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Thermochemical and Spectral Properties of Hydrates of Co(II), Ni(II) and Cu(II) Maleate. Crystal Structure of Co(II) Maleate Trihydrate

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The crystal and molecular structure of Co(II) maleate trihydrate, $Co(C_4H_2O_4)\cdot 3H_2O$, was determined by direct method and Fourier techniques. The structure was refined by full-matrix least-squares methods to a weighted R factor of 0.0263, based on independent reflections. The compound is a three-dimensional coordination polymer with distorted octahedron geometry at each cobalt(II) centre. Each cobalt atom is six-coordinated through two oxygen atoms from water molecules and four oxygen atoms from four different maleate groups. The thermal decompositions of Co(mal)$\cdot 3H_2O$, Ni(mal)$\cdot 3H_2O$ and Cu(mal)$\cdot H_2O$ (mal = maleate) have been investigated by means of TG, DTG, DSC and IR spectra. The release of volatile molecules after heating is either a three-step process for Co(mal)$\cdot 3H_2O$ and Ni(mal)$\cdot 3H_2O$ or a two-step process for Cu(mal)$\cdot H_2O$.

Key words: hydrates, maleate, transition metal, X-ray analysis, TG, DSC and IR spectra

Transition metal derivatives of unsaturated dicarboxylic acids rank among abundant groups of compounds that are of interest from the viewpoint of inorganic, macromolecular and coordination chemistry [1–4]. This is determined in many respects by the practical significance of maleates, which are used as coatings with specific properties and also as adhesion promoters in rubber technologies [5,6].

In previous papers we described the influence of the temperature on the curative interactions with the participation of Cu(II) and Co(II) carboxylates as adhesive promoters [7–9]. The effect of the structure of metal carboxylate complexes (including coordinate or lattice water molecules) on the thermal decomposition is of interest from the practical point of view. Therefore, this paper describes the preparation of the Co(II), Ni(II) and Cu(II) salts of maleic acid (HOOC-CH=CH-COOH), along with an X-ray analysis of Co(mal)$\cdot 3H_2O$, spectral and thermal analyses (TG, DTG, DSC) of all compounds prepared.

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EXPERIMENTAL

Preparation of the compounds: Co(mal)·$3H_2O$, Ni(mal)·$3H_2O$ and Cu(mal)·H_2O were prepared in the reaction between the aqueous solution of the sodium salt (pH 7) of maleic acid (0.05 mol) with the aqueous solution of M(II) sulphate (0.05 mol), where M(II) = Co, Ni or Cu. The fine compounds which precipitated were filtered off (*ca* 75% yield), washed with cold water and dried at room temperature. The crude products were recrystallized from hot water – a yield of 60%. We found violet crystals of $Co(C_4H_2O_4)\cdot 3H_2O$, the green $Ni(C_4H_2O_4)\cdot 3H_2O$ and blue $Cu(C_4H_2O_4)\cdot H_2O$. The analytical data confirm the calculated composition of the prepared complexes.

Structure determination: Data collection and cell refinement of the $Co(C_4H_2O_4)\cdot 3H_2O$ were carried out using SYNTEX $P2_1$ diffractometer software [10]. Intensity data were connected for Lorentz and polarization factors. The structure was solved by the heavy atom method with SHELXS86 [11] and subsequent Fourier synthesis using SHELXL93 [12], anisotropic thermal parameters were refined for all non-hydrogen atoms. Geometrical analysis was performed using SHELXL93 [12]. The structure was drawn using ORTEP [13]. The final parameters after refinement are summarized in Table 1. Selected inter-atomic distances and bond angles are given in Table 2. Supplementary material including hydrogen atomic coordinates ($\times 10^4$) and anisotropic displacement parameters for the non-hydrogen atoms (Å$\times 10^3$) have been deposited at the Cambridge Crystallographic Data Centre (CCDC 160788). Observed and calculated structural factors are available on request from the authors.

Table 1. Crystal data and structure refinement for $[Co(C_4H_2O_4)]\cdot 3H_2O$.

Identification code	puch
Empirical formula	$C_4H_8CoO_7$
Formula weight	227.04
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*Cc*
Unit cell dimensions	a = 8.118(2) Å
	b = 13.175(3) Å β = 115.17(3)°
	c = 7.4970(10) Å
Volume	725.7(3) $Å^3$
Z	2
Calculated density	2.078 Mg/m^3
Absorption coefficient	2.364 mm^{-1}
F(000)	460
Crystal size	0.65 × 0.40 × 0.20 mm
θ range for data collection	3.09 to 32.56°
Limiting indices	$0 <= h <= 12, -19 <= k <= 19, -11 <= l <= 10$
Reflections collected/unique	1605/1369 [*R*(int) = 0.0535]
Completeness to θ = 32.56	98.9 %
Absorption correction	Experimental

Table 1 (continuation)

Max. and min. transmission	0.346 and 0.502
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1369/2/109
Goodness-of-fit on F^2	1.050
Final R indices [I>2σ(I)]	$R1 = 0.0263$, $wR2 = 0.0657$
R indices (all data)	$R1 = 0.0273$, $wR2 = 0.0659$
Absolute structure parameter	0.041(16)
Largest diff. peak and hole	0.754 and –0.789 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for $Co(C_4H_2O_4)\cdot 3H_2O$.

Co(1)–O(4)	2.067(2)
Co(1)–O(5)#1	2.0730(19)
Co(1)–O(7)	2.074(3)
Co(1)–O(2)	2.0857(19)
Co(1)–O(6)	2.087(2)
Co(1)–O(3)#2	2.137(2)
O(2)–C(8)	1.250(3)
O(3)–C(8)	1.261(3)
O(4)–Co(1)–O(5)#1	82.28(8)
O(4)–Co(1)–O(7)	91.26(10)
O(5)#1–Co(1)–O(7)	95.12(11)
O(4)–Co(1)–O(2)	86.53(8)
O(5)#1–Co(1)–O(2)	168.79(8)
O(7)–Co(1)–O(2)	84.53(11)
O(4)–Co(1)–O(6)	176.84(8)
O(5)#1–Co(1)–O(6)	100.81(8)
O(7)–Co(1)–O(6)	89.18(10)
O(2)–Co(1)–O(6)	90.39(8)
O(4)–Co(1)–O(3)#2	91.89(8)
O(5)#1–Co(1)–O(3)#2	84.18(8)
O(7)–Co(1)–O(3)#2	176.66(11)
O(2)–Co(1)–O(3)#2	96.80(9)
O(6)–Co(1)–O(3)#2	87.75(9)
C(8)–O(2)–Co(1)	129.21(16)

Table 2 (continuation)

C(8)–O(3)–Co(1)#3	130.55(18)
C(11)–O(4)–Co(1)	132.43(16)
C(11)–O(5)–Co(1)#4	127.80(16)
O(2)–C(8)–O(3)	123.7(2)
O(2)–C(8)–C(9)	122.2(2)
O(3)–C(8)–C(9)	114.0(2)
C(10)–C(9)–C(8)	127.5(2)
C(9)–C(10)–C(11)	126.3(2)
O(4)–C(11)–O(5)	123.1(2)
O(4)–C(11)–C(10)	122.2(2)
O(5)–C(11)–C(10)	114.7(2)

Symmetry transformations used to generate equivalent atoms:
#1 x – 1/2, –y + 1/2, z – 1/2 #2 x, –y + 1, z – 1/2
#3 x, –y + 1, z + 1/2 #4 x + 1/2, –y + 1/2, z + 1/2.

Thermal studies: Thermal decomposition of the complexes, under dynamic conditions, was studied using Derivatograph (Type OD 102, MOM Budapest). The sample (100 mg) was heated in static air at a heating rate of 5°C min^{-1} in open ceramic crucibles from 20°C to 500°C. The Perkin-Elmer Differential Scanning Calorimeter DSC-7 was used for DSC studies with a sample weight *ca* 5 mg, pure nitrogen and a scanning rate of 10°C min^{-1}. Calibration of the temperature and change of enthalpy axes were made with pure indium with the melting point of 156.6°C and $\Delta_f H = 28.47$ Jg^{-1}.

Spectral measurements: The IR spectra were measured in Nujol suspension in the region of 4000–200 cm^{-1} with the MAGNA FTIR 750 spectrometer (Nicolet).

RESULTS AND DISCUSSION

All three complexes are hydrated. The thermal decomposition of these compounds was initiated by elimination of water. The loss of volatile components occurs (on the TG and DTG curves) in three steps for $Co(mal)\cdot 3H_2O$ and $Ni(mal)\cdot 3H_2O$ and in two steps for $Cu(mal)\cdot H_2O$ (Table 3). $Co(mal)\cdot 3H_2O$ and $Ni(mal)\cdot 3H_2O$ are stable up to 70°C, when starts their thermal decomposition. TG curves show two bendings at $Co(mal)\cdot 3H_2O$ at ~ 80, 220°C and $Ni(mal)\cdot 3H_2O$ at ~ 120, 200°C corresponding to two intermediate decomposition products, respectively: $M(mal)\cdot 2H_2O$ and M(mal), where M = Co(II) or Ni(II). The first and the second steps are attributed to the gradual dehydration process. The third step is attributed to the decomposition of the anhydrous salt to CoO or NiO as the final products. The stoichiometry of thermal decomposition of these compounds can be represented as:

$$\mathrm{M(mal)\cdot 3H_2O} \xrightarrow[(1)]{70\text{–}130^\circ\mathrm{C}} \mathrm{M(mal)\cdot 2H_2O} \xrightarrow[(2)]{130\text{ –}260^\circ\mathrm{C}} \mathrm{M(mal)} \xrightarrow[(3)]{260\text{–}450^\circ\mathrm{C}} \mathrm{MO,\ (M = Co(II),\ Ni(II))}$$

$Cu(mal)\cdot H_2O$ is stable up to 100°C, when decomposition to CuO starts, as final solid product. The stoichiometry of $Cu(mal)\cdot H_2O$ can be expressed by:

$$\mathrm{Cu(mal)\cdot H_2O} \xrightarrow[(1)]{100\text{–}200^\circ\mathrm{C}} \mathrm{Cu(mal)} \xrightarrow[(2)]{200\text{–}400^\circ\mathrm{C}} \mathrm{CuO}$$

The observed residual mass for these compounds corresponds approximately to MO as the final product of thermal decompositon. The experimental data are in good agreement with calculated data.

Table 3. Data on thermal decomposition of $M(mal)\cdot xH_2O$.

Starting compound	Resulting intermediate	TG / %		DTG results	DSC results	
		Calcd.	Found	T_p/°C	T_p/°C	ΔH/kJ mol^{-1}
$Co(mal)\cdot 3H_2O$	$Co(mal)\cdot 2H_2O$	7.93	8.00	125	120	57.9
	Co(mal)	15.87	16.00	170	169	145.0
	CoO	41.17	40.00	315	–	–
$Ni(mal)\cdot 3H_2O$	$Ni(mal)\cdot 2H_2O$	8.22	8.50	125	128	65.2
	Ni(mal)	15.88	16.00	208	220	143.1
	NiO	41.22	40.00	320	–	–
$Cu(mal)\cdot H_2O$	Cu(mal)	9.24	9.00	190	171	74.8
	CuO	50.12	50.00	260	–	–

The values of the decomposition enthalpies ($\Delta_{dec}H$) of the solid complexes (DSC data) can be used in the investigation of some bond strengths in the compounds (Table 3). Variations in the values of $\Delta_{dec}H$ registered for the compounds studied with various metal ions may, however, be attributed not only to changes in bond strengths, but also to recrystallization processes, polarization effects, and especially to crystal lattice energy [14,15]. The $\Delta_{dec}H$ values corresponding to the release of one mole of water (the first step of decomposition) from these compounds fall in the order (according to M): Co (II) < Ni (II) < Cu (II) (–1 mole of H_2O).

In the temperature range of 50–240°C, the DSC curve of $Co(mal)\cdot 3H_2O$ exhibits maxima at ~120 and 169°C, DSC curve of $Ni(mal)\cdot 3H_2O$ exhibits maxima at ~128 and 220°C and DSC curve of $Cu(mal)\cdot H_2O$ exhibits one maximum at ~171°C (Table 3). These maxima correspond to the dehydration processes.

Table 4. Important vibrations (cm^{-1}) in infrared spectra of the compounds studied.

Compound	ν(OH)	ν(C–H)	ν(C=C)	δ(HOH)	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta(\nu_{as} - \nu_s)$	$\nu(M–OH_2)$
Co(mal)·3H_2O	3554, 3370	2866	1682	1603	1546	1434	112	349
Co(mal)·2H_2O	3554, 3366	2700	1668	1600	1541	1462	79	370, 349
Co(mal)	–	2700	1660(sh)	–	1551	1456	95	–
Ni(mal)·3H_2O	3549, 3358	2720	1677	1606	1545	1436	109	351
Ni(mal)·2H_2O	3546, 3369	2730	1647	1600	1580, 1536	1444, 1433	120(ϕ)	378, 350
Ni(mal)	–	2750	1650(sh)	–	1558	1432	126	–
Cu(mal)·H_2O	3541, 3398	2730	1655, 1624	1610	1577, 1547	1443, 1425	128(ϕ)	376
Cu(mal)	–		1656, 1624	–	1578, 1548	1442	106	–

sh – short, ϕ – average, s – symmetric, as – asymmetric.

The IR spectra of all three compounds showed absorption bands within the range of 3554–3200 cm^{-1}. These frequencies correspond to the asymmetric and symmetric OH stretching. These bands clearly confirm the presence of crystal water in these compounds. The absorption bands which occur in the range 1000–600 cm^{-1} (rocking and wagging stretching) and ~ 350 cm^{-1} (ν(M–O)) confirm the presence of coordinated water in these complexes [15,16]. After the first step of dehydration ($-H_2O$) of compounds $Co(mal)\cdot 3H_2O$ and $Ni(mal)\cdot 3H_2O$, new band at ~ 370–380 cm^{-1} is observed. This indicates that already the release of 1 mole of H_2O is accompanied by structural changes. After the second step of the dehydration ($-2H_2O$), all these peaks disappeared and M(II) maleate was formed. The important infrared spectral data of the starting compounds and their intermediate decomposition products are reported in Table 4.

Carboxylate ions can coordinate to the metal ions in a number of ways, such as unidentate, bidentate (chelating or bridging). The analysis of COO^- group bands allowed for the determination of the parameter $\Delta(COO^-) = \nu_{as}(COO^-) - \nu_s(COO^-)$. The magnitude of $\Delta(COO^-)$ has been aproximately used [16] as a criterion of the way by which the carboxylates bind to the metal ions. From the IR spectra of the compounds studied, the calculated values of ΔCOO^- were in the range 109–128 cm^{-1} for the starting compounds. The values $\Delta(COO^-)$ correspond to the polymeric (bridging) bonded maleate groups, which is in agreement with the X-ray structure data of the starting complexes.

The values of ΔCOO^- were in the range 79–126 cm^{-1} for the compounds after heating. The values $\Delta(COO^-)$ changed slightly after heating, being below 150 cm^{-1}. Thus, we assume, that the polymeric structure will be remained and structures, which are loosing or which lost the molecule of water, will be next to cross-link. We assume, that the cross-link causes the changes in $\nu(COO^-)$ vibrations, but the coordination of maleate groups stays bridging to M(II) ions. In compounds $Ni(mal)\cdot 2H_2O$, $Cu(mal)\cdot H_2O$ and Cu(mal) a splitting of absorption bands $\nu(COO^-)$ is observed. Splitting of $\nu_{asym}(COO^-)$ absorptions has been attributed to many causes, *e.g.* two coordination modes, polymer-dimer equilibria, coupling between neighbouring carboxylate groups, or “solid state effects“ [18], however, we prefer the third and the fourth cases for splitting of absorption bands $\nu(COO^-)$ for our compounds.

The crystal and molecular structure of the Co(II) maleate trihydrate was determined by X-ray analyses. The crystallographic data show that the complex is monoclinic with the space group *Cc* (Table 1). The structure and numbering scheme of the compound are shown in Fig. 1. The coordination geometry around the central cobalt(II) atom is a distorted octahedron. Three of the square-planar coordination sites are occupied by the carboxylate anion from maleic groups, a carboxylate O(2), O(3a) and O(5a) atoms (O(2)–Co 2.0857(19), O(3a)–Co 2.137(2) and O(5a)–Co 2.0730(19)). The fourth site of the square plane is occupied by an O(7) atom from a water molecule at a distance O(7)–Co equal to 2.074(3) Å. The fifth coordinated atom is an O(6) atom of a second water molecule O(6)–Co at a distance of 2.087(2)) Å. The sixth coordinated atom is an O(4) atom of carboxylate anion (O(4)–Co 2.067(2)).

These atoms lie at the apexes of the octahedron. The coordination bond distances and angles around the Co(II) atom are given in Table 2. The O(3a) and O(5a) atoms are from the other carboxylate groups and the O(1) atom is from the non-coordinated water molecule. The chelate seven-membered ring are forming the atoms Co, O(4), O(2), C(8), C(9), C(10) and C(11). The planar structure of the maleate ligand is stabilized by the intramolecular hydrogen bond. In this case, maleic acid acts as the tetradentate ligand similarly to the Cu(II) maleate complex [17], where the copper atom is in the five-coordination square-pyramidal surrounding.

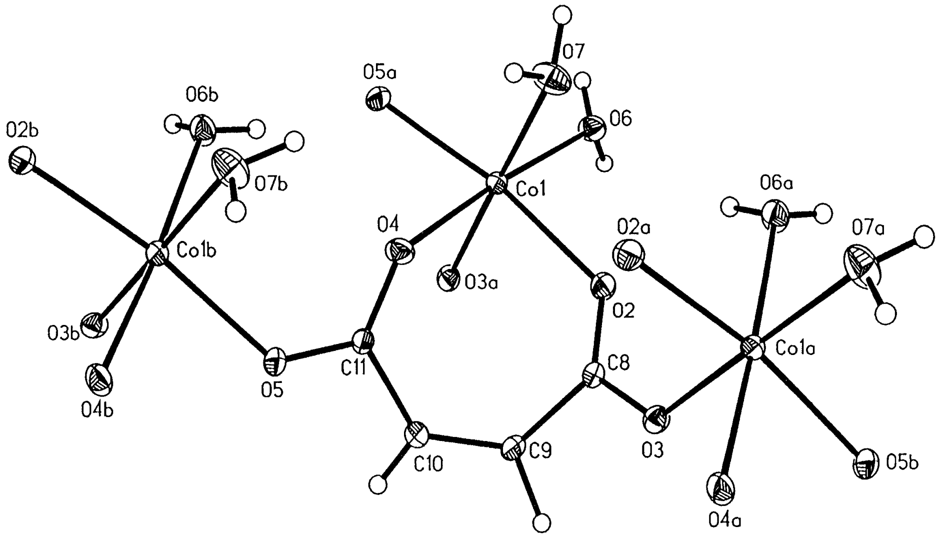

Figure 1. ORTEP plot of $Co(C_4H_2O_4)\cdot 3H_2O$.

It can be assumed, on the basis of X-ray analysis, that each crystal constitutes one macromolecule made up of structural units $[CoC_4H_2O_4\cdot 2H_2O]_n\cdot nH_2O$, which are connected into layers through oxygen O(3) atom of the carboxylate anion. The three-dimensional macromolecule is rich in the hydrogen bond system. It contains two types of hydrogen atoms participating in the formation of this system. They are hydrogen atoms from the non-coordinated water and hydrogen atoms from one coordinated water. Of interest is also the other coordinated water, which does not participate in the hydrogen bond.

The coordination geometry around central nickel(II) atom is approximately an octahedron in the $Ni(C_4H_2O_4)\cdot 3H_2O$ complex, as central cobalt(II) atom in $Co(C_4H_2O_4)\cdot 3H_2O$ complex, as reported previously [2]. On the other hand, in $Cu(C_4H_2O_4)\cdot H_2O$ the copper(II) atom is in a five coordinate square – pyramidal environment, where the ligands are a water molecule, a chelate ring and two oxygen atoms of two other maleate groups. In the basal plane the average copper–oxygen bond length is 1.99 Å. Each maleate group is bonded to three copper atoms to form a polymeric sheet. The sheets are joined by a hydrogen bond [17].

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