Synthesis and reactivity of metal-containing monomers
47.* Synthesis and structure of salts of unsaturated dicarboxylic acids

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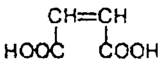
Acid and neutral Co^{II}, Cu^{II}, Ni^{II}, Zn^{II}, Fe^{II}, and Fe^{III} maleates, fumarates, and itaconates were obtained and characterized. The methods for their synthesis were optimized, and the valence state and coordination of metals were studied. Co^{II} and Fe^{II} hydrogen maleates, Co^{II} maleate, and Co^{II} fumarate were examined by X-ray diffraction analysis. The ligands based on unsaturated dicarboxylic acids can be mono-, bi-, and tetradentate, which results in the formation of acid salts, chain and three-dimensional coordination polymers, whose double bond is not involved in the coordination. The strong antiferromagnetic exchange (μ_{eff} = 1.41 and 0.34 μ_B at 290 and 80 K, respectively) was detected in Cu^{II} itaconate. Based on the data of Mössbauer spectroscopy, the partial reduction of Fe^{III} to Fe^{II} during the synthesis of Fe^{III} maleate was shown to occur: δFe = 0.43 and 1.27 mm s^{-1}, ΔE_Q = 0.57 and 3.13 mm s^{-1} and Γ = 0.37 and 0.28 mm s^{-1} at T = 298 K for Fe^{III} and Fe^{II}, respectively.

Key words: acid and neutral transition-metal maleates, fumarates, itaconates; coordination polymer; metal-containing monomers; X-ray diffraction analysis.

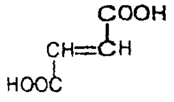
Metal derivatives of unsaturated dicarboxylic acids constitute an abundant group of compounds that are of interest from the viewpoint of both coordination and macromolecular chemistry.[1—4] This is determined in many respects by the practical significance of maleates, fumarates, and itaconates, which are used as coatings with specific properties, efficient catalysts, and medicinals.[5—8]

By virtue of the multiple bond, salts of unsaturated dicarboxylic acids are also potential metal-containing monomers (MCM), whose polymerization transformations can open new routes for the preparation of valuable products. However, data on the synthesis, structure, and reactivity of these compounds are scarce, unlike MCM based on unsaturated monocarboxylic acids, whose structure and polymerization properties are fairly well studied.[9] In the present work, the methods for their synthesis were optimized, and the structure and properties of Co^{II}, Cu^{II}, Ni^{II}, Zn^{II}, Fe^{III}, and Fe^{II} salts of maleic (**1**), fumaric (**2**), and itaconic (**3**) acids were compared and analyzed.



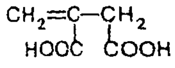
$HOOC{-}CH{=}CH{-}COOH$

1



$HOOC{-}CH{=}CH{-}COOH$

2



$CH_2{=}C(COOH){-}CH_2{-}COOH$

3

Results and Discussion

Synthesis and composition of salts of unsaturated acids 1—3

The general method for the preparation of salts of unsaturated dicarboxylic acids is the reaction of metal hydroxides, carbonates, or acetates with the corresponding acids. The effect of the molar ratios of the initial components and their concentrations, the reaction temperature, the nature of the solvent, and time of synthesis was studied to optimize the conditions of the synthesis.

Maleates. The maximum yield of the target products (up to 95%) was achieved[10] when Co^{II}, Ni^{II}, and Zn^{II} carbonates and Cu^{II} and Fe^{III} hydroxides were dissolved in a twofold excess of a methanolic solution of **1**, and the salts formed were precipitated with diethyl ether. When water is traditionally used as the solvent[11,12] and the

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solution is concentrated, the purification of the reaction product from the unconsumed acid becomes considerably more difficult, and the yield is lower. The reactions of concentrated aqueous solutions of Co^{II}, Ni^{II}, and Zn^{II} acetates with maleic acid (in molar ratios of 1 : 2) turned out also to be convenient: the salts precipitated, because their solubility is considerably lower than that of the initial acetates. We established that the use of transition metal acetates or carbonates in the synthesis results in the formation of MCM, which differ in composition, *viz.*, acid salts or coordination polymers, respectively, as has been shown for Co^{II}, Ni^{II}, and Zn^{II} salts.

The reaction of maleic acid with $Fe(OH)_3$ in water occurs in an unusual way. According to the data of Mössbauer spectroscopy, a mixture of Fe^{III} maleate and Fe^{II} hydrogen maleate (9 : 1) was obtained instead of the expected Fe^{III} maleate at various ratios of the reagents (1 : 1, 2 : 1, 3 : 1) and at temperatures of 40—50 °C and 80—90 °C. Evidently, the partial reduction of Fe^{III} to Fe^{II} occurs during the synthesis. It is noteworthy that when finely dispersed metallic iron was dissolved in an aqueous solution of maleic acid in an inert atmosphere, acid Fe^{II} maleate was obtained as a crystalline substance stable in air.

Fumarates. For the preparation of fumarates, the use of an excess of soluble salts (Co^{II}, Cu^{II}, Ni^{II}, and Zn^{II} acetates and Fe^{III} sulfate) as the initial substances and reaction in an aqueous solution at 80—90 °C due to the limited solubility of fumaric acid turned out to be the method of choice. The products of the same composition ($MC_4H_2O_4 \cdot nH_2O$) (Table 1) were obtained for all ratios of the initial components.

Itaconates. The same methods as those for the preparation of maleates are efficient for the synthesis of these salts. However, as in the case of fumarates, the use of different salts and the variation of molar ratios of the initial components give products of the same composition $MC_5H_4O_4 \cdot nH_2O$ (see Table 1).

Table 1. Data from elemental analysis of MCM

Initial acid	Salt obtained	$\frac{\text{Found}}{\text{Calculated}}$ (%)			Molecular formula
		C	H	M	
Maleic (1)	$Co(C_4H_3O_4)_2 \cdot 4H_2O$	26.93 26.59	4.11 3.88	16.70 16.34	$C_8H_{14}CoO_{12}$
1	$CoC_4H_2O_4 \cdot 3H_2O$	21.33 21.15	3.29 3.52	26.07 25.99	$C_4H_8CoO_7$
1	$CuC_4H_2O_4 \cdot H_2O$	24.81 24.49	2.51 2.04	33.01 32.65	$C_4H_4CuO_5$
1	$Ni(C_4H_3O_4)_2 \cdot 4H_2O$	26.59 26.59	4.22 3.88	16.22 16.34	$C_8H_{14}NiO_{12}$
1	$NiC_4H_2O_4 \cdot 2H_2O$	22.59 22.97	3.01 2.87	27.96 28.23	$C_4H_6NiO_6$
1	$Zn(C_4H_3O_4)_2 \cdot 4H_2O$	26.01 26.16	3.52 3.81	17.25 17.71	$C_8H_{14}O_{12}Zn$
1	$ZnC_4H_2O_4 \cdot 2H_2O$	22.15 22.33	2.37 2.79	30.03 30.23	$C_4H_6O_6Zn$
1	$Fe(C_4H_3O_4)_2 \cdot 4H_2O$	26.55 26.82	4.07 3.91	16.11 15.64	$C_8H_{14}FeO_{12}$
Fumaric (2)	$CoC_4H_2O_4 \cdot 5H_2O$	18.51 18.25	4.28 4.56	22.21 22.43	$C_4H_{12}CoO_9$
2	$CuC_4H_2O_4 \cdot 2H_2O$	22.81 22.43	2.28 2.80	30.03 29.91	$C_4H_6CuO_6$
2	$NiC_4H_2O_4 \cdot 2H_2O$	23.17 22.97	3.13 2.87	27.89 28.23	$C_4H_6NiO_6$
2	$ZnC_4H_2O_4 \cdot 2H_2O$	22.07 22.33	3.17 2.79	29.81 30.23	$C_4H_6O_6Zn$
Itaconic (3)	$CoC_5H_4O_4 \cdot H_2O$	28.82 29.27	3.16 2.93	29.03 28.78	$C_5H_6CoO_5$
3	$CuC_5H_4O_4 \cdot H_2O$	28.43 28.57	2.79 2.86	30.42 30.48	$C_5H_6CuO_5$
3	$NiC_5H_4O_4 \cdot H_2O$	28.91 29.27	2.80 2.93	28.86 28.78	$C_5H_6NiO_5$
3	$ZnC_5H_4O_4 \cdot 2H_2O$	26.14 26.20	3.02 3.49	28.26 28.38	$C_5H_8O_6Zn$

The data from elemental analysis do not allow one to draw an unambiguous conclusion on the composition and structure of Fe^{III} maleate, fumarate, and itaconate synthesized in this work, and therefore the corresponding values are not included in Table 1.

The compounds obtained are stable in air and colored as the corresponding transition metal ions, they are poorly soluble in water and almost insoluble in organic solvents (except for acid Co^{II}, Ni^{II}, Zn^{II}, and Fe^{II} maleates and neutral Co^{II} maleate, which are soluble in water and MeOH).

Valence state of the transition metal and coordination

It is known that the carboxyl group can be mono- and bidentate, which determines the variety of structural functions of compounds **1**, **2**, and **3** as the ligands. IR spectroscopy is most often used to elucidate the type of coordination. For example, the spectra of acid Co^{II}, Ni^{II}, Fe^{II}, and Zn^{II} maleates, fumarates, and itaconates contain a broad absorption band in the region of 1580—1590 cm^{-1} and 1366—1400 cm^{-1} caused by the asymmetric (ν_{as}(COO$^-$)) and symmetric (ν_s(COO$^-$)) stretching vibrations of the monodentate carboxylate ion.[13] However, Co^{II}, Cu^{II}, Ni^{II}, and Zn^{II} maleates exhibit absorption in the region of 1540—1560 cm^{-1} and 1425—1435 cm^{-1} assigned to the ν_{as}(COO$^-$) and ν_s(COO$^-$) stretching vibrations of the carboxyl group with the bidentate type of coordination (Table 2).

The frequencies of the stretching vibrations of the >C=C< bond do not substantially change when the nature of the ligand and metal is varied. All compounds synthesized are crystal hydrates ($\nu_{OH}(H_2O)$ = 2992—3572 cm^{-1}), which is also confirmed by the data from elemental analysis (see Table 1).

The magnetic properties of the complexes were studied in order to examine the state of the transition metal in the complexes. The μ_{eff} values obtained were interpreted using ligand field theory, which made it possible to establish not only the valence state but the coordination of the metal as well. According to the data from magnetic measurements, the valence states of the initial metal ions underwent no changes. In the majority of cases, the μ_{eff} values indicate the octahedral configuration of the ligand surrounding (Table 3). The magnetic

Table 2. Characteristic frequencies (ν/cm^{-1}) in the IR spectra of MCM

Compound	$\nu_{OH}(H_2O)$	ν(COOH)	ν(C=C)	ν(COO$^-$)	
				ν_s	ν_{as}
Maleic acid	—	1708 (s)	1635 (w)	—	—
Co hydrogen maleate	3046 (br.s)	1684 (w)	1637 (w)	1366 (s) 1398 (s)	1589 (br.s)
Co maleate	3407 (br)	—	1638 (w)	1435 (s) 1366 (m)	1544 (br.s)
Cu maleate	3404 (br.s)	—	1625 (w)	1426 (s)	1559 (br.s)
Ni hydrogen maleate	3412 (br.s)	1682 (w)	1638 (w)	1399 (m) 1599 (br.s)	1366 (s)
Ni maleate	3051 (br.s)	—	1637 (w)	1428 (s)	1549 (br.s)
Fe^{II} hydrogen maleate	3045 (br.s)	1689 (w)	1637 (w)	1344 (s)	1588 (br.s)
Fe^{III} maleate	3405 (br.m)	1700 (s)	1638 (w)	1444 (s) 1399 (m) 1366 (m)	1592 (br.s)
Zn hydrogen maleate	3398 (br.s)	1680 (w)	1654 (w)	1389 (s)	1603 (br.s)
Zn maleate	3410 (br.s)	—	1638 (w)	11429 (s)	1555 (br.s)
Fumaric acid	—	1685 (s)	1621 (w)	—	—
Co fumarate	3045 (br.s)	—	1650 (w)	1392 (s)	1589 (br.s)
Cu fumarate	2922 (br.s)	—	1638 (w)	1397 (s)	1599 (br.s)
Ni fumarate	3401 (br.s)	—	1638 (w)	1397 (s)	1589 (br.s)
Fe^{III} fumarate	3413 (s)	—	1638 (w)	1397 (s)	1597 (br.s)
Zn fumarate	3410 (br.s)	—	1638 (w)	1381 (s)	1582 (br.s)
Itaconic acid	—	1703 (s)	1636 (s)	—	—
Co itaconate	3399 (br.s)	—	1638 (m)	1402 (s)	1576 (br.s)
Cu itaconate	3401 (br.s)	—	1656 (w)	1401 (s)	1616 (br.s)
Ni itaconate	3400 (br.s)	—	1647 (w)	1400 (s)	1577 (br.s)
Fe^{III} itaconate	3408 (br.s)	1708 (s)	1637 (m)	1398 (s)	1599 (br.s)
Zn itaconate	3572 (br.s)	—	1622 (w)	1391 (s)	1580 (br.s)

Table 3. Magnetic properties of transition-metal maleates, fumarates, and itaconates

Salt	μ_{eff}/μ_B		Valence state of metal	Coordination
	290 K	80 K		
Co hydrogen maleate	5.01	5.04	Co^{II}	High-spin octahedron
Co maleate	4.84	4.65	Co^{II}	High-spin octahedron
Ni maleate	2.83	2.89	Ni^{II}	Octahedron
Cu maleate	1.97	1.96	Cu^{II}	Octahedron
Fe hydrogen maleate	5.83	5.71	Fe^{II}	High-spin octahedron
Fe maleate	2.53	2.42	Fe^{III}	Octahedron
Co fumarate	5.08	5.04	Co^{II}	High-spin octahedron
Ni fumarate	2.87	2.86	Ni^{II}	Octahedron
Cu fumarate	1.91	1.92	Cu^{II}	Octahedron
Fe fumarate	3.08	2.41	Fe^{III}	—
Co itaconate	5.05	4.78	Co^{II}	High-spin octahedron
Ni itaconate	3.07	3.06	Ni^{II}	Octahedron
Cu itaconate	1.41	0.34	Cu^{II}	Octahedron
Fe itaconate	2.47	2.03	Fe^{III}	—

measurement data for itaconates agree with the published data.[14] The exception is copper itaconate for which a strong antiferromagnetic exchange was detected (μ_{eff} = 1.41 and 0.34 μ_B at 290 and 80 K per copper atom). Such a change in the magnetic moment can be explained assuming that copper itaconate is a binuclear complex with two electronic levels, whose energies differ insignificantly: the upper level is triplet and the lower level is singlet. This conclusion is in good agreement with the ESR spectra. For example, the numbers of the paramagnetic centers for copper maleate and fumarate (mononuclear complexes) determined at different temperatures correspond to the content of copper in the complexes, while no signal in the ESR spectrum was detected for copper itaconate.

The reduction of Fe^{III} to Fe^{II} during the synthesis of iron maleate was established. According to the data from Mössbauer spectroscopy, there are two states of iron at 298 K: high-spin Fe^{III} with the parameters of the isomer shift δFe = 0.43 mm s^{-1}, quadrupole splitting ΔE_Q = 0.57 mm s^{-1}, and linewidth Γ = 0.37 mm s^{-1} and high-spin Fe^{II} with the parameters δFe = 1.27 mm s^{-1}, ΔE_Q = 3.13 mm s^{-1}, and Γ = 0.28 mm s^{-1}. The ratio of the intensities of the peaks in the spectrum is Fe^{III} : Fe^{II} = 9 : 1. The parameters of the Mössbauer spectrum of Fe^{II} hydrogen maleate obtained by dissolv-

Table 4. Crystallographic data of salts

Parameter	Co^{II} maleate	Co^{II} hydrogen maleate	Fe^{II} hydrogen maleate	Co^{II} fumarate
a/Å	8.132(2)	5.222(6)	5.2650(10)	5.283(2)
b/Å	13.224(3)	7.340(2)	7.3630(10)	13.193(2)
c/Å	7.537(2)	9.239(4)	9.265(2)	13.335(2)
α/deg		109.17(3)	109.21(3)	
β/deg	115.31(3)	104.52(9)	104.78(3)	95.280(10)
γ/deg		93.31(9)	93.32(3)	
V/Å^3	732.7(3)	320.0(4)	323.97(10)	925.5(4)
M	225.02	361.12	358.04	263.06
Z	1	1	4	4
d/g cm^{-3}	2.040	1.874	1.835	1.888
Radiation	Cu	Cu	Mo	Mo
Space group	Cc	$P1$	$P1$	$C2$
Number of reflections, n	1545	1125	2924	1166
R-factor	0.0591	0.102	0.0305	0.0220

Table 5. Coordinates of atoms (×10^4) and equivalent isotropic heat parameters (×10^3) in Fe hydrogen maleate, Co maleate, and Co fumarate

Atom	*x*	*y*	*z*	U_{eq}/Å^2
		Fe maleate		
Fe	0	0	0	23(1)
O(2)	3190(3)	−1350(2)	965(2)	29(1)
O(3)	2460(3)	2652(2)	773(2)	33(1)
O(4)	−1467(3)	596(2)	2054(2)	30(1)
O(5)	1984(3)	2694(3)	3826(2)	41(1)
O(6)	2011(4)	4751(3)	8742(2)	41(1)
O(7)	3406(4)	4560(3)	6663(2)	44(1)
C(8)	−274(4)	1706(3)	3453(2)	25(1)
C(9)	−1665(4)	1786(3)	4685(2)	30(1)
C(10)	−840(4)	2745(3)	6265(2)	30(1)
C(11)	1672(4)	4085(3)	7299(2)	28(1)
H(21)	4749(73)	−788(54)	1236(42)	38(9)
H(22)	3149(84)	−2455(62)	289(51)	55(11)
H(31)	3223(90)	3206(65)	1696(56)	63(12)
H(32)	2223(83)	3369(61)	270(52)	58(11)
H(7)	2741(121)	3710(88)	5398(76)	93(18)
H(9)	−3279(73)	966(52)	4250(43)	42(9)
H(10)	−2066(67)	2637(48)	6796(40)	38(8)
		Co maleate		
Co	5000	6393(1)	5000	6(1)
O(2)	4712(5)	4918(3)	3888(6)	16(1)
O(3)	3327(5)	3791(3)	1535(6)	12(1)
O(4)	2779(5)	6769(3)	2419(5)	13(1)
O(5)	−124(5)	7078(3)	578(6)	14(1)
O(6)	7211(5)	5930(3)	7595(6)	16(1)
O(7)	6767(6)	6585(5)	3680(7)	24(1)
C(8)	3311(6)	4477(4)	2706(7)	6(1)
C(9)	1482(7)	4667(4)	2663(7)	8(1)
C(10)	547(6)	5525(4)	2216(7)	10(1)
C(11)	1146(7)	6523(4)	1720(7)	7(1)
O(12)	314(6)	2545(3)	62(7)	20(1)
		Co fumarate		
Co(1)	0	10000	0	17(1)
Co(2)	5000	4630(1)	5000	16(1)
O(1)	7035(4)	3521(2)	5896(1)	27(1)
O(2)	2068(4)	11089(2)	929(2)	19(1)
O(3)	1641(3)	8902(2)	971(1)	25(1)
O(4)	3313(3)	5736(2)	4014(1)	24(1)
O(5)	−2955(4)	10068(2)	911(2)	25(1)
O(6)	2042(5)	4571(2)	5929(2)	35(1)
O(7)	−1082(3)	8583(2)	2114(1)	24(1)
O(8)	6070(3)	6001(2)	2872(1)	30(1)
O(9)	0	12778(2)	0	26(1)
O(10)	5000	1846(3)	5000	31(1)
C(1)	4047(3)	6187(2)	3246(1)	22(1)
C(2)	1005(3)	8470(2)	1764(1)	16(1)
C(3)	2128(6)	6901(2)	2757(2)	21(1)
C(4)	2805(6)	7682(3)	2222(2)	19(1)
H(3)	416(80)	6806(34)	2810(32)	20(11)
H(4)	4570(92)	7803(37)	2097(36)	28(13)
H(51)	−4537(104)	10306(42)	863(40)	65(16)
H(52)	−2781(123)	9543(44)	1255(48)	80(18)
H(61)	617(107)	4319(43)	5885(39)	38(15)
H(62)	2176(118)	5006(43)	6409(48)	52(16)
H(9)	917(99)	13144(47)	−338(37)	50(15)
H(10)	5880(90)	1478(39)	4704(35)	49(14)
H(21)	1535(95)	11787(40)	638(37)	55(15)
H(22)	1657(106)	11072(44)	1588(43)	77(16)
H(11)	7051(127)	2992(53)	5735(51)	80(21)
H(12)	6558(109)	3502(44)	6492(46)	55(16)

ing metallic iron in the acid are the following: δFe = 1.25 mm s^{-1}, ΔE_Q = 3.19 mm s^{-1}, and Γ = 0.26 mm s^{-1}. Only one state, high-spin Fe^{III}, was revealed in iron fumarate and itaconate (δFe = 0.42 mm s^{-1}, ΔE_Q = 0.63 mm s^{-1}, Γ = 0.41 mm s^{-1} and δFe = 0.43 mm s^{-1}, ΔE_Q = 0.57 mm s^{-1}, Γ = 0.40 mm s^{-1} for fumarate and itaconate, respectively).

Molecular and crystal structure of the salts

Since unsaturated dicarboxylic acids have diverse ligand possibilities, the total information on the structure of their salts can be obtained only on the basis of XDA. With Cd^{II} maleate as an example, it is shown[15,16] that the same compound can exist in two crystallographic modifications and with different coordination surroundings of the metal. We performed the X-ray diffraction study of crystals of Co^{II} and Fe^{II} hydrogen maleates of the composition $M(C_4H_3O_4)_2 \cdot 4H_2O$, Co^{II} maleate $CoC_4H_2O_4 \cdot 3H_2O$, and Co^{II} fumarate $CoC_4H_2O_4 \cdot 5H_2O$. The main crystallographic data are presented in Table 4, and atomic coordinates, bond lengths, and bond angles are presented in Tables 5—8.

Acid Co and Fe maleates are isostructural to similar Zn^{II} and Mn^{II} compounds.[17,18] In the center-symmetric complex, two monodentate residues of compound **1** are linked with the metal atom (the Co—O(4) bond length is equal to 2.123 Å, the Fe—O(4) bond length is equal to 2.157 Å (see Table 6)), and the coordination is supplemented to the octahedron by four water molecules (Fig. 1). The planar structure of the maleate ligand is stabilized by the intramolecular hydrogen bond (for example, for the Fe complex the H(7)...O(5) bond length is equal to 1.87 Å), and the bond lengths and

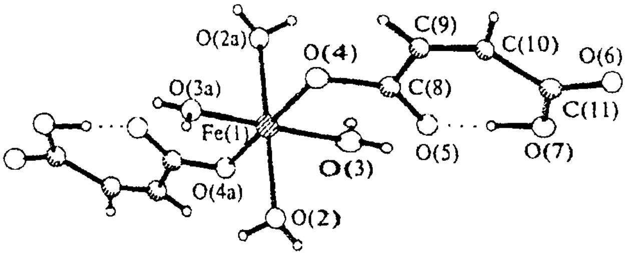

Fig. 1. Molecular structure of Fe^{II} hydrogen maleate.

Table 6. Bond lengths (*d*) and bond angles (ω) in Co (A) and Fe (B) hydrogen maleates

Bond	*d*/Å		Bond	*d*/Å	
	A	B		A	B
M—O(2)	2.128(4)	2.149(2)	O(6)—C(11)	1.245(6)	1.223(2)
M—O(3)	2.044(4)	2.078(2)	O(7)—C(11)	1.307(7)	1.294(3)
M—O(4)	2.123(4)	2.157(2)	C(8)—C(9)	1.512(7)	1.493(3)
O(4)—C(8)	1.239(5)	1.253(2)	C(9)—C(10)	1.350(6)	1.338(3)
O(5)—C(8)	1.259(6)	1.260(3)	C(10)—C(11)	1.454(7)	1.491(3)

Angle	ω/deg		Angle	ω/deg	
	A	B		A	B
O(4)—M—O(2)	91.8(2)	93.27(6)	O(5)—C(8)—C(9)	120.3(4)	121.0(2)
O(3)—M—O(2)	91.4(2)	92.35(7)	C(10)—C(9)—C(8)	129.1(4)	129.7(2)
O(3)—M—O(4)	96.4(2)	96.93(7)	C(9)—C(10)—C(11)	130.8(5)	130.6(2)
C(8)—O(4)—M	127.8(3)	126.6(1)	O(6)—C(11)—O(7)	119.8(5)	121.4(2)
O(4)—C(8)—O(5)	123.5(4)	122.8(2)	O(6)—C(11)—C(10)	118.7(5)	118.5(2)
O(4)—C(8)—C(9)	116.2(4)	116.3(2)	O(7)—C(11)—C(10)	121.5(4)	120.0(2)

bond angles have common values. The bond lengths between the metal atoms and oxygen atoms of water molecules differ sharply (for example, the Fe—O(2) bond length is equal to 2.149 Å and the Fe—O(3) bond length is equal to 2.078 Å (see Table 6)). In the absence of intermolecular hydrogen and other shortened contacts in crystals, the nonequivalence of bonds is likely determined by intramolecular steric factors.

In the condensed phase, Co^{II} maleate is a three-dimensional coordination polymer. The crystals of $[CoC_4H_2O_4 \cdot 2H_2O]_n \cdot nH_2O$ belong to the monoclinic syngony. The unit cell parameters are presented in Table 4. The coordination polyhedron of cobalt is a somewhat distorted octahedron, where the residue of **1** is linked with the metal ion by two oxygen atoms of both carboxyl groups (the O(2)—Co bond length is equal to 2.096 Å, the O(4)—Co bond length is equal to 2.071 Å (see Table 7)) to form the chelate seven-membered ring (Fig. 2), and the coordination of O(3) and O(5) with the Co atoms results in the formation of the three-dimensional cage structure (Fig. 3). In this case, maleic acid acts as the tetradentate ligand similarly to the Cu^{II} maleate complex described previously, where the metal atom is in the five-coordination square-pyramidal surrounding.[11] The polyhedron is completed to the octahedron by two H_2O molecules (O(6) and O(7)) arranged in *cis*-orientation to each other. The third H_2O molecule (not shown in order to simplify the figures) is the water of crystallization. The O(12) atom of the water molecule of crystallization has three shortened intermolecular contacts: with the carboxyl O(3) atom, which is not incorporated in the chelate cycle (2.76 Å), and two O(7) atoms (2.77 Å and 2.86 Å) of coordination H_2O molecules of adjacent Co atoms. Despite the fact that hydrogen atoms were not localized, these intermolecular contacts, judging from the bond lengths and bond angles at oxygen atoms, are close to tetrahedral and can prob-

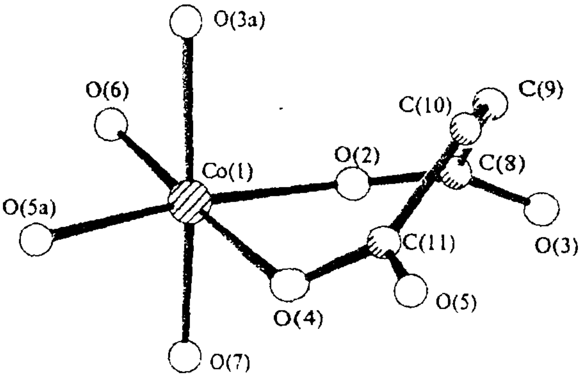

Fig. 2. Fragment of the coordination polyhedron of Co^{II} maleate.

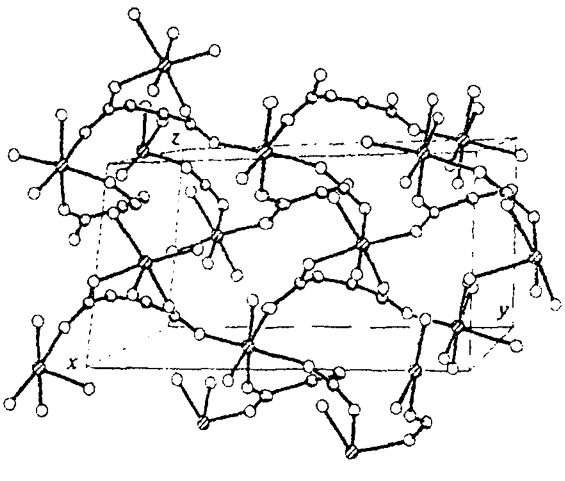

Fig. 3. Structure of the three-dimensional coordination polymer of Co^{II} maleate.

Table 7. Bond lengths (*d*) in Co maleate and Co fumarate

Bond	*d*/Å	Bond	*d*/Å
Co maleate			
Co—O(4)	2.071(4)		
Co—O(5)[a]	2.079(4)	O(3)—C(8)	1.270(6)
Co—O(7)	2.083(4)	O(4)—C(11)	1.245(6)
Co—O(2)	2.096(4)	O(5)—C(11)	1.260(7)
Co—O(6)	2.104(4)	C(8)—C(9)	1.494(6)
Co—O(3)[b]	2.144(4)	C(9)—C(10)	1.327(8)
O(2)—C(8)	1.251(6)	C(10)—C(11)	1.508(7)
Co fumarate			
Co(1)—O(5)	2.066(2)	C(1)—O(4)	1.275(2)
Co(1)—O(3)	2.078(2)	C(1)—C(3)	1.490(3)
Co(1)—O(2)	2.131(2)	C(2)—O(7)	1.245(2)
Co(2)—O(6)	2.083(3)	C(2)—O(3)	1.273(2)
Co(2)—O(4)	2.106(2)	C(2)—C(4)	1.501(3)
Co(2)—O(1)	2.119(2)	C(3)—C(4)	1.321(3)
C(1)—O(8)	1.245(2)		

[a] $x + 1/2, -y + 3/2, z + 1/2$. [b] $x, -y + 1, z + 1/2$.

ably be considered as fairly strong hydrogen bonds, due to which an infinite hydrogen-linked chain of alternating coordination and crystallization water molecules forms.

Fumaric acid acts as the bidentate ligand. The crystals of Co^{II} fumarate have the composition $[CoC_4H_2O_4 \cdot 4H_2O]_n \cdot nH_2O$. The crystallographic data are presented in Table 4. Two O atoms of the carboxyl groups are linked with two Co atoms (the O(3)—Co(1) and O(4)—Co(2) bond lengths are equal to 2.078 Å and 2.106 Å, respectively (see Table 6)). Four H_2O molecules supplement the coordination of the metal to the octahedron, and the fifth molecule is the water of crystallization. Two crystallographically independent Co atoms are localized in particular sites on the double axis, which results in the formation of an infinite chain of the coordination polymer with the *cis*-arranged residues of fumaric acid, whose fragment is presented in Fig. 4. The molecule of water of crystallization is also arranged in two particular sites on double axes and form strong (2.69—2.73 Å) hydrogen bonds with the polymeric chain to link them to a three-dimensional network. It is noteworthy that the systems of hydrogen bonds observed in Co^{II} maleate and fumarate can turn out to be promising proton conductors.

Thus, the compounds obtained have both the monomeric (acid salts) and polymeric chain or three-dimensional structure (coordination polymers), whose double bond is not involved in the coordination, which is important for subsequent polymerization transformations of salts based on unsaturated dicarboxylic acids.

Experimental

$Co(MeCOO)_2$, $Ni(MeCOO)_2 \cdot 4H_2O$, $Cu(MeCOO)_2 \cdot H_2O$, $Zn(MeCOO)_2$ (analytically pure grade); $Fe_2(SO_4)_3 \cdot H_2O$ (analytically pure grade); $CoCO_3$, $NiCO_3$, $ZnCO_3$, $Cu(OH)_2$, $Fe(OH)_3$, and metallic Fe (pure grade) and maleic, fumaric, and itaconic acids (recrystallized from water) were used.

Acid Co^{II}, Ni^{II}, and Zn^{II} maleates were prepared in reactions of concentrated aqueous solutions of metal acetates with **1** (molar ratios were 1 : 1 and 1 : 2). The reaction mixtures were stirred for 5 h at 40—50 °C. The precipitates formed were filtered off, washed with acetone, and dried *in vacuo* for 3 h at 40—50 °C.

Neutral maleates were synthesized by dissolving Co^{II}, Ni^{II}, and Zn^{II} carbonates and Cu^{II} hydroxide in a methanolic solution of a twofold excess of **1** with vigorous stirring at 50—60 °C for 24 h. Then the solution was filtered off from the unconsumed carbonate (hydroxide), and the final product was precipitated by a threefold excess of diethyl ether, washed

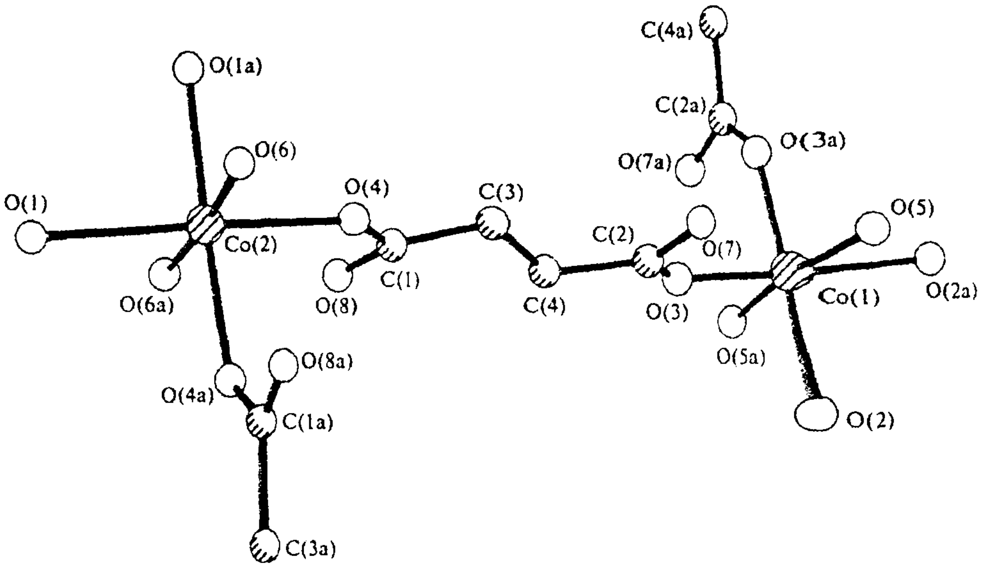

Fig. 4. Fragment of the chain of the coordination polymer of Co^{II} fumarate.

Table 8. Bond angles (ω) in Co maleate and Co fumarate

Angle	ω/deg	Angle	ω/deg
		Co maleate	
O(4)—Co—O(5)^a	82.1(2)	O(2)—Co—O(3)^b	97.0(2)
O(4)—Co—O(7)	91.4(2)	O(6)—Co—O(3)^b	87.3(2)
O(5)^a—Co—O(7)	95.0(2)	C(8)—O(2)—Co	129.1(3)
O(4)—Co—O(2)	86.8(2)	C(8)—O(3)—Co^c	130.8(3)
O(5)^a—Co—O(2)	168.9(2)	C(11)—O(4)—Co	132.7(3)
O(7)—Co—O(2)	84.5(2)	C(11)—O(5)—Co^d	127.6(3)
O(4)—Co—O(6)	176.9(2)	O(2)—C(8)—O(3)	123.4(4)
O(5)^a—Co—O(6)	100.8	O(2)—C(8)—C(9)	122.2(4)
O(7)—Co—O(6)	89.4(2)	O(3)—C(8)—C(9)	114.3(4)
O(2)—Co—O(6)	90.3(2)	C(10)—C(9)—C(10)	127.3(4)
O(4)—Co—O(3)^b	92.0(2)	C(9)—C(10)—C(11)	126.9(4)
O(5)^a—Co—O(3)^b	84.2(2)	O(4)—C(11)—O(5)	123.5(5)
O(7)—Co—O(3)^b	176.4(2)	O(4)—C(11)—C(10)	121.5(5)
		O(5)—C(11)—C(10)	115.0(5)
		Co fumarate	
O(5)^e—Co(1)—O(5)	175.03(13)	O(4)^f—Co(2)—O(4)	92.32(10)
O(5)^e—Co(1)—O(3)^e	87.62(7)	O(6)^f—Co(2)—O(1)^f	90.48(10)
O(5)—Co(1)—O(3)^e	95.86(7)	O(6)—Co(2)—O(1)^f	86.55(10)
O(5)^e—Co(1)—O(3)	95.86(7)	O(4)—Co(2)—O(1)^f	173.80(7)
O(5)—Co(1)—O(3)	87.62(7)	O(4)—Co(2)—O(1)^f	87.86(8)
O(3)^e—Co(1)—O(3)	91.64(11)	O(6)^f—Co(2)—O(1)	86.55(10)
O(5)^e—Co(1)—O(2)	86.42(9)	O(6)—Co(2)—O(1)	90.48(10)
O(5)—Co(1)—O(2)	90.22(9)	O(4)^f—Co(2)—O(1)	87.86(8)
O(3)^e—Co(1)—O(2)	173.69(7)	O(4)—Co(2)—O(1)	173.80(7)
O(3)—Co(1)—O(2)	86.90(8)	O(1)^f—Co(2)—O(1)	92.63(13)
O(5)^e—Co(1)—O(2)^e	90.22(9)	O(8)—C(1)—O(4)	124.5(2)
O(5)—Co(1)—O(2)^e	86.42(9)	O(8)—C(1)—C(3)	121.6(2)
O(3)^e—Co(1)—O(2)^e	86.90(8)	O(4)—C(1)—C(3)	113.7(2)
O(3)—Co(1)—O(2)^e	173.69(7)	C(1)—O(4)—Co(2)	133.02(13)
O(2)—Co(1)—O(2)^e	95.21(11)	O(7)—C(2)—O(3)	124.6(2)
O(6)^f—Co(2)—O(6)	175.7(2)	O(7)—C(2)—C(4)	118.7(2)
O(6)^f—Co(2)—O(4)^f	95.72(9)	O(3)—C(2)—C(4)	116.3(2)
O(6)—Co(2)—O(4)^f	87.26(9)	C(2)—O(3)—Co(1)	134.64(13)
O(6)^f—Co(2)—O(4)	87.26(9)	C(4)—C(3)—C(1)	121.5(2)
O(6)—Co(2)—O(4)	95.72(9)	C(3)—C(4)—C(2)	124.6(2)

[a] $x + 1/2, -y + 3/2, z + 1/2$.

[b] $x, -y + 1, z + 1/2$.

[c] $3x, -y + 1, z - 1/2$.

[d] $4x - 1/2, -y + 3/2, z - 1/2$.

[e] $-x, y, -z$. [f] $-x + 1, y, -z + 1$.

with ether, and dried *in vacuo* for 1 h at 40—50 °C. The yields were 90—95% and 65—70% for Cu^{II} maleate.

Fe^{II} hydrogen maleate was obtained by dissolving finely disperse metallic Fe in an aqueous solution of **1** (in a molar ratio of 1 : 2) in an inert atmosphere with vigorous stirring for 5 h at 40—50 °C. The unconsumed iron was removed by filtration, and the mother liquor was kept for 24 h. The crystals precipitated were filtered off and dried *in vacuo* for 3 h at 40—50 °C. The salt obtained was stable in air.

Mixed-valence **Fe maleate** (Fe^{II} and Fe^{III}) was synthesized by dissolving freshly precipitated Fe^{III} hydroxide in an aqueous solution of **1** (in molar ratios of 1 : 1, 1 : 2, and 1 : 3) for 24 h at 40—50 °C and 80—90 °C. The solution was filtered from the unconsumed hydroxide and concentrated until the precipitate was formed. The salt was washed with ether and dried *in vacuo* for 3 h at 40—50 °C.

Fe^{III} maleate was obtained in a way similar to the synthesis of Cu^{II} maleate.

Fumarates were synthesized by the reactions of a twofold excess of Co^{II}, Ni^{II}, Zn^{II}, and Cu^{II} acetates and Fe^{III} sulfate with an aqueous solution of compound **2** at 80—90 °C, the reaction time was 30—40 h. The precipitate formed was washed with acetone and dried *in vacuo* for 3 h at 40—50 °C. The yields were 75—80%.

Itaconates were prepared according to procedures described for acid and neutral maleates.

IR spectra were recorded on a Perkin—Elmer 325 spectrophotometer, and samples were prepared as pellets with KBr. Elemental analysis was performed by the atomic absorption method on a Saturn instrument and by the combustion method.

The magnetic susceptibility was measured by the Faraday method at 80 and 290 K. The magnetic moment was calculated by the formula $\mu_{\rm eff} = 2.84\sqrt{\chi_{\rm at}T}$, where $\chi_{\rm at}$ is the magnetic susceptibility referred to 1 g-at. metal.

ESR spectra were recorded on an SE/X-2544 radiospectrometer (Radiopan). The number of paramagnetic centers was determined comparing second integrals of the ESR spectra of samples studied and of the standard sample of $CuSO_4 \cdot 5H_2O$ with the known mass.

Mössbauer spectra were recorded on a spectrometer (WISSEL) with a Co^{57}(Rh) source in the constant acceleration regime. The calibration by rates was performed relative to the spectrum of metallic α-Fe.

X-ray diffraction analysis was carried out on a KM-4 automated four-circle diffractometer (KUMA DIFFRACTION). Structures were solved by the direct method using the SHELX-93 complex of programs.[19] In Fe^{II} hydrogen maleate and Co^{II} fumarate, hydrogen atoms were directly localized from differential syntheses. The least-squares refinement was performed in the full-matrix anisotropic (isotropic for H) approximation. Absorption was not taken into account.

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