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New Complexes of 4-[(4-Fluorophenyl)amino]-4-oxobut-2-enoic Acid with Selected Transition Metal Ions: Synthesis, Thermal, and Magnetic Properties[1]

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Abstract—Complexes of 4-[(4-fluorophenyl)amino]-4-oxobut-2-enoic acid, HL, with Mn(II), Co(II), Ni(II), Cu(II), Nd(III), Gd(III), and Er(III) were synthesized and characterized by various physico-chemical methods: elemental analysis, FT-IR, TG, DTG, DSC, TG/FT-IR, XRF, XRD, and magnetic measurements using the Gouy's method and a SQUID-VSM magnetometer. The complexes were found to be hydrates (except Er(III) complex) containing 1 to 4 molecules of water. The carboxylate groups acted as bidentate ligands.

Keywords: 4-[(4-fluorophenyl)amino]-4-oxobut-2-enoic acid, selected 3*d*- and 4*f*-metals, IR and X-ray spectra, thermal stability, magnetic properties

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Transition metals carboxylates demonstrate variable stereochemistry depending upon the mechanism of their formation. Their activity is modulated by the nature of substituents at the basic ligand and kinds of coordinated metal ions [1–3].

Maleic acid is used in pharmacology for producing corresponding maleates that make the drugs more stable. In biochemistry maleate ion acts as an inhibitor of transaminase reactions that catalyze transfer of the amino group of an amino acid to a carbonyl compound, commonly an α-keto acid. The maleinic acid derivatives demonstrate cytotoxic activity towards leukaemic cells and a strong antifungal activity [4]. Those may also act as inhibitors of aldose reductase [5].

According to the literature survey, the complexes of maleic acid with Tl(I), Sn(IV), Mo(IV), and Co(II) ions and its various amido derivatives with Cu(II) ion were prepared and characterized [6–10]. The thermodynamic functions of compounds of 4-nitro- and 4-methoxymaleanilic acids with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) were determined [11]. The new complexes of maleanilic and phtalanilic acids with Cr(III), and Sb(III) were synthesized and studies as well [12–15]. (*Z*)-4-Oxo-4-(phenylamino)but-2-enoic acid and its compounds with La(III), Eu(III), Tb(III), and Yb(III) were prepared and characterized by some physicochemical methods [16].

Complexes of selected transition metal ions with 4-oxo-4-{[3-(trifluoromethyl)phenyl]amino}but-2-enoic acid anion have been studied [17].

The current study targeted synthesis of new Mn(II), Co(II), Ni(II), Cu(II), Nd(III), Gd(III), and Er(III) complexes with 4-[(4-fluorophenyl)amino]-4-oxobut-2-enoic acid anion and elucidation of their molecular structures. Because of poor crystallization of the compounds in neutral solvents the molecular structures of the complexes were not determined. Instead, their diffractograms are presented. The particular attention was directed towards determination of stoichiometry of the complexes by elemental analysis, X-ray fluorescence spectroscopy (XRF) and thermogravimetric methods. IR spectroscopy was used for determining possible centers of coordination of HL anion. IR spectroscopy and magnetic susceptibility data were used for determining geometry around Mn(II), Co(II), Ni(II), Cu(II), Nd(III), Gd(III), and Er(III) ions.

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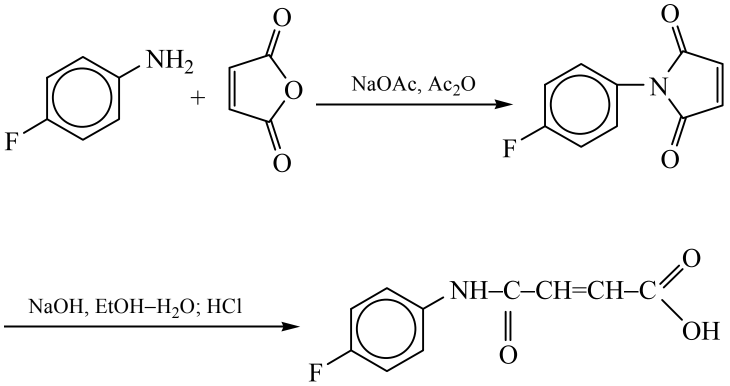
[1] The text was submitted by the authors in English.

Scheme 1. synthesis of 4-[(4-fluorophenyl)amino]-4-oxobut-2-enoic acid.



EXPERIMENTAL

Chemicals and solvents used in the synthesis were commercially available, reagent grade and used without purification. CHN analysis was carried out on a CHN 2400 Perkin-Elmer analyzer. The amounts of Ln(III) and M(II) metals and fluorine were determined by X-ray fluorescence XRF method using an energy dispersion spectrophotometer XRF-1510 (Canberra-Packard). FT-IR spectra (KBr discs) were recorded over the range of 4000–400 cm^{-1} on a M–80 Perkin–Elmer spectrophotometer. ^1H NMR spectrum for HL in DMSO-d_6 was measured on a Bruker Avance 300 MHz NMR spectrometer at 298.1 K.

X-Ray diffraction patterns of compounds and the products of their decomposition were determined on a HZG–4 (Carl Zeiss, Jena) diffractometer using Ni filtered CuK_α radiation. The measurements were made within the range of $2\theta = 4^\circ–80^\circ$ by means of the Bragg-Brentano method. For interpretation of diffractograms the Dicvol 06 programme was used. Thermal stability and decomposition processes of complexes were studied using a Setsys 16/18 (Setaram), TG, DTG and DSC instrument. The experiments were carried out under the air flow in the temperature range of 293–1173 K at a heating rate of 5 K/min. The initial masses of complexes samples changed from 3.69 to 4.74 mg. The compounds were heated in Al_2O_3 crucibles.

Magnetic susceptibility of samples was studied at the temperature ranges of 76–303 and 2–300 K. The measurements were carried out using the Gouy's method and with the use of a Quantum Design SQUID-VSM magnetometer. A superconducting magnet was generally operated at a field strength ranging from 0 to 7 T. Measurements of samples were made at magnetic field 0.1 T. A SQUID magnetometer was calibrated with the palladium rod sample. In the case of the Gouy's method the mass changes were determined on a Cahn RM-2 electrobalance. The calibrate employed was $Hg[Co(SCN)_4]$ for which the magnetic susceptibility was assumed to be 1.644×10^{-5} cm^3/g. The measurements were made at a magnetic field strength of 0.99 T. Corrections for diamagnetism of the constituent atoms were calculated using the Pascal's constants [18, 19]. Effective magnetic moment values were calculated by the equation:

$$\mu_{eff} = 2.83\,(\chi_m^{corr}T)^{1/2},$$

where μ_{eff} is an effective magnetic moment, χ_m^{corr} is a magnetic susceptibility per molecule, and T ia sn absolute temperature.

Synthesis. HL was prepared by the two-steps process (Scheme 1). At first *N*-(4-fluorophenyl) maleimide was obtained in the following way. A mixture of 11.1 g (0.1 mol) of 4-fluoroaniline with 10.0 g (0.105 mol) of maleic anhydride, 8.2 g sodium acetate, and 50 mL acetic acid was stirred over 1 h at room temperature. Then the mixture was heated at 80–85ºC for 5 h. Upon following cooling down the flask content was poured onto ice. The colourless precipitate was filtered off and washed with water. Yield 18.3 g (95.5%), mp 147.5ºC [20].

In the second step thus obtained *N*-(4-fluorophenyl) maleimide was hydrolyzed in a solution of NaOH. *N*-(4-fluorophenyl)maleimide (9.6 g, 0.05 mol) were mixed with 100 mL of ethanol, 60 mL of water, and 2 g (0.05 mol) of NaOH. The mixture was boiled for 1.5 h, then it was cooled down and acidified with 10% HCl (pH = 1). The obtained crystalline solid was filtered off and purified by crystallization from methanol–water solution. Yield 8.3 g (79%), mp 211–212ºC [21]. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.36 s (2H, CH=CH), 7.17–7.63 m (4H, Ar-H), 10.43 s (1H, NH,), 12.86 s (1H, COOH). Found, %: C 57.51; H 3.90; N 6.71. $C_{10}H_8FNO_3$ Calculated, %: C 57.42; H 3.85; N 6.70. *M* 209.17.

Ammonium salt of HL (pH~5) of 0.1 mol/L concentration was prepared by adding NH_{3aq} solution (25% pure, Polish Chemical Reagents in Gliwice, Poland) to water solution of HL. For obtaining the 4f element(III) chlorides the samples of 0.8 g of those elements oxides (99.9% pure, Aldrich Chemical Company) were digested in the equivalent amount of concentrated HCl (35–36% pure, Polish Chemical Reagents in Gliwice–Poland). The formed chlorides were dried, dissolved in water giving the solutions of corresponding chlorides, concentration 0.1 mol/L, pH ca 5.

The complexes of 3*d*- and 4*f*-electron metal ions with HL were prepared by adding the equivalent amounts of 0.1 mol/L ammonium salt of HL (pH ca 5) to warm solutions of the corresponding element chlorides and crystallized at 293 K. Certain volumes of solutions, 39, 84, 84, 116, 142, 132, and 125 cm^3, of 0.1 M ammonium 4-[(4-fluorophenyl)amino]-4-oxobut-2-enoate were added to the certain chloride solutions of Mn(II), Co(II), Ni(II), Cu(II), Nd(III), Gd(III), and Er(III). For reaching equilibrium state the solids were constantly stirred for 1 h, then filtered off, washed with warm water to remove ammonium chloride and dried at 303 K until reaching the constant mass.

Sodium salt of HL acid was synthesized by the reaction of the equivalent amount of 0.1 mol/L ammonium salt of HL acid with the solution containing 0.1 g of NaOH (analytically pure, Polish Chemical Reagents in Gliwice–Poland) and crystallized.

$MnL_2·2H_2O$. Grey solid. IR spectrum, ν, cm^{-1}: 3436 ($\nu_{N–H}$), 3228 (ν_{OH}), 1672 ($\nu_{C=O}$), 1636 ($\nu_{C=C}$), 1612 [$\nu_{as}(COO^-)$], 1508 [$\nu(C_{Ar}=C_{Ar})$], 1408 ($\nu_{C=C}$), 1356 [$\nu_s(COO^-)$], 1228 (ω_{CH}), 1096 ($\nu_{C–F}$), 828 (ω_{CH}), 620 ($\delta_{N–H}$), 488 ($\nu_{Mn–O}$). Found, %: C 46.46; H 4.02; N 5.45; F 7.38; Mn 10.60. Calculated, %: C 46.89; H 3.93; N 5.47; F 7.42; Mn 10.73.

$CoL_2·H_2O$. Light-brown crystals. IR spectrum, ν, cm^{-1}: 3460 ($\nu_{N–H}$), 3328 (ν_{OH}), 1684 ($\nu_{C=O}$), 1636 ($\nu_{C=C}$), 1612 [$\nu_{as}(COO^-)$], 1512 [$\nu(C_{Ar}=C_{Ar})$], 1408 ($\nu_{C=C}$), 1356 [$\nu_s(COO^-)$], 1224 (ω_{CH}), 1100 ($\nu_{C–F}$), 836 (ω_{CH}), 620 ($\delta_{N–H}$), 492 ($\nu_{Co–O}$). Found, %: C 48.55; H 3.58; N 5.58; F 7.60; Co 11.55. Calculated, %: C 48.70; H 3.68; N 5.68; F 7.70; Co 11.95.

$NiL_2·H_2O$. Light-green crystals. IR spectrum, ν, cm^{-1}: 3359 ($\nu_{N–H}$), 3228 (ν_{OH}), 1672 ($\nu_{C=O}$), 1632 ($\nu_{C=C}$), 1612 [$\nu_{as}(COO^-)$], 1508 [$\nu(C_{Ar}=C_{Ar})$], 1408 ($\nu_{C=C}$), 1352 [$\nu_s(COO^-)$], 1224 (ω_{CH}), 1098 ($\nu_{C–F}$), 832 (ω_{CH}), 640 ($\delta_{N–H}$), 488 ($\nu_{Ni–O}$). Found, %: C 48.09; H 3.60; N 5.58; F 7.68; Ni 11.60. Calculated, %: C 48.72; H 3.68; N 5.68; F 7.71; Ni 11.90.

$CuL_2·4H_2O$. Green crystals. IR spectrum, ν, cm^{-1}: 3412 ($\nu_{N–H}$), 3132 (ν_{OH}), 1676 ($\nu_{C=O}$), 1632 ($\nu_{C=C}$), 1612 [$\nu_{as}(COO^-)$], 1492 [$\nu(C_{Ar}=C_{Ar})$], 1408 ($\nu_{C=C}$), 1364 [$\nu_s(COO^-)$], 1224 (ω_{CH}), 1100 ($\nu_{C–F}$), 836 (ω_{CH}), 640 ($\delta_{N–H}$), 486 ($\nu_{Cu–O}$). Found, %: C 43.43; H 4.27; N 5.00; F 6.80; Cu 11.42. Calculated, %: C 43.52; H 4.37; N 5.08; F 6.89; Cu 11.52.

$NdL_3·2H_2O$. Light-green crystals. IR spectrum, ν, cm^{-1}: 3372 ($\nu_{N–H}$), 3300 (ν_{OH}), 1664 ($\nu_{C=O}$), 1632 ($\nu_{C=C}$), 1600 [$\nu_{as}(COO^-)$], 1508 [$\nu(C_{Ar}=C_{Ar})$], 1408 ($\nu_{C=C}$), 1352 [$\nu_s(COO^-)$], 1232 (ω_{CH}), 1100 ($\nu_{C–F}$), 836 (ω_{CH}), 632 ($\delta_{N–H}$), 488 ($\nu_{Nd–O}$). Found, %: C 44.36; H 3.46; N 5.20; F 7.06; Nd 17.82. Calculated, %: C 44.70; H 3.50; N 5.22; F 7.08; Nd 17.92.

$GdL_3·3H_2O$. Creamy crystals. IR spectrum, ν, cm^{-1}: 3364 ($\nu_{N–H}$), 3292 (ν_{OH}), 1664 ($\nu_{C=O}$), 1632 ($\nu_{C=C}$), 1612 [$\nu_{as}(COO^-)$], 1508 [$\nu(C_{Ar}=C_{Ar})$], 1408 ($\nu_{C=C}$), 1356 [$\nu_s(COO^-)$], 1232 (ω_{CH}), 1100 ($\nu_{C–F}$), 832 (ω_{CH}), 628 ($\delta_{N–H}$), 480 ($\nu_{Gd–O}$). Found, %: C 43.33; H 3.51; N 5.00; F 6.68; Gd 18.62. Calculated, %: C 43.11; H 3.61; N 5.03; F 6.82; Gd 18.82.

ErL_3. Creamy crystals. IR spectrum, ν, cm^{-1}: 3368 ($\nu_{N–H}$), 1664 ($\nu_{C=O}$), 1632 ($\nu_{C=C}$), 1616 [$\nu_{as}(COO^-)$], 1508 [$\nu(C_{Ar}=C_{Ar})$], 1408 ($\nu_{C=C}$), 1356 [$\nu_s(COO^-)$], 1228 (ω_{CH}), 1100 ($\nu_{C–F}$), 828 (ω_{CH}), 624 ($\delta_{N–H}$), 482 ($\nu_{Er–O}$). Found, %: C 45.40; H 3.05; N 5.30; F 7.18; Er 21.03. Calculated, %: C 45.50; H 3.06; N 5.31; F 7.20; Er 21.13.

RESULTS AND DISCUSSION

IR spectra of HL, its complexes and sodium salt were recorded for monitorring the complexation process and identifying the atoms of ligand carboxylate coordinated to the appropriate cations. For parent carboxylic ligand, HL, broad bands with the maxima at 3408 and 2940 cm^{-1} indicated the N–H and $–CH_2$ stretching bonds vibrations, respectively [22–27]. In its complex spectra the bands at 3328–3128 cm^{-1} indicated the presence of water molecules (except of Er(III)) in the compounds and those at 3464–3359 cm^{-1} originated from the N–H bond vibrations. The band at 1700 cm^{-1} was attributed to stretching vibrations of the COOH group of HL. Upon deprotonation two strong bands at 1616–1600 and 1364–1352 cm^{-1} were

Table 1. The unit cell parameters for polycrystalline series of 4-[(4-fluorophenyl)amino]-4-oxobut-2-enoic acid with Mn(II), Co(II), Ni(II), Cu(II), Nd(III), Gd(III), and Er(III)

Complex $L^- = C_{10}H_7O_3FN$	Crystal system	a, Å	b, Å	c, Å	α, deg	β, deg	γ, deg	V, Å^3
$MnL_2 \cdot 2H_2O$	Triclinic	7.7901	17.1655	20.2041	70.583	86.964	81.139	2517.64
$CoL_2 \cdot H_2O$	Monoclinic	13.8315	7.9569	19.2611	90.000	97.486	90.000	2101.72
$NiL_2 \cdot H_2O$	Triclinic	9.2713	14.0216	19.2483	92.494	98.150	101.609	2419.60
$CuL_2 \cdot 4H_2O$	Monoclinic	13.6829	12.7944	16.6121	90.000	92.968	90.000	2904.30
$NdL_3 \cdot 2H_2O$	Triclinic	10.3250	12.9079	15.0070	73.430	73.091	68.679	1746.10
$GdL_3 \cdot 3H_2O$	Triclinic	9.7889	12.8367	15.1010	93.485	108.712	109.349	1665.84
ErL_3	Triclinic	8.2255	12.1803	14.3824	99.815	97.626	90.128	1406.86

attributed to COO^- asymmetric and symmetric stretching vibrations, respectively. The bands of C=C valency vibrations were recorded at 1636–1632 cm^{-1}. The –C=C– stretching ring vibrations, $\nu_{C=C}$, were recorded at 1512–1452 cm^{-1}. The C–F stretching vibrations, ν_{C-F}, were recorded at 1100–1096 cm^{-1}. The bands characteristic for –*N*-H deformation vibrations, δ_{N-H}, appeared at 640–620 cm^{-1} and those at 836–828 cm^{-1} were attributed to C–H valency vibrations in the 1 : 4 substituted ring. The bands at 492–480 cm^{-1} confirmed the presence of the ionic metal–oxygen bond [22–27]. In the spectra of complexes the bands of $\nu_{as}(OCO^-)$ and $\nu_s(OCO^-)$ were shifted to lower frequencies compared to those of sodium salt [$\nu_{as}(OCO^-)$ = 1672 cm^{-1}, $\nu_s(OCO^-)$ = 1332 cm^{-1}] [27]. With reference to Nakamoto criterion, the carboxylate ion acted as a bidentate chelating group [1, 3, 27]. The values of $\Delta\nu_{OCO}$ for the analyzed compounds were smaller ($\Delta\nu_{OCO}$ = 260–248 cm^{-1}) than those for sodium salt ($\Delta\nu_{OCO}$ = 340 cm^{-1}).

Position of the C–F stretching vibrations in the complexes spectra (1100 cm^{-1}) was practically in the same position as that in the parent ligand spectrum (1096 cm^{-1}), which suggested that F atom did not coordinate with the metal center. The fingerprint regions have been also compared. Several bands present in the HL spectrum (for example, ν_{N-H} or δ_{N-H}) were observed in different positions compared to those in its metal complexes IR spectra due to interactions of these groups vibrations with neighbouring atoms or ions in the molecules.

The X–ray powder diffraction patterns of complexes indicated the crystalline nature of those [28, 29]. In order to determine their unit cell parameters the X–ray powder diffractions data were calculated by applying the Dicvol06 program [30] (Table 1).

Thermogravimetric studies of analyzed transition metal complexes were carried out in the air in the range of 293–1273 K (Table 2, Fig. 1). TG, DTG, and DSC curves were recorded using the DSC/TG technique. Upon heating to 1273 K the compounds decomposed in three steps. They were stable up 310–410 K. In the range of 310–439 K they dehydrated in one step with endothermic effects (DSC curves) losing molecules of water and forming anhydrous compounds. The mass losses calculated from TG curves were equal to 4.25–13.00% corresponding to the loss of two and four molecules of water (calculated 3.65–13.05%).

Energy effects accompanying the dehydration processes were also determined. Enthalpy values, Δ*H*, changed from 9.65 to 185.9 kJ/mol and from 2.41 to 93.98 kJ/mol per one molecule of water. The values demonstrated that water molecules were bounded in these compounds with different strengths depending on their positions in the complexes coordination spheres and nature of the central ions.

Upon heating the anhydrous complexes of 3*d*- and 4*f*-electrons metals ions formed intermediates, oxyfluorides (427–785 K), that ultimately yielded the oxides of the appropriate metals. Mass losses calculated from TG curves were in the range of 30.09–76.19% indicating formation of oxyfluorides (calculated values changed from 29.13 to 77.87%). The intermediate compounds decomposed into the oxides of respective metals MO and Ln_2O_3, where M(II) = Mn, Co, Ni, Cu and Ln(III) = Nd, Gd, Er. Temperature

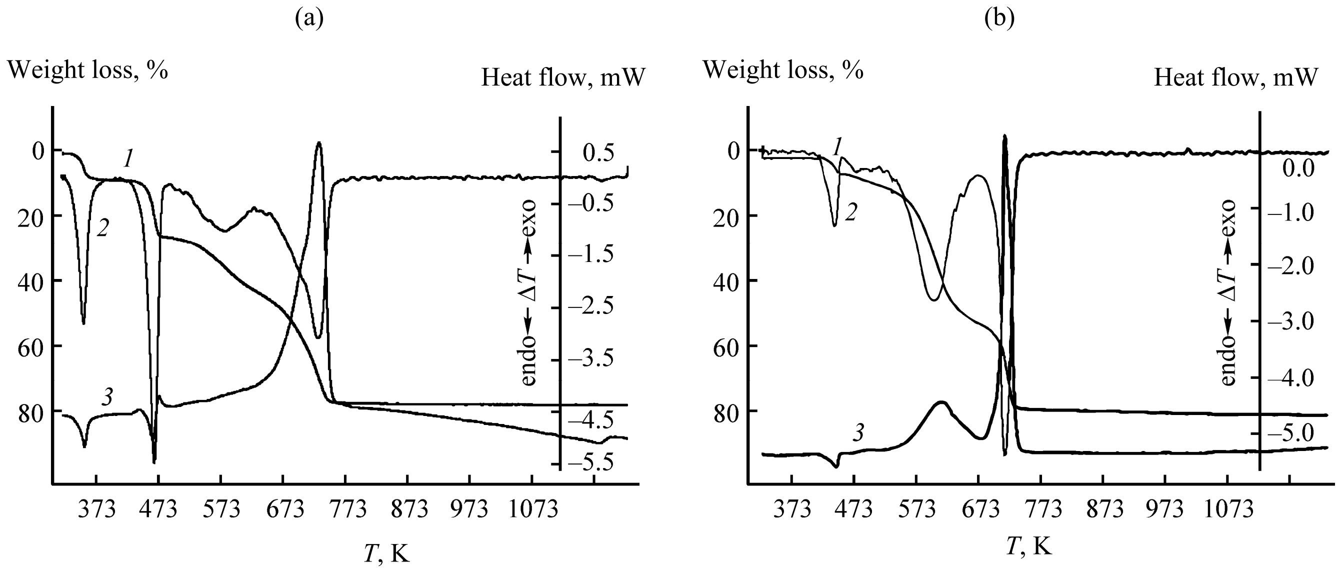


Fig. 1. (*1*) TG, (*2*) DTG, and (*3*) DSC curves for (a) Mn(II) and (b) Nd(III) complexes.

of their formation was in the range of 706–1273 K. The masses of residues determined from TG curves were in the range of 9.47–23.10% (theoretical values changed from 9.02 to 24.14%). Those were obtained as metal oxides and verified by comparing their FT-IR spectra and powder diffractograms with those of pure oxides. The results indicated that thermal decomposition of analyzed complexes in the air proceeded along the following pathways:

$$ML_2{\cdot}nH_2O \rightarrow ML_2 \rightarrow M_2OF_2 \rightarrow MO,$$

M(II) = Mn, Co, Ni, Cu; $n = 1$ for Co, Ni;
$n = 2$ for Mn; $n = 4$ for Cu;

$$LnL_3{\cdot}nH_2O \rightarrow LnL_3 \rightarrow LnOF \rightarrow Ln_2O_3,$$

Ln(III) = Nd, Gd, Er; $n = 2$ for Nd; $n = 3$ for Gd;
$n = 0$ for Er.

The accumulated data demonstrated that the coordination numbers of central ions were probably equal to 6, 8 or 9 for trivalent ions. In the case of Nd(III) and Gd(III) the water molecules seemed to be aqua ligands [31, 32]. For Mn(II), Co(II), Ni(II), and Cu(II) complexes the coordination numbers could be equal to 5, 6 or 8 depending on nature of the central ion.

Data accumulated for the complete structures of the complexes could give fair information about positions

Table 2. Temperature ranges for thermal stability in the air at 293–1273 K and enthalpy values of dehydration processes for the studied complexes[a]

Complex $L^- = C_{10}H_7O_3FN$	ΔT_1, K	Weight loss, %		nH_2O	ΔT_2, K	Weight loss, %		Residue, %		T_k, K	ΔH, kJ/mol	ΔH^0, kJ/mol
		calculated	found			calculated	found	calculated	found			
$MnL_2{\cdot}2H_2O$	331–352	7.10	7.90	2	431–473	29.13	30.09	10.63	10.52	773	185.9	92.95
$CoL_2{\cdot}H_2O$	327–360	3.85	4.25	1	431–493	33.07	34.00	11.28	11.37	752	93.98	93.98
$NiL_2{\cdot}H_2O$	310–373	3.65	4.35	1	427–514	48.23	49.76	9.02	9.47	752	87.74	87.74
$CuL_2{\cdot}4H_2O$	310–423	13.05	13.00	4	493–680	46.18	46.02	14.50	15.01	706	9.65	2.41
$NdL_3{\cdot}2H_2O$	385–439	4.47	4.84	2	693–773	77.87	76.19	20.89	21.95	1073	91.98	45.99
$GdL_3{\cdot}3H_2O$	410–439	6.46	6.34	3	452–773	77.01	73.21	22.22	21.65	1273	112.72	37.57
ErL_3	–	–	–	–	535–785	74.59	74.60	24.14	23.10	1273	–	–

[a] (ΔT_1) temperature range of dehydration; (n) number of water molecules; (ΔT_2) temperature range of anhydrous complex decomposition; (T_k) final temperature of decomposition, (ΔH) enthalpy value for dehydration process, (ΔH^0) enthalpy value per one water molecule.

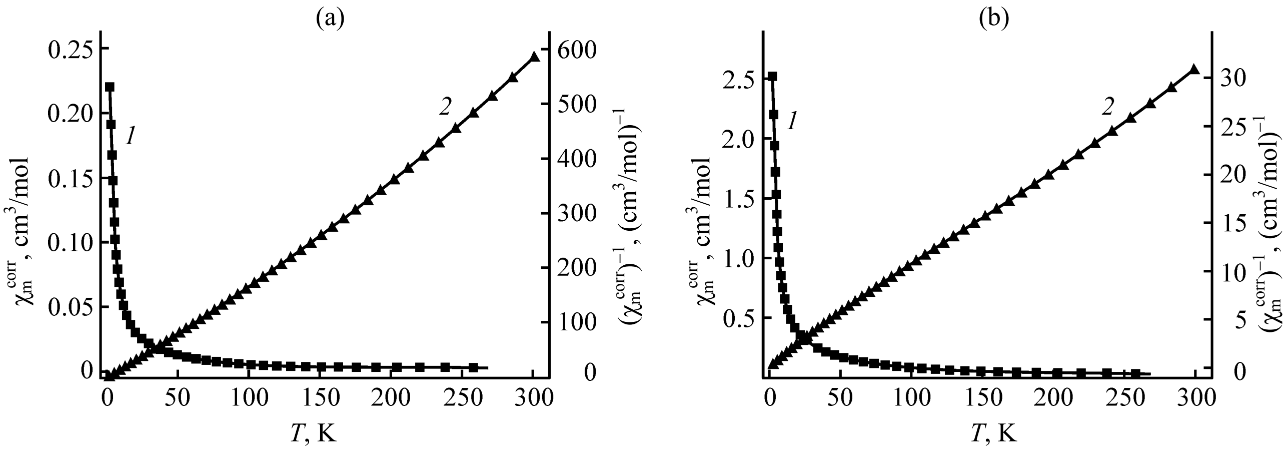


Fig. 2. Relashionships between (*1*) χ_m^{corr} and (*2*) $(\chi_m^{corr})^{-1}$ values, and *T* for (a) Ni(II) and (b) Er(III) complexes.

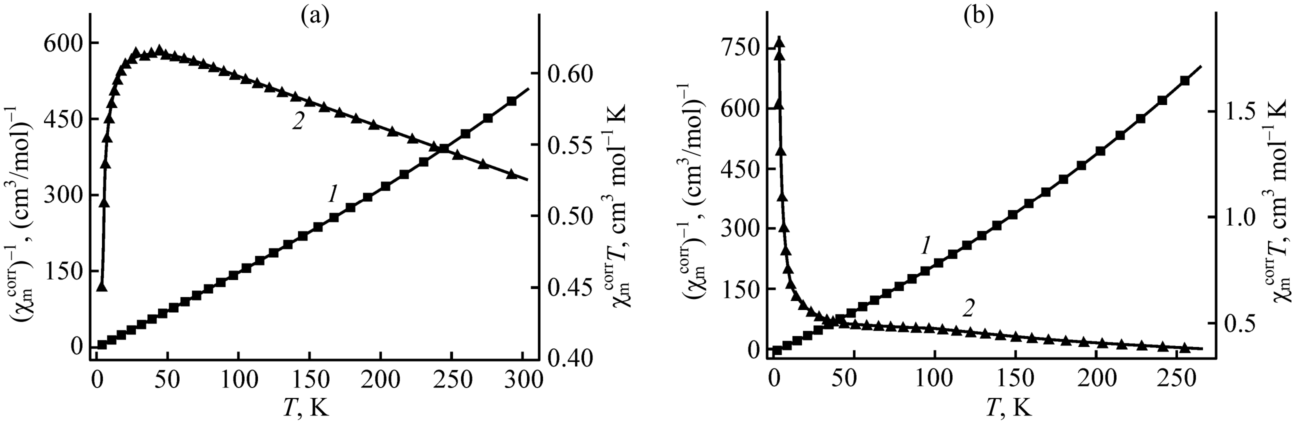


Fig. 3. Relashionships between (*1*) $(\chi_m^{corr})^{-1}$ and (*2*) $\chi_m^{corr}T$ values, and *T* for (a) Ni(II) and (b) Cu(II) complexes.

of water molecules in the compounds but their single crystals have not been isolated so far from various solvents (H_2O, alcohols, DMSO, DMF) and using different metal:ligand ratios.

The initial dehydration temperature values for complexes indicated that the water molecules could be also lattice water because it was released below 423 K [33].

Magnetic measurements. For estimation of metal ligand bonding nature in analyzed complexes and determining the reason for their colour to be typical for 4*f*-electron metal(III) ions and for studying of the surrounding of coordination ions the magnetic susceptibility of compounds was measured over the ranges of 76–303 K [34–40], and of 2–300 K for determining whether the nature of atomic magnetic interaction changed at low temperatures (Figs. 2, 3).

The accumulated data indicated that the complexes obeyed the Curie–Weiss law. The effective magnetic moment values experimentally determined in the range of 76–303 K changed from: 2.1 μ_B to 1.77 μ_B for Cu(II); 3.40 to 3.70 μ_B for Co(II); 2.31 to 2.35 μ_B for Ni(II); 4.45 to 4.55 μ_B for Mn(II); 3.08 to 3.49 μ_B for Nd(III); 5.85 to 5.83 μ_B for Gd(III), and from 8.34 to 8.70 μ_B for Er(III) complexes.

In Nd(III), Gd(III) and Er(III) complexes the paramagnetic central ions remained practically unaffected by diamagnetic ligands. The 4*f* orbitals were effectively shielded by $5s^2$ and $5p^6$ orbitals. They were not involved in the bonds between Ln(III) ions and their close neighbours. Accordingly the metal–ligand bonding in Ln(III) compounds appeared to be predominantly electrostatic [39–41] as it was deduced from IR spectra.

Due to the fact that the 4*f* orbitals were well shielded by the surroundings of the ions, various states arising from $4f^n$ configurations were split by external fields only to ca 100 cm^{-1}. Therefore the electronic *f*–*f* transitions caused the absorption bands to be very sharp being similar to those of free atoms. As the colours were determined by the *f–f* transitions, they did not depend upon the environment of the ions [41]. The magnetic properties could be considered as those of the ground state alone. Therefore 4*f*-electron meatal(III) ions in the compounds acted the same way as free ions. The values of μ_{eff} determined for the studied complexes of 4*f* metals(III) were close to those calculated by the Hund and Van Vleck [2, 34] for Ln(III) ions.

The magnetic moments experimentally determined at 76–303 and 2–299 K for Mn(II), Co(II), Ni(II), and Cu(II) complexes seemed close to spin only values for the respective ions calculated from the equation $\mu_{\text{eff}} = [4s(s + 1)]^{1/2}$ ($s = n/2$) in the absence of the magnetic interactions for present spin-system. The theoretical values calculated at room temperature for Mn(II), Co(II), Ni(II), and Cu(II) ions were equal to 5.9, 3.88, 2.83, and 1.73 μ_B, respectively.

The magnetic moments determined at 2–300 K for complexes changed from 3.57 to 4.56 μ_B for Mn(II), 2.64 to 3.81 μ_B for Co(II); 1.9 to 2.03 μ_B for Ni(II), 3.51 to 1.69 μ_B for Cu(II), 2.31 to 3.32 μ_B for Nd(III), 8.81 to 8.09 μ_B for Gd(III), and from 6.46 to 8.80 μ_B for Er(III).

The magnetic moments for Mn(II) ion complex were lower than the spin–only value, which could be due to the fact that the vectors L and S were aligned by the strong field of the heavy atom in opposite directions and this diminished the resulting magnetic moment. The experimental data demonstrated that Mn(II) compound seemed to be the high–spin complex with octahedral symmetry around the central ion and the weak ligand field [1, 37, 40, 42, 43]. At 300 K the $\chi_m T$ value was equal to 2.5977 cm^3 K mol^{-1} (μ_{eff} = 4.56 μ_B). Upon lowering of temperature the $\chi_m T$ value and the magnetic moment decreased to 1.5956 cm^3 K mol^{-1} (μ_{eff} = 3.57 μ_B) at 2.02 K, which suggested an antiferromagnetic interaction between Mn(II) centres [44] or weak intermolecular hydrogen bonds in the compound lattice. Around the central ion there were probably four oxygen atoms from two carboxylate bidentate groups and two atoms of water molecules.

In the case of Co(II) complex the values of magnetic moments changed from 2.64 (at 2.03 K) to 3.81 μ_B (at 299 K). The experimental data indicated the Co(II) complex to be high–spin compound with the weak ligand field. At 300 K the $\chi_m T$ value was equal to 1.8113 cm^3 K mol^{-1} (μ_{eff} = 3.81 μ_B). Upon temperature lowering the $\chi_m T$ and the magnetic moment values decreased to 0.8729 cm^3 K mol^{-1} (μ_{eff} = 2.64 μ_B) at 2 K, which indicated the weak antiferromagnetic order between Co(II) centers or the intermolecular hydrogen bonds in the compound crystal lattice.

For Ni(II) ion complex the magnetic moments changed from 1.9 (at 2.029 K) to 2.03 μ_B (at 300 K). At 300 K the $\chi_m T$ value was equal to 0.5126 cm^3 K mol^{-1}, which increased to 0.6129 cm^3 K mol^{-1} at 47.40 K at lower temperature. This could be due to weak ferromagnetic order between Ni(II) centres of crystal lattice. In the range of 47.4–2.029 K the magnetic moments changed from 2.22 to 1.9 μ_B. These values were lower than those of calculated theoretically, which could indicate the antiferromagnetic interaction among Ni(II) ions (θ negative). The reason for this could be the second order spin–coupling splitting the $^3A_{2g}$ ground state of Ni(II) ion, or perhaps it was combined with an antiferromagnetic super–exchange interaction [44]. The higher values in the range of 48–300 K probably resulted from the ferromagnetic effects. The lower values of magnetic moments than theoretically calculated could also originate from the alignment of the vectors L and S caused by the strong field of the heavy atom in opposite directions. It diminished the resultant magnetic moment. The analyzed Ni(II) complex was expected to be high–spin with the weak ligand field [1, 37, 40] and tetrahedral environment of central ion with its sp^3 hybridization [40].

The magnetic interpretation of data for Cu(II) complex is presented in Fig. 3. At 300 K $\chi_m T$ values were equal to 0.3564 cm^3 K mol^{-1} (μ_{eff} = 1.69 μ_B), being typical for non–coupled S=1/2 Cu(II) centres. Upon temperature lowering the $\chi_m T$ value and the magnetic moment increased to $\chi_m T$ = 1.8861 cm^3 K mol^{-1} (μ_{eff} = 3.88 μ_B) at 3.43 K. It suggested a weak ferromagnetic interaction between Cu(II) ions [45] or intermolecular hydrogen bonds in molecular crystal lattice [46]. The study of magnetostructural data indicated that weak ferromagnetic or antiferromagnetic coupling between adjacent copper ions depended on the nature of magnetic orbitals (built up from d orbitals of the metal ions and the symmetry adapted linear contribution of the orbitals of the ligands) on Cu neighboring ions [1, 47]. The complex could have a distorted tetragonal pyramid geometry. According to IR spectra, the carboxylate group was bidentate with an equatorial position at one copper ion and a pseudo equatorial position at the other. This feature could cause the exchange coupling through the carboxylate group to be less operative in comparison with the geometry close to the square–planar pyramid with the carboxylate group in two equatorial positions at copper ions. Therefore any deviation of the atom from the Cu–ligand best plane would lead to a poor overlap with the $d_{x^2-y^2}$ magnetic orbital of copper ions, thus reducing the antiferromagnetic contribution and making the ferromagnetic one to be dominant [1, 47]. Due to the fact that Cu(II) complex could have a distorted geometry, analysis of magnetic interactions on the basis of structural data became difficult and rather speculative.

CONCLUSIONS

Complexes of Mn(II), Co(II), Ni(II), Cu(II), Nd(III), Gd(III), and Er(III) ions with 4-[(4-fluorophenyl)amino]-4-oxobut-2-enoic acid anion form hydrated or anhydrous crystalline compounds that crystallize in a monoclinic or triclinic system. The carboxylate groups act as bidentate ligands.

Thermal stability of analysed compounds was studied in the air at 293–1273 K. The complexes decomposed in three steps. At first they dehydrated and formed anhydrous salts, which was followed by decomposition with formation of the oxides of appropriate metals via intermediate formation of oxyfluorides. Enthalpy values of dehydration processes were determined. The magnetic susceptibility of compounds was studied in the temperature ranges of 76–303 K and 2–300 K. All of those obeyed the Curie–Weiss law, demonstrating the paramagnetic properties. In the molecular centres the ferromagnetic interactions took place.

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