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Synthesis and Characterization of Coordination Compounds of 3*d*-Metal Malonates with Phenylacetyl Hydrazide. Crystal Structure of $[Cu(L)_2][Cu(Mal)_2] \cdot 4.5H_2O$ (L Is Phenylacetyl Hydrazide, Mal^{2-} Is Malonic Acid Anion)

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Abstract—Three phenylacetyl hydrazide malonate complexes $[M(L_3)](Mal)$ of cobalt(II) (**I**), nickel(II) (**II**), and zinc(II) (**III**), as well as complex $[Cu(L)_2][Cu(Mal)_2] \cdot 4.5H_2O$ (**IV**) are synthesized. The obtained compounds are characterized by chemical analysis, IR spectroscopy, diffuse reflectance spectroscopy, and thermogravimetry. Compound **IV** (where L is phenylacetyl hydrazide, and Mal^{2-} is malonic acid anion) is studied by X-ray diffraction analysis (CIF file CCDC no. 1844502).

Keywords: synthesis, IR spectroscopy, diffuse reflectance spectroscopy, thermogravimetry, X-ray diffraction analysis, phenylacetyl hydrazide, 3*d*-metal malonates

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INTRODUCTION

The behavior of a malonate anion (malonic acid dianion) differs from that of anions of other dicarboxylate ligands. It was found [1] that the malonate anion with 3*d*-metal ions can manifest various coordination modes: bidentate, bidentate + monodentate, bidentate + bis(monodentate), and bidentate + bis(monodentate) + μ-oxo. In the last case, one of the oxygen atoms acts as a μ-oxo bridge between two metal centers in addition to the bidentate and bis(monodentate) coordination modes. We have previously synthesized and structurally characterized $[Co(R)(Mal)(H_2O)_2]H_2O$ [2] (R is benzhydrazide, and the malonate anion enters the composition of the intracomplex compound to form a chelate six-membered cycle [2]) and $[Ni(Z)_2][Ni(Mal)_2(H_2O)_2]_2 \cdot 3.51H_2O$ (Z is thiosemicarbazide, and the malonate ion also forms six-membered rings but in the composition of the complex anion [3]). A few complexes with phenylacetyl hydrazide were described, in particular, we determined the structures of the 1 : 3 hydrated nickel complexes based on benzoate [4] and 5-sulfosalicylate [5].

In this work, we describe the syntheses, IR and diffuse reflectance spectra, and thermogravigrams of the malonate complexes with phenylacetyl hydrazide $[M(L)_3]Mal$ (M = Co (**I**), Ni (**II**), and Zn (**III**); L is phenylacetyl hydrazide, and Mal^{2-} is malonic acid anion) and $[Cu(L)_2][Cu(Mal)_2] \cdot 4.5H_2O$ (**IV**). The crystal and molecular structures of compound **IV** were determined by X-ray diffraction analysis.

EXPERIMENTAL

Synthesis of complexes I–IV. Phenylacetyl hydrazide (4.5 g, 0.03 mol) was dissolved in methanol (50 mL), dry powdered malonate of the corresponding metal (0.01 mol) was added, and the mixture was stirred to complete dissolution. The mixture was left to stay for a week for the spontaneous evaporation of the solvent. The precipitate formed was separated, washed with a water–methanol (1 : 1) mixture, and dried in air to a constant weight. In the case of copper(II), the precipitated crystals turned out to be suitable for X-ray diffraction analysis.

The initial malonates were obtained by the reaction of sodium malonate with the corresponding 3*d*-metal nitrate.

For $C_{27}H_{32}N_6O_7Co$ (**I**)

Anal. calcd., %	C, 53.02	H, 5.24	N, 13.75	Co, 9.66
Found, %	C, 53.05	H, 5.03	N, 13.46	Co, 9.79

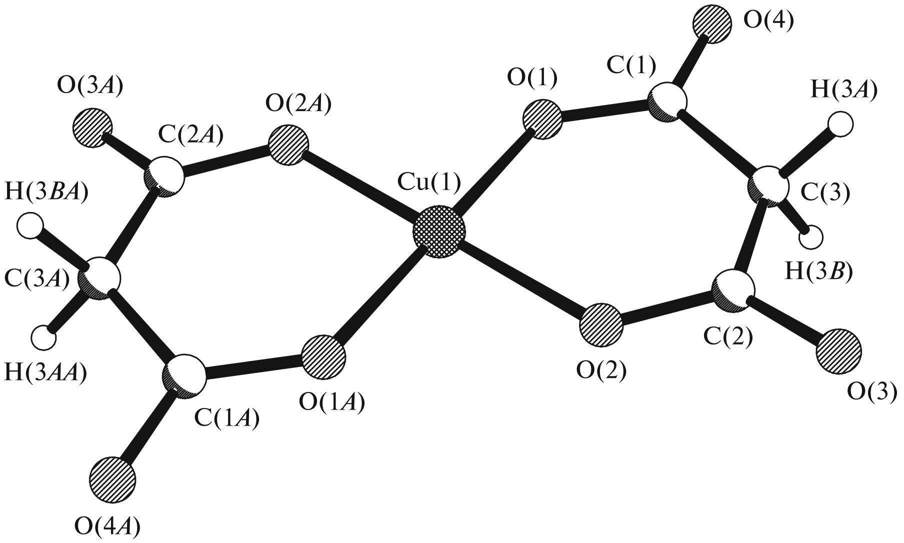

Fig. 1. Structure of complex anion $[Cu(1)(Mal)_2]^{2-}$.

For $C_{27}H_{32}N_6O_7Ni$ (**II**)

Anal. calcd., %	C, 53.02	H, 5.24	N, 13.75	Ni, 9.66
Found, %	C, 53.01	H, 5.37	N, 13.43	Ni, 9.63

For $C_{27}H_{32}N_6O_7Zn$ (**III**)

Anal. calcd., %	C, 52.51	H, 5.19	N, 13.61	Zn, 10.53
Found, %	C, 52.30	H, 5.50	N, 13.77	Zn, 10.95

For $C_{22}H_{33}N_4O_{14.5}Cu_2$ (**IV**)

Anal. calcd., %	C, 37.03	H, 4.63	N, 7.85	Cu, 17.95
Found, %	C, 37.05	H, 4.37	N, 7.46	Cu, 17.79

Elemental analysis to metal was conducted by atomic emission spectrometry with inductively coupled plasma on a Perkin-Elmer Optima 8000 instrument, and elemental analyses to carbon, hydrogen, and nitrogen were carried out on a CHN analyzer.

IR spectra were recorded on a Perkin-Elmer Spectrum BX II FT-IR System instrument for samples in KBr pellets. Diffuse reflectance spectra were detected on a Lambda-9 spectrometer (Perkin-Elmer) using MgO as a standard ($\beta_{MgO} = 100\%$).

Thermogravigrams were recorded on a Paulik–Paulik–Erdey derivatograph in air with a heating rate of 10 deg/min.

X-ray diffraction analysis of compound IV. The structure was solved by a direct method and refined by least squares in the full-matrix anisotropic approximation for all non-hydrogen atoms. The positions of all hydrogen atoms (including hydrogen atoms of water molecules) were calculated geometrically and included into the refinement by the riding model. The crystallographic data and experimental characteristics for the crystals of compound **IV** are presented in Table 1. Selected interatomic distances and bond angles are given in Table 2. The geometric parameters of hydrogen bonds are presented in Table 3.

The coordinates of atoms and other parameters for the structure of compound **IV** were deposited with the Cambridge Structural Database (CSD) in the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1844502; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The chemical analysis results show that the metal to phenylacetyl hydrazide ratio is 1 : 1 for Cu(II) in complex **IV** and 1 : 3 for Co(II), Ni(II), and Zn(II) in compounds **I–III**. According to the X-ray diffraction data, the structural units in compound **IV** are complex cations $[Cu(1)(L_2)]^{2+}$ (Fig. 1), complex anions $[Cu(2)(Mal)_2]^{2-}$ (Fig. 2), and crystallization water molecules. Both centrosymmetric complex ions have a distorted square coordination mode: the coordination environment of the Cu(1) atom of the cation is formed by four oxygen atoms of two bidentate-chelating malonate ions (average Cu(1)–O 1.900(4) ± 0.013 Å), and the Cu(2) atom of the anion is coordinated by two oxygen atoms and two nitrogen atoms of two bidentate-chelating phenylacetyl hydrazide molecules (Cu(2)–O(5) 1.958(4), Cu(2)–N(1) 1.983(5) Å, chelate angle O(5)Cu(2)N(1) 83.8(2)°). When the copper atoms are coordinated by the Mal^{2-} ions and L molecules, two equivalent metallocycles for each copper atom undergo ring closure: six-membered $Cu(1)OC_3O$ (A) and five-membered $Cu(2)N_2CO$ (B), respectively. Chelate A is almost planar (±0.004–0.014 Å), and metallocycle B is somewhat corrugated (±0.027–0.065 Å, the average deviation of the atoms from the mean plane is 0.040 Å).

Table 1. Crystallographic characteristics and experimental and structure refinement data for compound **IV**

Parameter	Value
FW	712.60
Temperature, K	293(2)
Crystal system; space group	Triclinic; $P\bar{1}$
Cell parameters:	
a, Å	7.904(2)
b, Å	10.191(3)
c, Å	11.143(3)
α, deg	110.12(2)
β, deg	97.254(10)
γ, deg	111.98(2)
V, Å^3	747.3(4)
Z; ρ_{calcd}, g/cm^3	1; 1.584
F(000)	367
μ, mm^{-1}	2.414
Crystal size, mm	0.18 × 0.08 × 0.03
Diffractometer	Enraf-Nonius CAD4
Scan mode	ω
Radiation; λ , Å	CuK_α; 1.5418
θ_{min}–θ_{max}, deg	4.42– 62.47
Index ranges	$-9 \le h \le 9$, $-11 \le k \le 11$, $-20 \le l \le 20$
Number of reflections:	
Measured/independent	3380/1880
R_{int}	0.0231
Completeness for θ, %	79.3
Absorption correction	ψ scan
T_{min}, T_{max}	0.6705, 0.9311
Refinement method	Full-matrix least squares for F^2
Number of refined parameters	203
GOOF (F^2)	1.03
R_{hkl} ($I > 2\sigma(I)$)	$R_1 = 0.0552$, $wR_2 = 0.1471$
R_{hkl} (for all reflections)	$R_1 = 0.0654$, $wR_2 = 0.1576$
$\Delta_{max}/\Delta_{min}$ e/Å^3	1.286/–0.590

The CSD (6, version 5.38, November, 2017) contains no results about the structure of the $[Cu(L)_2]^{2+}$ and $[Cu(Mal)_2]^{2-}$ complex ions. However, there are data on the crystal structures of four compounds containing the copper(II) diaquadimalonate dianion, $[Cu(Mal)_2(H_2O)_2]^{2-}$ (An), and one neutral complex with monoprotonated single-charge malonate ions HMal$^-$, all of which are characterized by the extended (due to the Jahn–Teller effect) tetragonal bipyramidal coordination mode of the metal atom. Three original variants of the structure of $[Cu(H_2O)_6]$ · An (**V**) are known [7–9], as well as the X-ray diffraction results for the $[Cu(HMal)_2(H_2O)_2]$ complex (**VI**) at two temperatures, 120 and 294 K [10]. In addition, the CSD contains data on the crystal structures of three compounds with a more complicated composition of the

Table 2. Selected bond lengths (Å) and bond angles (deg) in the structure of compound **IV**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(1)	1.912(4)	N(2)–N(1)	1.422(6)
Cu(1)–O(2)	1.887(4)	N(2)–C(4)	1.310(8)
O(1)–C(1)	1.275(7)	C(4)–C(5)	1.509(8)
O(2)–C(2)	1.272(7)	C(5)–C(6)	1.518(8)
O(3)–C(2)	1.239(7)	C(6)–C(7)	1.375(9)
O(4)–C(1)	1.234(7)	C(7)–C(8)	1.374(10)
C(1)–C(3)	1.484(8)	C(8)–C(9)	1.334(11)
C(2)–C(3)	1.492(8)	C(9)–C(10)	1.374(12)
Cu(2)–O(5)	1.958(4)	C(6)–C(11)	1.366(9)
Cu(2)–N(1)	1.983(5)	C(11)–C(10)	1.378(11)
O(5)–C(4)	1.255(7)		
Angle	**ω, deg**	**Angle**	**ω, deg**
O(2)Cu(1)O(1)	93.76(16)	N(2)N(1)Cu(2)	105.9(3)
C(1)O(1)Cu(1)	128.4(4)	O(5)C(4)N(2)	121.4(6)
C(2)O(2)Cu(1)	129.7(3)	O(5)C(4)C(5)	120.6(6)
O(4)C(1)O(1)	122.0(5)	N(2)C(4)C(5)	118.0(6)
O(4)C(1)C(3)	116.1(5)	C(4)–C(5)–C(6)	111.4(5)
O(1)C(1)C(3)	121.8(5)	C(11)C(6)C(7)	119.2(6)
O(3)C(2)O(2)	121.6(5)	C(11)C(6)C(5)	120.2(6)
O(3)C(2)C(3)	117.8(5)	C(7)C(6)C(5)	120.5(6)
O(2)C(2)C(3)	120.6(5)	C(6)C(11)C(10)	119.0(8)
C(1)C(3)C(2)	123.4(5)	C(6)C(7)C(8)	120.5(7)
O(5)Cu(2)N(1)	83.79(18)	C(9)C(8)C(7)	120.7(8)
C(4)O(5)Cu(2)	111.2(4)	C(8)C(9)C(10)	119.2(7)
C(4)N(2)N(1)	117.7(5)	C(9)C(10)C(11)	121.2(8)

Table 3. Geometric parameters of hydrogen bonds in compound **IV***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
N(1)–H(1*B*)···O(8)	0.90	2.12	2.80(2)	132
N(1)–H(1*A*)···O(2)	0.90	2.08	2.862(6)	144
N(2)–H(2*A*)···O(6)	0.86	1.84	2.688(8)	169
O(7)–H(71)···O(8)$^{\#1}$	0.85	1.55	2.40(2)	179
N(1)–(1*A*)···O(1)$^{\#2}$	0.90	2.53	3.311(6)	146
O(6)–H(6)···O(4)$^{\#2}$	0.86	1.90	2.761(7)	179
N(1)–H(1*B*)···O(7)$^{\#3}$	0.90	2.20	3.056(8)	160
O(6)–H(61)···O(7)$^{\#4}$	0.85	2.02	2.866(9)	179
O(7)–H(7)···O(3)$^{\#5}$	0.85	1.86	2.712(7)	179

* Symmetry transforms of equivalent atoms: $^{\#1}$ $x, y, z - 1$; $^{\#2}$ $-x + 1, -y, -z$; $^{\#3}$ $x, y, z + 1$; $^{\#4}$ $x + 1, y, z + 1$; $^{\#5}$ $-x, -y - 1, -z - 1$.

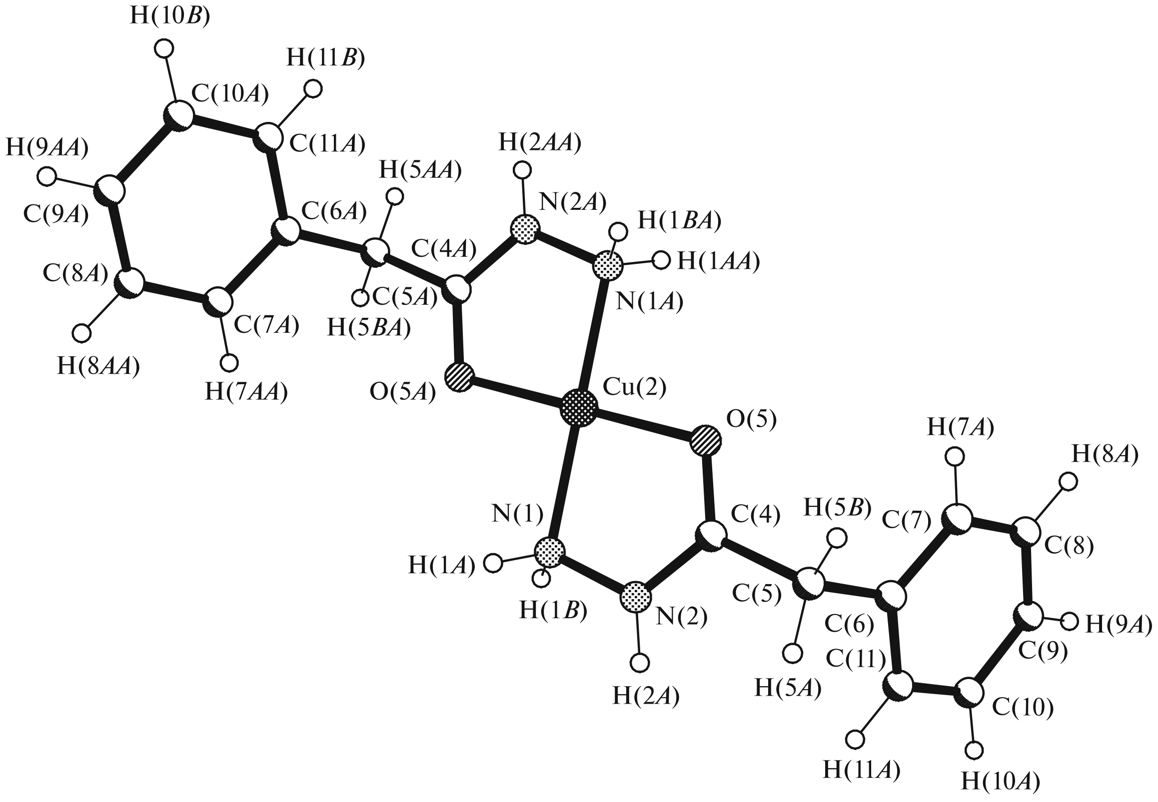

Fig. 2. Structure of complex cation $[Cu(2)(L)_2]^{2+}$.

general formula $\{Cu(H_2O)_n(\mu\text{-}Mal)_2\{Cu(H_2O)_4\}_2]^{2+}$-$[Cu(Mal)_2(H_2O)_2]^{2-}$ · $[\{Cu(H_2O)_2(Mal)(\mu\text{-}Mal)\}$-$\{Cu(H_2O)_4\}]$ bearing the neutral binuclear molecules together with the trinuclear complex anions and the mononuclear anionic complex. The structures of two monoclinic modifications were determined for the compounds with $n = 2$: space group C_2/c, $Z = 8$ **(VII)** [11] and space group $P2_1/c$, $Z =$ **(VIII)** [12]. For the complex with $n = 1$ **(IX)** [13], the central copper atom in the trinuclear complex cation has an extended tetragonal pyramidal coordination mode, whereas the coordination mode is an extended tetragonal bipyramid for a similar Cu atom in the structures of compounds **VII** and **VIII**.

The Cu–O(Mal) bonds in the $[Cu(Mal)_2]^{2-}$ complex of the studied structure of compound **IV** are much shorter, on the average, than those in the complex anions of the structures of compounds **V–IX** (1.900 and 1.936–1.994 Å, respectively). The ranges of lengths of the axial $Cu–O(H_2O)_{ax}$ bonds and O(Mal)CuO(Mal) chelate angles in the structures of compounds **V–IX** are 2.409–2.480 Å and 91.0°–93.5°, respectively. The O(Mal)CuO(Mal) angle in the structure of compound **IV** is 93.8(2)°.

The packing of structural units in the crystal of compound **IV** is shown in Fig. 3. The complex cations and anions and crystallization water molecules are connected by a branched network of hydrogen bonds: acceptor (involving the nitrogen atoms of ligand L and water molecules) and donor (involving the oxygen atoms of ligands Mal^{2-} and L and H_2O molecules). The O(7)–H(71)···O(8) hydrogen bond between the water molecules (H···O 1.55, O···O 2.40 Å, angle OHO 180°) is very strong.

A comparison of the IR spectra of phenylacetyl hydrazide and synthesized complexes with 3*d*-metal malonates (Table 4) was performed taking into account the published data [14–17] and showed an increase in the ν(C=O) absorption frequency. However, this frequency usually decreases upon coordination via the oxygen atom [18–24]. The unusual behavior of ν(C=O) for the synthesized complexes is related to the fact that this band in the spectrum of the initial phenylacetyl hydrazide is lowered because of the presence of intra- and intermolecular hydrogen bonds. The presence of hydrogen bonds in phenylacetyl hydrazide both in the solid state and even in concentrated chloroform solutions was confirmed as early as in 1956 [15]. It was established [15] that the ν(C=O) absorption should be observed about 1710 cm^{-1} in the absence of hydrogen bonds. Thus, it can be asserted that the ν(C=O) frequency decreases because of complex formation, but the shift caused by complex formation is inferior to that caused by hydrogen bonding. An increase in ν(C=O) due to complex formation is

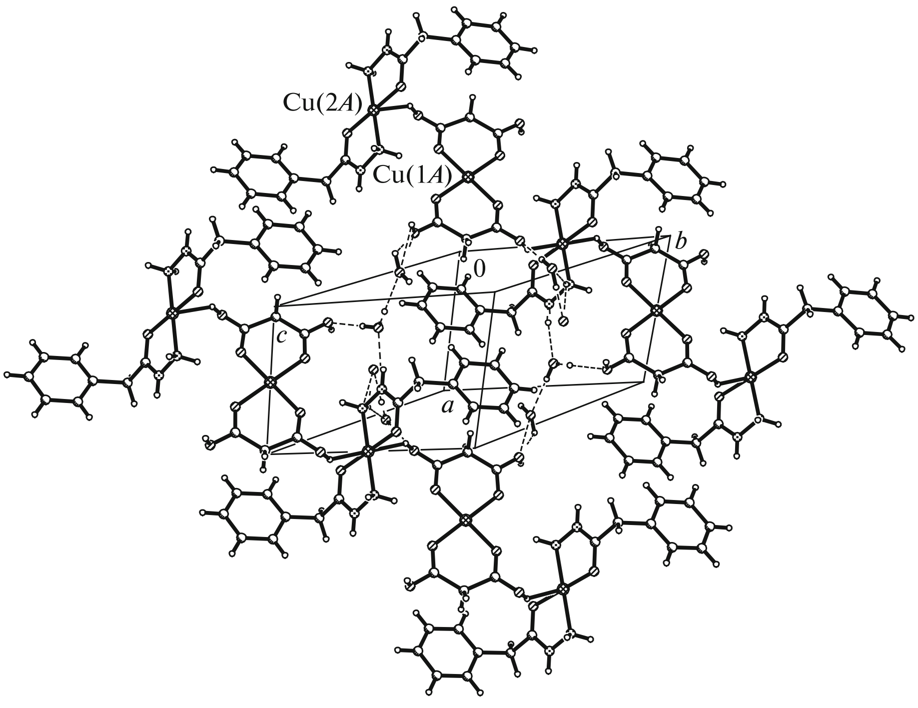

Fig. 3. Packing of structural units in the crystal of compound **IV**.

13–15 cm^{-1} for 1 : 3 complexes **I–III** and 25 cm^{-1} for complex **IV**. One more distinction in the spectrum of the latter is the absence of the ν_{as}(C–H), δ(NH_2), and ν(C–C) bands of the aromatic ring, which are observed at nearly the same frequencies in the spectra of complexes **I–III**. The δ(CH_2) bands in the spectra of complexes **I–III** (1 : 3) almost coincide with the corresponding band in the spectrum of organic molecule L, and for copper complex **IV** the frequency of this band decreases. The doublet for the ν(NH) stretching vibrations disappears from the IR spectra of all the four complexes synthesized by us, which corresponds to the participation of nitrogen in coordination and the cleavage of hydrogen bonds. The number of bands also decreases in a range of 1100–1200 cm^{-1}, where the bands of the bonds involving nitrogen are also observed, and the position of the bands is almost the same for all complexes **I–IV**. For the doublet in a range of 1000–1100 cm^{-1}, which is also contributed by the bond involving nitrogen, a decrease in the difference in the frequencies between two bands is approximately the same for all complexes **I–IV**. For copper complex **IV**, the δ(CNH) + δ(CCC) frequency is a little higher and δ(CCN) + (δ(NCO) is a little lower than those for complexes **I–III**.

Thus, the changes in the bands in the IR spectra are consistent with the X-ray diffraction data for complex **IV** on the participation of oxygen and nitrogen in the formation of the chelate cycle in the complex cations.

We earlier compared the data of IR spectroscopy and X-ray diffraction analysis [25–27] and showed that the ΔΔν(COO^-) value, the difference Δν(COO^-) between the mixed-ligand complex and initial metal carboxylate (where Δν(COO^-) = ν_{as}(COO^-) – ν_s(COO^-)), can characterize the type of binding of carboxylate ions in coordination compounds. The high values of ΔΔν(COO^-) are characteristic of the monodentate coordination mode of carboxylate, and much lower values are observed for the bidentate coordination mode and out-of-sphere anions. For the synthesized 1 : 3 compounds **I–III**, ΔΔν(COO^-) is fairly low, which corresponds to the out-of-sphere character of the malonate ions. For compound **IV**, this difference is negative, since the initial copper malonate contains the identical complex anion (Table 5).

The diffuse reflectance spectral data (Table 6) for complexes **I** and **II** are consistent with their octahedral structure. The broad band with a maximum at 15400 cm^{-1} in the spectrum of compound **IV** is characteristic of the square copper(II) complexes [28].

The thermogravigrams (Table 7) of 1 : 3 compounds **I–III** are rather similar: the endoeffect with a minor mass loss is observed at 120–140°C, then the exoeffect with the mass loss somewhat larger than 20% is observed at ~200°C, and more than 50% of the overall mass loss fall on the exoeffect at ~400°C. Obviously, the endoeffects correspond to the destruction of the complexes, and the exoeffects correspond to the burning out of the organic moiety. Complex **IV** demonstrates more effects in the thermogravigram,

Table 4. Assignment of absorption bands (cm^{-1}) in the IR spectra of phenylacetyl hydrazide and its complexes with 3*d*-metal malonates

Assignment	L	$[Co(L)_3]Mal$	$[Ni(L)_3]Mal$	$[Zn(L)_3]Mal$	$[Cu(L)_2][Cu(Mal)_2] \cdot 4.5H_2O$
$\nu(NH)$, $\nu(NH_2)$	3294, 3200	3221	3214	3224	3205
$\nu_{as}(C{-}H)$ (CH_2)	3030	3062, 3031	3062, 3030	3062, 3031	
$\nu_s(C{-}H)$ (CH_2)	2917			2951	2896
$\nu(C{=}O)$	1644	1659	1657	1659	1669
$\delta(NH_2)$		1607	1609	1610	
$\nu(C{-}C)_{arom.ring}$	1529	1545	1543	1542	
$\delta(CH_2)$	1455	1454	1454	1454	1433
$\omega(NH_2)$	1352, 1265	1358	1360, 1277	1354, 1277	1369, 1275
$\nu(CN) + \nu(N{-}N) + \tau(NH_2) + \delta(CCH)$	1205, 1156, 1137	1195, 1165	1196, 1171	1190, 1162	1195, 1163
$\nu_{puls.ring} + \rho(NH_2) + \tau(NH_2)$	1074, 1007	1060, 1032	1062, 1033	1064, 1033	1063, 1033
$\rho(CCH) + \delta(CCH)$	773			780	784
$\delta(CNH) + \delta(CCC)$	705, 623	696	696	696	702
$\delta(CCN) + \delta(NCO)$		539	542	547	530

Table 5. Absorption bands (cm^{-1}) of carboxylate ions in the IR spectra of 3*d*-metal malonates and their complexes with phenylacetyl hydrazide

Compound	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu(COO^-)$	$\Delta\Delta\nu(COO^-)$
$Co(Mal) \cdot 2H_2O$	1567	1374	193	
$[Co(L)_3]Mal$	1594	1358	236	43
$Ni(Mal) \cdot 2H_2O$	1567	1380	187	
$[Ni(L)_3]Mal$	1595	1360	235	48
$Zn(Mal) \cdot 2H_2O$	1566	1378	188	
$[Zn(L)_3]Mal$	1596	1354	242	54
$Na_2[Cu(Mal)_2] \cdot 2H_2O$	1592	1366	226	
$[Cu(L)_2][Cu(Mal)_2] \cdot 4.5H_2O$	1584	1369	215	–11

Table 6. Diffuse reflectance spectra for the phenylacetyl hydrazide complexes with 3*d*-metal malonates

Compound	ν, cm^{-1}	Assignment
$[Co(L)_3]Mal$	19850	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	8750	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$
$[Ni(L)_3]Mal$	16300	$^3A_{2g} \rightarrow {}^3T_{1g}$
	9600	$^3A_{2g} \rightarrow {}^3T_{2g}$
$[Cu(L)_2][Cu(Mal)_2] \cdot 4.5H_2O$	15400	

Table 7. Thermogravimetric data for the phenylacetyl hydrazide complexes with 3*d*-metal malonates

Compound	Endoeffect		Exoeffect		Total mass loss, %
	T, °C*	Δ*m*, %	*T*, °C*	Δ*m*, %	
$[Co(L)_3]Mal$	120–140(130)	4.4	190–260(240)	22.2	78.8
			400–570(540)	42.8	
$[Ni(L)_3]Mal$	140–160(150)	3.5	210–260(230)	3.5	80.0
			260–270(265)	28.2	
			400–530(500)	40.5	
$[Zn(L)_3]Mal$	120–140(130)	2.4	190–250(220)	20.4	78.8
			330–360(350)	4.9	
			420–570(560)	42.3	
$[Cu(L)_2][Cu(Mal)_2] \cdot 4.5H_2O$	110–140(130)	12.3	200–270(250)	5.4	73.8
	140–200(190)	35.7	330–400(360)	11.3	
			400–510(450)	7.4	

* The temperature of the effect maximum is given in parentheses.

which is probably related to a more complicated structure (two coordination spheres). Depending on the complexing agent, the thermal stability decreases in the order $Ni^{2+} > Co^{2+} \approx Zn^{2+} > Cu^{2+}$.

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