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PREPARATION, IR SPECTRA AND THERMAL DECOMPOSITION OF MALATOAQUO COMPLEXES OF Mn(II), Co(II), Ni(II) AND Cu(II)

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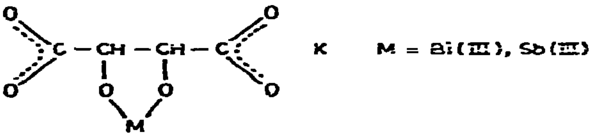
ABSTRACT

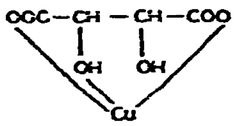
Reaction of malate ion with Mn(II), Co(II) and Ni(II) gave malatotriaquo complexes of these ions, while Cu(II) gave the malatoaquo complex. The structures of these complexes were predicted from elemental analysis and IR spectra. Thermal decomposition of the complexes using TG, DTG and DTA gave supporting evidence for the predicted structures. A correlation between the thermal stability of these complexes and the covalency of the M–O bond was made.

INTRODUCTION

The IR spectra of metal salts of oxy-acids such as lactic, citric and tartaric acids have been studied by several investigators[1a, b, c]. Goulden[2] has found that the OH in-plane bending band of the hydroxyl group in the lactate ion (1275 cm^{-1}) is shifted to 1390 cm^{-1} upon chelation to zinc. Girard and Lecomte[3] have studied the IR spectra of potassium salts of bismuth and antimony tartrates and proposed the structures



Kirschner and Kiesling[4] concluded from the IR spectrum that the structure of copper tartrate is



Several authors have reported recently on the behaviour of malic acid complexes of a few metal ions in aqueous media such as Ni(II), Ba(II) and Cu(II)[5-7]. Parenthetically it is of interest to note that no study has been done on the solid salts obtained through the reaction of malic acid and transition metal ions. We wish to report on the preparation of the complexes $M'M \cdot nH_2O$ (M' = Mn(II), Co(II), Ni(II), and Cu(II); M = malate ion $C_4H_4O_5^{2-}$; $n = 1$ or 3), the IR spectra of these complexes and their thermal decomposition by TG, DTG and DTA.

EXPERIMENTAL

Preparation of the complexes. The complexes malatotriaquonickel(II), malatotriaquomanganese(II), malatotriaquocobalt(II) and malatoaquocopper(II) were prepared according to the following procedure. 50 mmol of sodium hydroxide dissolved in the minimum amount of distilled water were added to a solution containing 25 mmol of malic acid in the minimum amount of water. The solution was placed in an ice bath and an aqueous solution of 25 mmol of MCl_2 was then added with stirring. The copper complex separated after about 5 min, while the other complexes needed longer times and scratching of the container was necessary. The neutral complexes were isolated by filtration, washed with water, ethanol and diethyl ether and dried in vacuo over $CaCl_2$.

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES

Complex	*Color*	*C%*		*H%*		*Metal%*	
		Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
$Mn(C_4H_4O_5)(H_2O)_3$	Pale pink	19.92	20.84	4.15	4.21	22.80	23.79
$Co(C_4H_4O_5)(H_2O)_3$	Violet	19.59	19.80	4.07	3.98	24.04	24.30
$Ni(C_4H_4O_5)(H_2O)_3$	Bluish green	19.61	19.22	4.08	4.03	23.95	24.41
$Cu(C_4H_4O_5)(H_2O)$	Pale blue	22.50	21.90	2.81	2.96	29.74	30.53

TABLE 2

SOME CHARACTERISTIC BANDS OF THE COMPLEXES (cm^{-1})

Material	*νCOO asym.*	*νCOO asym.*	*Δ*	*νC–O alcoh.*	*νO–H st.*
MH_2 (acid)	1740	1412	—	1160	3480
$MnM.3H_2O$	1600	1440	160	1095	3520
$CoM.3H_2O$	1612	1450	162	1088	3500
$NiM.3H_2O$	1610	1445	165	1090	3490
$CuM.H_2O$	1600	1435	165	1100	3508

TABLE 3

TG AND DTA DATA FOR MALATOAQUO COMPLEXES[a]

Process		*TG*			*DTA*		
		Temp. range °C	*Residue %*		*Temp. range °C*	*Peak temp. °C*	*Peak nature*[b]
			Found	*Calc.*			
$(C_4H_4O_5)Mn.3H_2O$ →	$(C_4H_4O_5)Mn$	90–210	77.4	77.59	90–218	160	endo
$(C_4H_4O_5)Mn$ →	$(C_4H_2O_4)Mn$	235–293	69.72	70.12	218–300	280	endo
$(C_4H_2O_4)Mn$ →	MnO_2	297–433	35.62	35.92	300–440	347	exo[c]
MnO_2		433			400–		
$(C_4H_4O_5)Co.3H_2O$ →	$(C_4H_4O_5)Co$	45–235	77.6	77.96	62–200	115	endo[c]
$(C_4H_4O_5)Co$ →	$(C_4H_2O_4)Co$	247–300	70.3	70.61	—	135	endo
$(C_4H_2O_4)Co$ →	Co_3O_4	312–425	32.1	32.72	312–436	344	exo[c]
Co_3O_4					336		
$(C_4H_4O_5)Ni.3H_2O$ →	$(C_4H_2O_4)Ni$	40–295	70.5	70.58	56–220	118	endo
$(C_4H_2O_4)Ni$ →	NiO	303–400	30.82	30.52	295–425	342	exo[c]
NiO		400–					
$(C_4H_4O_5)Cu.H_2O$ →	$(C_4H_2O_4)Cu$	40–180	83.6	83.14	62–180	103	endo
$(C_4H_2O_4)Cu$ →	CuO	190–432	37.4	37.25	190–435	240[d]	exo[c]
CuO		432			435		

[a] Each value is the mean of five determinations.
[b] Endo = endothermic; exo = exothermic.
[c] The process is defined by more than one peak.
[d] In such cases the first peak temperature is considered.

Analyses. Carbon, hydrogen and metal microanalyses were performed by the Alfred Bernhardt microanalytical laboratory, Mulheim, Germany. The results of the analyses are shown in Table 1. No conductivity or NMR spectra of these complexes were measured because of their low solubility in the usual solvents.

IR measurements. The spectra of the complexes were recorded on a Pye Unicam SP 1100 recording IR spectrophotometer. The samples were analysed as KBr discs. The exact position of the peaks was checked by expansion of the peaks and the results are shown in Table 2.

Thermal analyses. TG, DTG and DTA were carried out in a Paulik-Erdey MOM derivatograph under static (air) atmosphere and dynamic nitrogen at a flow rate of 20 ml min^{-1}. The samples weighing 100 mg were placed in platinum crucibles and heated at a rate of 5°C min^{-1}. α-Al_2O_3 was employed as a reference material for the DTA measurements. The results are tabulated in Table 3 and are shown in Fig. 1.

RESULTS AND DISCUSSION

(A) *IR spectra*

All the complexes prepared in this study behave as non-electrolytes in the

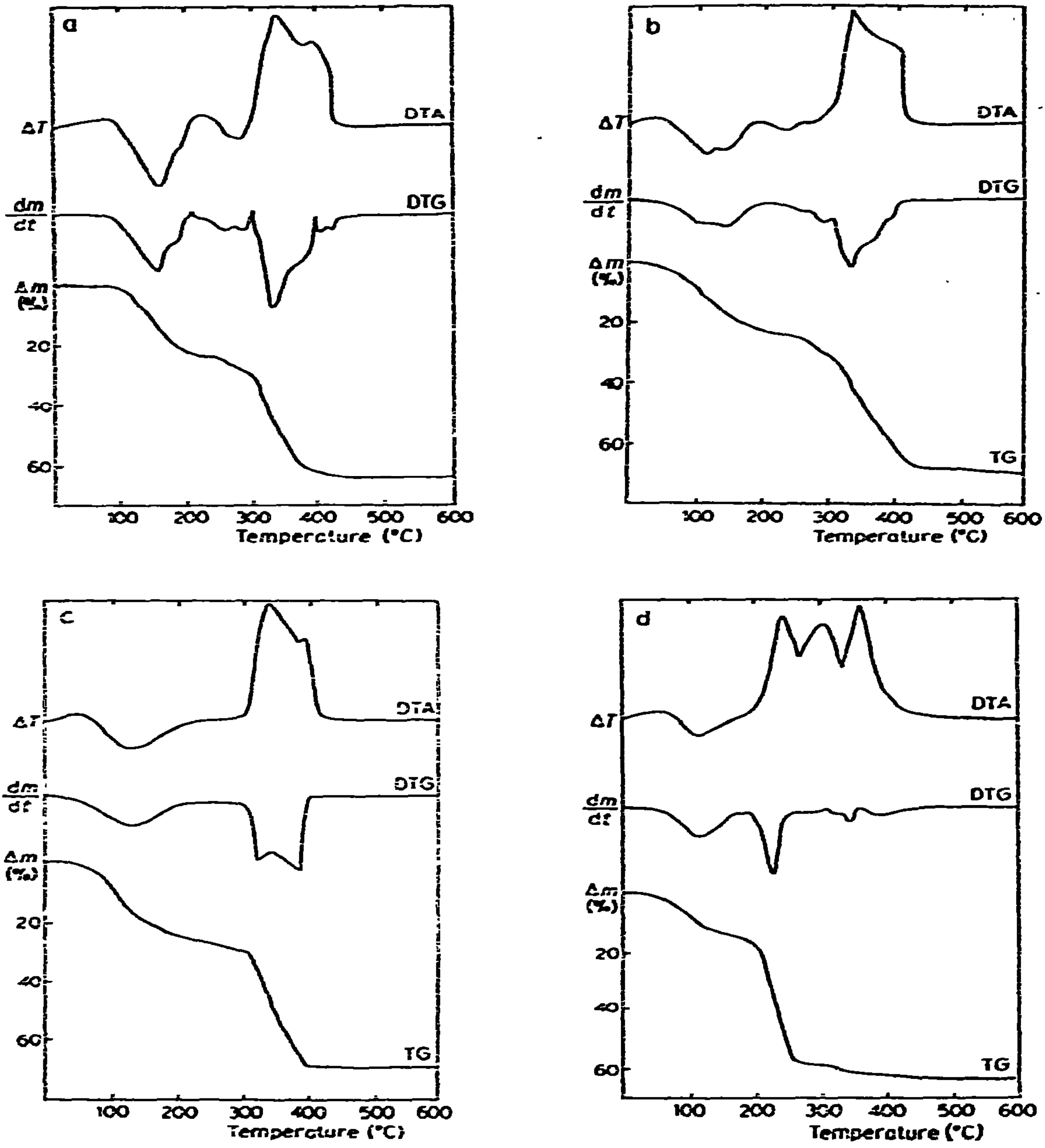


Fig. 1. The TG, DTG and DTA Curves of malato aquo-complexes of (a) Mn(II), (b) Co(II), (c) Ni(II) and Cu(II).

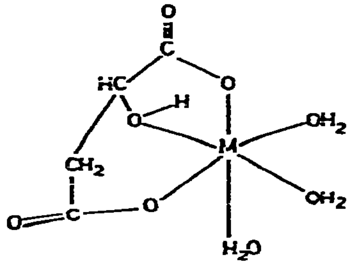
usual organic solvents, i.e., nitrobenzene, DMF, etc. Table 2 lists the $\nu_{COO\ asym.}$, $\nu_{COO\ asym.}$, $\nu_{C-O\ alcoh.}$ and ν_{O-H} stretching bands for malic acid and for the complexes. The IR spectrum of *d*-tartaric acid shows a peak at 1750 cm^{-1}, which is indicative of free carboxyl groups[8]. Upon coordination of *d*-tartrate to copper(II), a shift in this peak to lower frequency (1634 cm^{-1}) was observed. This band was interpreted by Bailar Jr. et al.[9] and by Kirschner[10] as being due to coordinated carboxylate groups. The IR spectrum of malic acid shows the corresponding $\nu_{COO\ asym.}$ at 1740 cm^{-1}, whereas the complexes under investigation show a strong peak at 1600–1612 cm^{-1} and none at 1740 cm^{-1}. It was thus concluded that both carboxylate groups of malic acid are coordinated to the transition metal ion in the complexes.

Comparing the C–O stretching frequencies of the secondary alcohol group of *d*-tartaric acid with that of malic acid, it is found that there appears a sharp peak at 1097 cm^{-1} for the former while the latter appears at 1160 cm^{-1}. It was also noticed that upon coordination of *d*-tartaric acid to Cu(II), this band splits into two peaks at 1080 and 1063 cm^{-1}. This splitting was taken as an indication of a much stronger attraction by the copper ion for one hydroxyl group than for the other[4].

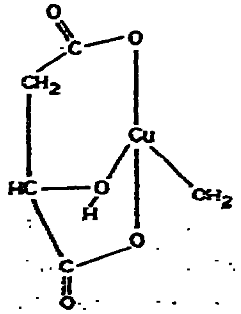
Complexes of malic acid showed one strong band at 1088–1100 cm^{-1}. This is an expected result because in malic acid there is only one alcoholic hydroxyl group and coordination of its oxygen to the metal ion will reduce its C–O stretching frequency. It may also be noted that the O–H bending peak at 1450 cm^{-1} remained almost at the same position for both malic acid and its complexes. This shows that there is no loss of proton by the alcoholic OH group upon coordination.

The metal ions under investigation are capable of extending their coordination number to six. Therefore, from the appearance of new bands of the wagging or rocking[11, 12] mode of coordinated water at 850, 820, 820 and 850 cm^{-1} in the IR spectra of the complexes of Mn(II), Co(II), Cu(II) and Ni(II) respectively, it is concluded that water molecules are coordinated to the metal ions.

By analogy with copper(II) tartrate trihydrate[4], we expect the malatotriaquo complexes of Mn(II), Co(II) and Ni(II) to have the following structure



While the malatoaquocopper(II) complex has the following structure



The increase in the difference between $\nu_{COO\ asym.}$ and $\nu_{COO\ sym.}$, (Δ), has been taken as a measure of increasing covalency of the M–O bond in the tartrate

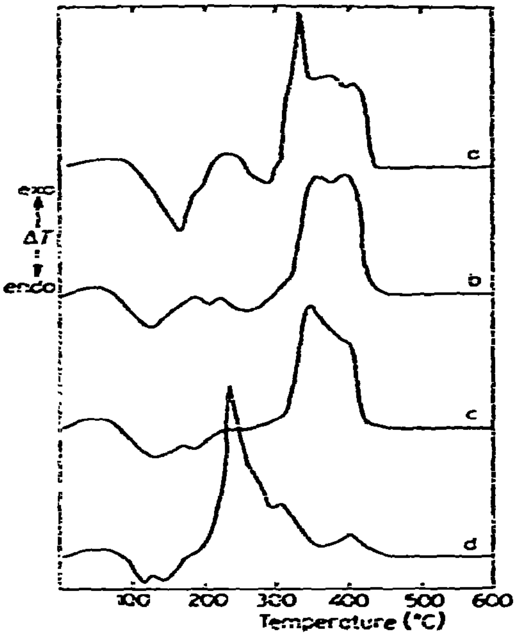


Fig. 2. The DTA curves of malato aquo-complexes of (a) Mn(II), (b) Co(II), (c) Ni(II) and (d) Cu(II), as recorded under a nitrogen atmosphere.

complexes of Co(II), Ni(II), Cu(II), Mn(II), and Zn(II)[13]. The malatoaquo complexes presented a band at 1600–1612 cm^{-1} (Table 2) for $\nu_{COO\ asym.}$, and at 1435–1450 cm^{-1} for $\nu_{COO\ sym.}$. Thus, the covalent character of the M–O bond follows the order: Mn < Co < Ni < Cu.

(B) *Thermal decomposition*

Results of the thermal decomposition of the complexes under investigation were not alike. Furthermore, for the same complex, the thermal decomposition may be changed by changing the atmosphere from air to dynamic nitrogen at a flow rate of 20 ml min^{-1}. The thermoanalytical curves, TG, DTG, and DTA for the complexes of Mn(II), Co(II), Ni(II) and Cu(II) are shown in Fig. 1 (a, b, c and d), while the DTA curves under nitrogen atmosphere are shown in Fig. 2 (a, b, c and d) for the same order of the metal ions. The general feature of the thermal decomposition for Mn(II) and Co(II) complexes are as follows

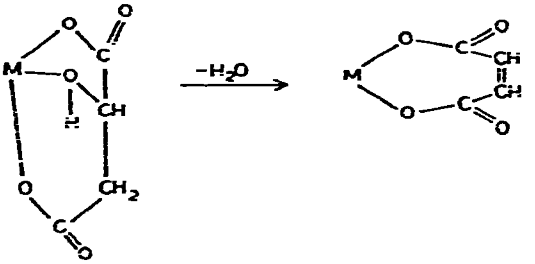
$M(Malato)(H_2O)_3 \rightarrow M(Malate) + 3H_2O$ (1)

$M(Malate) \rightarrow M(Maleate) + H_2O$ (2)

$M(Maleate) \rightarrow$ Metal Oxide (3)

The temperature ranges for reaction (1) are 90–210 and 45–235°C for Mn(II) and Co(II) complexes respectively as shown in Figs. 1 and 2, and Table 3. There are two overlapping peaks for the loss of the three water molecules. This result can be explained by assuming that the structure of the complexes changes from octahedral to tetrahedral $(-2H_2O)$ prior to the loss of the third water molecule.

Reaction (2) occurs at a temperature range 235–293 and 347–300 °C for Mn(II) and Co(II) complexes respectively. Another water molecule is lost in this reaction. In air or nitrogen the reaction occurs as follows



(4)

Both the first and the second reactions are endothermic. Reaction (3) is characterized by two exothermic peak maxima (DTA) in air or in nitrogen for both Mn(II) and Co(II) complexes (Figs. 1 and 2) which suggests that decomposition of the complexes is a multistep reaction. The residue of this decomposition was found to be MnO_2 and Co_3O_4 above 433 °C and 425 °C respectively (Table 3).

The thermal decomposition curves (TG, DTG, and DTA) in air and nitrogen for Ni(II) and Cu(II) complexes are shown in Figs. 1 (a, c and d) and 2 (c and d) and the data are presented in Table 3. The structure of the malatotriaquonickel complex is octahedral, while that for the Cu(II) complex is tetragonal. In both complexes, reactions (1) and (2) overlap. This is represented as

$$M(Malate)(H_2O)_n \rightarrow M(Maleato) + (n + 1)\ H_2O \qquad (5)$$

(where $n = 3$ in the Ni(II) complex and 1 in the Cu(II) complex).

The thermal decomposition of the maleatonickel(II) complex is similar in air and in nitrogen, while for the corresponding copper(II) complex different reactions occur. In air the third peak is the highest, while in nitrogen the DTA shows three overlapping exothermic peaks progressively decreasing in height. The last two peaks are much smaller in nitrogen than in air which indicates that in the last stages of decomposition atmospheric oxygen plays an important role. The decomposition of the maleatonickel(II) and copper(II) are exothermic and the residue was NiO and CuO (Table 3) above 400 and 432 °C respectively.

If the initial decomposition temperature is taken as a measure of the thermal stability of the complexes, we can conclude that the stability of the malate complexes decreases in the following order; Mn(90°) > Co(45°) > Ni(40°) ≈ Cu(40 °C), which is exactly opposite to the order of increasing covalency of the M–O bond.

REFERENCES

1 (a) Y. Kuroda and M. Kuba, *J. Phys. Chem.*, 64 (1960) 759; (b) K. Nakamoto, Y. Morimoto and A. B. Martell, *J. Am. Chem. Soc.*, 83 (1961) 4528; (c) M. J. Schmelz, I. Nakagawa, S. Mizushima and J. V. Quagliano, *J. Am. Chem. Soc.*, 81 (1959) 287.

2 J. D. S. Goulden, *Spectrochim. Acta*, 16 (1960) 715.

3 M. Girard and J. Lecomte, *C.R. Acad. Sci.*, 241 (1955) 292; 240 (1955) 415.

4 S. Kirschner and R. Kiesling, *J. Am. Chem. Soc.*, 82 (1960) 4174.

5 N. E. Milad, S. E. Morsi, S. T. Soliman and L. M. N. Saleem, *Egypt J. Chem.*, (1973) 101.
6 N. E. Milad, S. E. Morsi, S. T. Soliman and L. M. N. Saleem, *Egypt J. Chem.*, (1973) 395.
7 A. R. Das and V. S. K. Nair, *J. Inorg. Nucl. Chem.*, 37 (1975) 2121.
8 N. B. Colthup, *J. Opt. Soc. Am.*, 40 (1950) 397.
9 D. H. Busch and J. G. Bailar Jr., *J. Am. Chem. Soc.*, 75 (1953) 4574.
10 S. Kirschner, *J. Am. Chem. Soc.*, 78 (1956) 2372.
11 I. Game, *Bull. Chem. Soc. Jpn.*, 34 (1961) 760.
12 G. Sartri, C. Furlani and A. Damiani, *J. Inorg. Nucl. Chem.*, 8 (1959) 119.
13 A. Carillo, P. Vieles and A. Banniol., *C.R. Acad. Sci. Ser. C*, 274 (1972) 912.