in the metal–

sulfur bonds. This would further strengthen these bonds with respect to metal–oxygen bonds. In the previously mentioned work Gutnikov and Freiser found that the heat of formation of the metal–sulfur bond is greater than the heat of formation of the metal–oxygen bond. This supports these arguments.

Factors which indicate a more thermally stable system with an oxygen containing ligand include evidence on the entropy of formation of 1 :1 complexes and the lower basicity of the ring nitrogen in 8-MQ. In general, it was found that the entropies of formation of the 1 : 1 complexes are about 4 e.u. less for the 8-MQ complexes than for the 8-HQ complexes [9]. This negative entropy effect would, all other things being equal, lessen the thermodynamic and thermal stability of the 8-MQ chelates with respect to the 8-HQ chelates. In addition the greater electron withdrawing power of the sulfur atom with respect to the oxygen atom decreases the basicity of the ring nitrogen. One way of looking at this decreased basicity is as a decreased ability to donate the lone pair of electrons. Since the ability of the nitrogen in 8-MQ to donate its electrons is less than in the 8-HQ the nitrogen–metal bond in the 8-MQ chelates is weaker.

Since the thermal stability temperatures of the 8-MQ chelates are less than the thermal stability temperatures of the 8-HQ chelates the negative entropy effect and the decreased basicity of the nitrogen atom are relatively more important in determining thermal stability than the greater covalency and pi bonding interactions associated with the sulfur atom in the 8-MQ ligand.

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P. W. B. would like to express his appreciation to the Armco Steel Corporation, the National Merit Scholarship Corporation, and the Dow Corning Corporation for their financial assistance during his career at the University of Notre Dame.

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Résumé — Des chélates de métaux bivalents de la mercapto-8 quinoléine (8-MQ) ont été préparés avec le cuivre, le nickel, le cobalt, le zinc, le plomb, le fer, le cadmium et le mercure. Chacun d'eux a été étudié par thermogravimétrie et par analyse thermique différentielle et l'ordre suivant de stabilité thermique a été obtenu: Cd > Co > Ni > Zn > Pb > Hg > Fe > Cu. Cet ordre de succession est comparé à celui obtenu pour les chélates de l'hydroxy-8- quinoléine (8-HQ); les stabilités thermiques des différents termes de la série des chélates étudiés sont comparées et examinées en considérant les différences de coordinants.

Zusammenfassung — Zweiartige Metallchelate von 8-Mercaptochinolinen (8-MQ) wurden mit Kupfer, Nickel, Cobalt, Zink, Blei, Eisen, Cadmium und Quecksilber hergestellt. Die einzelnen Chelate wurden durch Thermogravimetrie und Differentialthermoanalyse untersucht und eine thermische Stabilitätsreihenfolge Cd > Co > Ni > Zn > Pb > Hg > Fe > Cu wurde erhalten. Diese Reihenfolge wird mit der für 8-Hydroxychinolin-Chelate (8-HQ) erhaltenen vergleichen und die relativen Thermostabilitätstemperaturen der Chelatreihen auf Grund der Ligand-Differenzen erörtert.

Резюме — Получены хелатные соединения 8-меркаптохинолина с двухвалентными металлами такими как медь, никель, кобальт, цинк, свинец, железо, кадмий и ртуть. Были изучены термогравиметрия и дифференциальный термический анализ каждого из этих хелатных соединений и был получен порядок их термической стабильности Cd > Co > Ni > > Zn > Pb > Hg > Fe > Cu. Этот порядок сопоставлен с порядком, полученным для хелатных соединений 8-оксихинолина и итносительные температуры термической стабильности этих хелатных серий обсуждены в смысле различия лигандов.