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THERMAL STUDIES OF SOME DIVALENT METAL CHELATES OF CROCONIC ACID*

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The thermal properties of chelates of croconic acid and squaric acid with divalent copper, cobalt, nickel and zinc have been investigated by TG and DTA. The decreasing order of thermal stability for the decomposition of the croconate chelates was Ni > > Zn > Co = Cu and for the squarate complexes, Zn > Co = Cu > Ni. The copper croconate TG showed water loss in two distinct steps. This was rationalized on the basis of the already known Jahn—Teller effect for this molecule. The nickel squarate was thought to have a different structure than the other squarate chelates. Activation energies were calculated for the croconate chelates from their DTA curves.

Croconic acid (4,5-dihydroxy-4-cyclopentene-1,2,3-trione) was one of the first enediolic acids to have been reported. Since its discovery by Gmelin in 1825 [1], it has engaged the attention of many workers. As pointed out by Hirata and coworkers [2], the dianion, $C_5O_5^{2-}$, has an unusual resonance structure. Molecular orbital calculations [3] and vibrational spectra and force constant studies [4] for the croconic acid dianion, as well as for the squaric acid dianion, $C_4O_4^{2-}$, have been performed.

West and Niu [5] have prepared and characterized some divalent and trivalent metal complexes of croconic acid by elemental analysis infrared spectroscopy, and magnetic susceptibility studies. No thermal studies, however, were reported. Structurally the croconate dianion, $C_5O_5^{2-}$, lies between the squarate dianion, $C_4O_4^{2-}$, and the rhodizonate dianion, $C_6O_6^{2-}$. Thermal studies have been performed in this laboratory by Bottei and Greene [6] on some divalent metal chelates of rhodizonic acid and by Tangredi and coworkers [7] on the thermal properties of the divalent metal chelate of squaric acid. It was therefore of interest to study the thermal properties of some croconic acid chelates and compare them where possible to those of the chelates of squaric and rhodizonic acids.

Since it was desirable to compare the procedural decomposition temperatures of the metal chelates of both croconic and squaric acids obtained with the same TG apparatus and in the same atmosphere (nitrogen), the synthesis and thermal studies of the squaric acid metal chelates were repeated.

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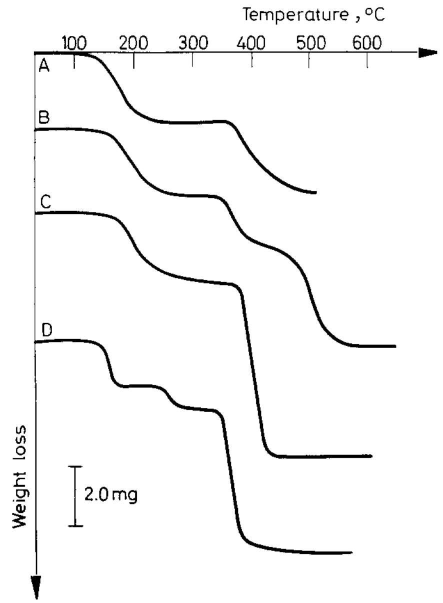


Fig. 1. Thermogravimetric analysis curves for the chelates of croconic acid: A Zinc chelate; B Cobalt chelate; C Nickel chelate; D Copper chelate

Experimental

Preparation of metal chelates. Dipotassium croconate was prepared by oxidation of tetrahydroxy-p-benzoquinone with specially prepared manganese dioxide [8] by a procedure similar to that of Fatiadi and coworkers [9]. The divalent copper, cobalt, zinc and nickel chelates were prepared following the procedure used by West and Niu [5]. The yields ranged from 0.9–1.0 g. The squaric acid chelates were prepared following the procedure of West and Niu [10], with the exception that the disodium salt was used instead of the dipotassium salt. The yields were nearly quantitative.

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. Infrared 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 one mg of sample with 200 mg of potassium bromide. The potassium bromide was dried at 160°.

Thermogravimetry. Thermal curves 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 immerzed 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 SCFH. The nominal heating rate was 10°/minute. A temperature correction table was used for the non-linearity of the chromel-alumel junction with temperature.

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

A stream of lamp nitrogen was passed continuously over the sample during the run at 2 SCFH. In each of seven quartz reference crucibles was placed 100 mg of alumina (α-Al_2O_3) which was previously fired at 1200°. 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 TG 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 Company, Massachusetts. Sample tubes were mounted in a 114.6 mm Debye-Scherer powder camera and irradiated with CuKα radiation for 1–4 hours. The *d* spacings were calculated after the film measurements were corrected for shrinkage. The ASTM tables were consulted to obtain the identity of the TG residues.

Calculation of energy parameters from DTA. The method of Borchardt and Daniels [11] was used. A compensating polar planimeter was used to obtain the areas under the DTA curves.

Results and discussion

Physical properties. All of the divalent metal chelates of squaric acid and croconic acid are powders which are insoluble in cold water, ethanol, and ether. The colors of the chelates are given in Table 1.

Composition of croconate chelates. Metal analyses for each of the croconate chelates are given in Table 1. All of the compounds were trihydrates with the general formula, $MC_5O_5 \cdot 3\ H_2O$.

The crystal structures for the copper and zinc chelates were determined previously by Dahl and coworkers [12]. These complexes are one dimensional coordi-

Table 1

color and Composition of the croconate and squarate chelates

Croconate chelates	Color	Element	Calculated	Experimental
CuL · $3H_2O$	blue	Cu	24.67	24.89
Col · $3H_2O$	purple	Co	23.30	23.08
ZnL · $3H_2O$	bright-yellow	Zn	25.20	25.16
NiL · $3H_2O$	yellow-green	Ni	23.23	23.22
Squarate chelates				
CuL · $2H_2O$	yellow-green	Cu	30.02	29.83
CoL · $2H_2O$	pink	Co	28.47	28.21
ZnL · $2H_2O$	white	Zn	30.62	30.58
NiL · H_2O	green	Ni	31.10	30.62

nation polymers with the infinite chains resulting from the bonding of each metal to two adjacent oxygens of one croconate and to a single oxygen of a second croconate such that two non-adjacent oxygens per croconate are not coordinated to the metal.

Composition of squarate complexes. Metal analyses for the squarate complexes are given in Table 1. With the exception of the nickel squarate chelate, compositions agree with those already reported by West and Niu [10]. The nickel chelate was found to be a monohydrate. This was confirmed by metal and TG analyses. The reported nickel squarate dihydrate of West and Niu was never analyzed for nickel. In the TG studies of the squarates by Tangredi and coworkers [7] it is stated, "The nickel compound is the only one here of questionable behavior, in that on long standing in a desiccator it exhibited a change in the TG curve in which roughly half of the water present came off at a lower temperature than normal. Apparently a partial rearrangement takes place with time."

Without ever placing the nickel squarate in a desiccator no more than one mole of coordinated water per mole of nickel squarate was ever found. This suggests that the nickel squarate exists as a monohydrate and might possibly have a different structural geometry than the copper, cobalt and zinc squarates.

Thermogravimetric studies. TG curves for the croconate complexes are given in Fig. 1. Thermal data are summarized in Table 2. From the curves and thermal data it can be seen that zinc, cobalt and nickel chelates lose the three coordinated waters all at one time while copper chelate, however, loses two molecules at 143° and remaining water molecule at 243°. This observation can probably be explained by the Jahn–Teller distortion of the copper ion in the complex observed in the crystal structure study of Dahl and coworkers [12]. Their comparison of the detailed structural parameters of the homologous compounds, manganese, copper and zinc croconates [12, 13] allows a separation of the metal-oxygen distortions in $C_5O_5Cu(H_2O)_3$ due to the static Jahn–Teller effect from those due to the unsym-

Table 2

Thermal decomposition of divalent metal croconates

Compound	T_{H_2O}*	Weight loss, %	H_2O, % calc.	T_{DEC}**	Final Product (by X-ray)
$CuL \cdot 3H_2O$	143	14.0	14.0 $(-2H_2O)$	343	Cu
	244	7.0	7.0 $(-H_2O)$		
$CoL \cdot 3H_2O$	160	20.7	21.3	343	Co
$NiL \cdot 3H_2O$	164	20.5	21.4	374	Ni and NiO
$ZnL \cdot 3H_2O$	141	20.1	20.8	360	ZnO

* Temperature for loss of H_2O
** Decomposition temperature

metrical oxygen environment of each metal. Inherent in such a comparison is the assumption that all disturbing influences about the central metal except those due to the Jahn–Teller effect are common to all croconate complexes.

The extra stability of the one water molecule in copper croconate cannot be understood from the standpoint of elongation of the bonds between the two axial waters and copper. Crystal structures show that the two oxygen atoms involved in the elongated M–O bonds come not from water molecules but rather from the two croconate molecules around the central copper metal in the $C_5O_5Cu(H_2O)_3$ entity. This can be attributed to either the lower field strength of the croconate oxygens relative to the waters and/or to a stereochemical "locking in" of this configuration in the polymer chain. Indeed the special stability of one water molecule of the copper chelate may arise from interchain hydrogen bonding in the polymer. The structural distortion of the copper chelate due to Jahn–Teller effects allows an oxygen atom of a coplanar croconate entity to get closer to the H_2O molecule of a neighboring copper croconate than is possible in the zinc croconate structure. This closeness results in a stronger hydrogen bond.

The decreasing order of thermal stability for the decomposition of the anhydrous croconate chelates is: Ni > Zn > CO = Cu while that for the anhydrous squarate chelates: Zn > Co = Cu > Ni. This study verifies the stability order of the squarate complexes reported by Tangredi and coworkers [7]. The thermal decomposition temperatures for the squaric acid chelates are: nickel, 255°; cobalt, copper, 311°; and zinc, 368°. With the exception of the nickel squarate chelate (vide infra) the thermal stability order of the metal croconates and squarates is the same. The copper and cobalt croconate chelates are, however, more stable to decomposition than the corresponding squarate chelates. This is probably due to the decrease of ring strain of the organic entity (five-membered ring in croconates versus four-membered ring in squarates). The zinc chelate of croconic acid, however, is about as stable as the zinc chelate of squaric acid. The nickel chelate of croconic acid is much more stable than the nickel squarate.

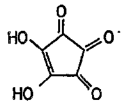
In the squaric acid series the nickel chelate is the least thermally stable. This low thermal stability of a nickel chelate is seldom, if ever, observed. The nickel chelate could perhaps have a different structure than the copper, cobalt or zinc chelates. Because of this difference in structure, the polymer layers of the nickel chelate would have differing interactions than those of the copper, cobalt and zinc chelates. This could account for the observed low thermal stability of the nickel chelate.

The divalent metal chelates of rhodizonic acid cannot be compared directly with the croconate chelates because of their different metal to ligand ratio. Unlike the croconates and squarates, the rhodizonates have a 2 : 1 ratio. The thermal decomposition temperatures for the rhodizonic acid chelates are: copper 183°; cobalt, 345°; zinc, 355°; and nickel, 386°. It is interesting to note that for the cobalt, zinc and nickel chelates, the thermal stability of the croconates and rhodizonates are approximately the same, while there is a difference of about 160° for the copper chelates.

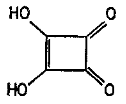
Residue analysis. X-ray diffraction analysis was performed on the TG residues. The results are listed in Table 2. In all cases the observed weight of the residue is greater than the calculated weight for the metal or metal oxide. Dissolution of the residues in acid left a small amount of non-crystalline black powder, which is carbonaceous in nature.

An attempt to obtain a powder pattern of the residue from the 450° region of the cobalt chelate (Fig. 1-B) using molybdenum radiation failed. It was thought that the sloping plateau region in the cobalt chelate thermogram might be due to cobalt oxide formation, Co_2O_3. This might arise from the decomposition of the cobalt croconate as follows:

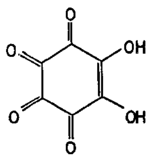
$$2\,CoC_5O_5 \rightarrow Co_2O_3 + 7\,CO + 3\,C$$



Croconic acid



Squaric acid



Rhodizonic acid

Theoretical calculations show that the weight remaining at this plateau should be 3.6 mg; the observed weight remaining was 6.5 mg. Carbon residue might account for this higher value.

Differential thermal studies. Differential thermal analysis plots for the croconate chelates are presented in Fig. 2. The procedural decomposition temperatures as determined from the peak maximum deflections are: copper, 322°; zinc, 336°; cobalt, 363°; and nickel, 406°. Except for the cobalt chelate this is the same thermal stability order as found in the TG studies. It can be seen from Fig. 2 that while the copper, zinc and nickel chelates all display a sharp decomposition exotherm, the cobalt chelate has a long sloping exotherm that starts at 320°. Taking this into account the relative thermal stability order for DTA matches that from the TG thermal studies.

All chelates except the copper chelate exhibit an endotherm just before decomposition. This could be due to the fusion of the chelate just before final decomposition.

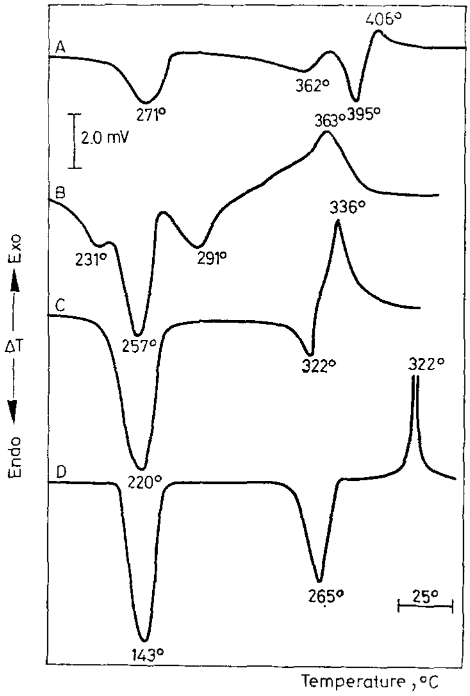


Fig. 2. Differential thermal analysis curves for the chelates of croconic acid: A Nickel chelate; B Cobalt chelate; C Zinc chelate; D Copper chelate

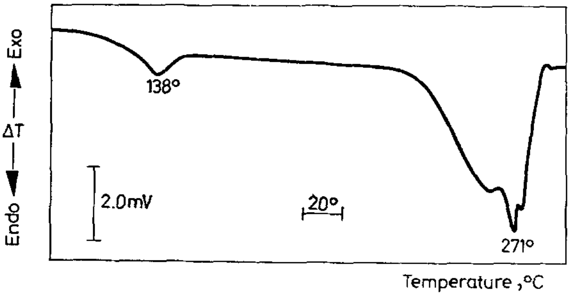


Fig. 3. Differential thermal analysis curve for nickel squarate

The stepwise dehydration of the copper complex, observed clearly in the TG curve, also appears in the DTA curve. The first endotherm (143°) due to the loss of two water molecules, is followed at 265° by the endothermic loss of the remaining water molecule. The two water loss endotherms observed for the cobalt chelate were not reflected by a stepwise weight loss in TG studies.

The cobalt chelate displays an endothermic peak (291°) which could be due to the decomposition of the anhydrous chelate to the cobalt oxide, Co_2O_3, as discussed earlier in the section on residue analysis.

DTA studies of nickel squarate. Tangredi and coworkers [7] have reported the DTA plots of a series of metal squarates. They reported that the nickel squarate gave only an irregular endotherm upon decomposition. This was in contrast to the other squarate complexes which gave only exothermic decomposition peaks. No graphical representation of the DTA plot for nickel squarate was given in Tangredi's work. Fig. 3 shows the DTA plot for nickel squarate prepared in this study. The dehydration peak occurs at 138° while the maximum temperature for the decomposition is 271°. Unlike the other squarate chelates there are no exothermic peaks for the nickel squarate decomposition. This is in agreement with nickel squarate results of Tangredi and coworkers. This observation seems to substantiate that we were both looking at the same complex. Tangredi has interpreted the nickel chelate to be a dihydrate, whereas, the nickel squarate prepared in this study is a monohydrate as evidenced by TG studies and nickel analysis.

Energy parameters from DTA. An attempt was made to calculate activation energies (E_a) for the dehydration reactions of the croconate chelates by the method of Borchardt and Daniels [11]. The energy parameters (kcal/mole) are: copper chelate, 24.6 for loss of two water molecules, 100.6 for loss of the remaining water molecule; cobalt chelate, 36.8; nickel chelate, 20.1; and zinc chelate, 12.5. While the parameters for the copper chelate follow the sequence of that chelate's water loss, no other correlation can be made with the procedural dehydration temperatures obtained from DTA and TG studies. Because of poor curve definition no energy parameters were calculated for decomposition reactions.

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RÉSUMÉ — Les propriétés thermiques des chélates formés par les acides croconique et squarique avec le cuivre, le cobalt, le nickel et le zinc ont été étudiées par TG et ATD. La stabilité thermique des chélates de l'acide croconique décroît dans l'ordre Ni > Zn > Co = Cu et pour l'acide squarique Zn > Co = Cu > Ni. L'étude TG du croconate de cuivre révèle une perte d'eau en deux étapes distinctes. Ceci s'explique par l'effet Jahn—Teller, déjà connu pour cette molécule. Le squarate de nickel possède sans dute une structure différente de celle des autres chélates de l'acide squarique. Les énergies d'activation des chélates de l'acide croconiqus ont été calculées à partir des courbes ATD.

ZUSAMMENFASSUNG — Die thermischen Eigenschaften der Chelate der Crocon- und Squarsäure mit zweiwertigem Kupfer, Cobalt, Nickel und Zink wurden durch TG und DTA untersucht. Die Abnahme der thermischen Stabilität bei der Zersetzung der Croconat-Chelate verlief von Ni > Zn > Co = Cu und der Squarat-Komplexe von Zn > Co = Cu > Ni. Die TG der Kupfercroconate wies eine Wasserabgabe in zwei deutlichen Stufen auf. Diese erklärt sich aufgrund des bereits bekannten Jahn—Teller Effekts für dieses Molekül. Für Nickelsquarat wurde eine andere Struktur angenommen als für die anderen Squaratkomplexe. Die Aktivierungsenergien für die Croconatchelate wurden aus ihren DTA-Kurven berechnet.

Резюме — С помощью TGA и DTA были исследованы термические свойства хелатных соединений кроконовой и скуаровой кислот с двухвалентными медью, кобальтом, никелем и цинком. Порядок уменьшения термической стабильность при разложении хелатных соединений кроконовой кислоты располагается в следующей последовательности Ni > > Zn > Co = Cu, а для комплексов скуаровой кислоты — Zn > Co = Cu > Ni. TGA кроконата меди показывает, что потеря воды протекает в две раздельные стадии. Это было объяснено на основе уже известного для этого соединения эффекта Ян — Теллера. Предполагается, что скуарат никеля имеет другую структуру, чем остальные скуараты. Из кривых DTA вычислены энергии активации для комплексов кроконовой кислоты.