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Dedicated to Full Member of the Russian Academy of Sciences
O.N. Chupakhin on his 80th anniversary

Metal Complexes Based on Functionalized 4-Hydroxypolyfluorocoumarins

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Abstract—4-Hydroxypolyfluorocoumarins containing an acetyl, 1-aminoethylidene, ethoxycarbonyl, or aminocarbonyl substituent on C^3 form coordination compounds with transition and rare earth metal cations. Some coumarin derivatives and their metal complexes show fluorescent properties.

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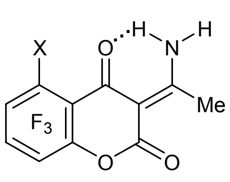
Coumarin derivatives are widely used in practice. They possess various biological and pharmacological properties [1]; in particular, 4-hydroxycoumarins are used in medicine as indirect anticoagulants [2]. Substituted coumarins display unique photochemical and photophysical properties and are characterized by blue–green luminescence, large Stokes shift, and high fluorescence quantum yield [3]. These properties underlie the applications of coumarins as laser dyes, optical bleaching agents, fluorescent pigments, and sensitizers for phototherapy [4].

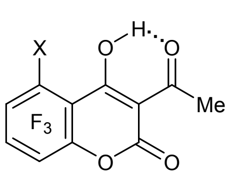
Functionalized coumarins are widely used as ligands to obtain metal complexes with different coordination modes. Complexation with coumarins is a promising line in the design of new therapeutic agents [5]. The resulting complexes are superior to free ligands in biological and optical activity [6]. Coumarins containing a 1,3-aminovinyl ketone fragment as substituent are the most attractive ligands for the preparation of biologically active complexes with metals [7].

In the present work we have demonstrated the possibility for synthesizing new coordination compounds on the basis of 3-substituted 4-hydroxypolyfluorocoumarins. We previously developed convenient methods for the preparation of 3-(1-aminoethylidene)-4-oxopolyfluorocoumarins **Ia** and **Ib**, 3-acetyl-4-hydroxypolyfluorocoumarins **IIa** and **IIb** [8], and 3-ethoxycarbonyl-4-hydroxypolyfluorocoumarins **IIIa** and **IIIb** [9]. By NMR and IR spectroscopy and X-ray analysis we found that compounds **Ia** and **Ib** exist as aminovinyl ketone tautomer with exocyclic double bond and that 3-acetyl- and 3-ethoxycarbonyl-substituted analogs **IIa**, **IIb**, **IIIa**, and **IIIb** have preferentially enol structure with endocyclic double bond [10]. These structural features determine the ability of compounds **I–III** to act as complexing ligands.

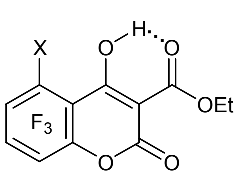
With a view to extend the series of potential ligands based on 4-hydroxypolyfluorocoumarins, coumarin **IIIb** was treated with benzylamine in boiling toluene (with simultaneous removal of water as azeotrope) to obtain *N*-benzyl-6,7,8-trifluoro-4-hydroxy-2-oxo-2*H*-



Ia, **Ib**



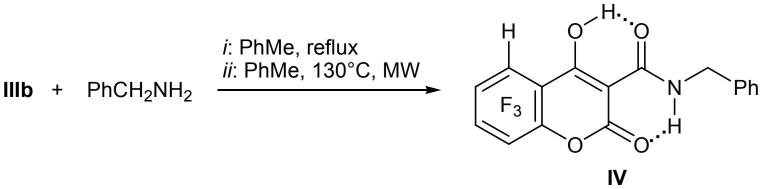
IIa, **IIb**



IIIa, **IIIb**

X = F (**a**), H (**b**).

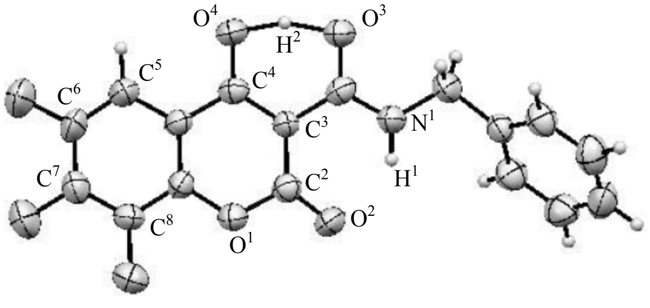
Scheme 1.



chromene-3-carboxamide (**IV**) (Scheme 1). When the reaction was carried out under microwave irradiation, the yield of **IV** increased from 59 to 85%.

Analogous reaction of coumarin **IIIb** under mild conditions (in ethanol at room temperature) afforded benzylammonium 3-ethoxycarbonyl-6,7,8-trifluoro-2-oxo-2*H*-chromen-4-olate which, like other structurally related salts, inhibited hydrogen chloride-induced corrosion of low-carbon steel at a low concentration [11]. Under more severe conditions, the product was amide **IV** rather than that resulting from concurrent nucleophilic substitution of the hydroxy group (unlike transformations of 4-hydroxycoumarin and its fluorinated analog [12]). Preferential formation of carboxamide **IV** is likely to be determined by electronic and steric factors which make the ester group in initial coumarin **IIIb** more accessible to nucleophilic attack.

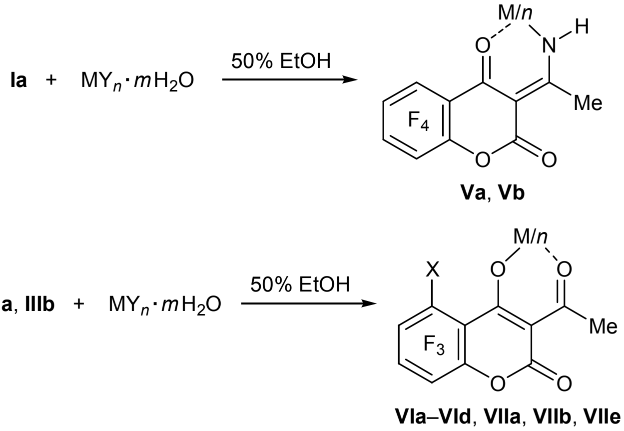
The structure of **IV** was proved by both spectral methods (see Experimental) and X-ray analysis (see figure). The H^2 proton in the keto–enol fragment of molecule **IV** is delocalized between the O^3 and O^4 oxygen atoms. The $O^3–H^2$ and $O^4–H^2$ bond lengths are 1.27(2) and 1.20(2) Å, respectively [$O^3\cdots O^4$ 2.430(1) Å]. Nearly symmetric position of H^2 conforms to leveling of bonds in the keto–enol fragment. The H^2 atom appears almost on the straight line connecting the O^3 and O^4 atoms, the $O^3H^2O^4$ bond angle being 159(1)°. The second intramolecular hydrogen bond in molecule **IV** involves the N^1 and O^2 atoms in the carboxamide fragment [$H^1\cdots O^2$ 2.03(1), $N^1\cdots O^2$ 2.711(1) Å, $\angle N^1H^1O^2$ 132.26°].



Structure of the molecule of *N*-benzyl-6,7,8-trifluoro-4-hydroxy-2-oxo-2*H*-chromene-3-carboxamide (**IV**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

4-Hydroxypolyfluorocoumarins **Ia**, **Ib**, **IIa**, **IIb**, **IIIa**, and **IIIb** may be regarded as cyclic analogs of enamino ketones, 1,3-diketones, and 1,3-oxo esters, respectively, which are capable of forming metal complexes with a stable six-membered O,O- or N,O-chelate ring. By treatment of solutions of coumarins **Ia**, **IIa**, and **IIIb** in 50% ethanol with copper(II), nickel(II), cobalt(II), iron(III), and europium(III) salts we obtained the corresponding metal complexes **Va**, **Vb**, **VIa–VId**, **VIIa**, **VIIb**, and **VIIe** (Scheme 2).

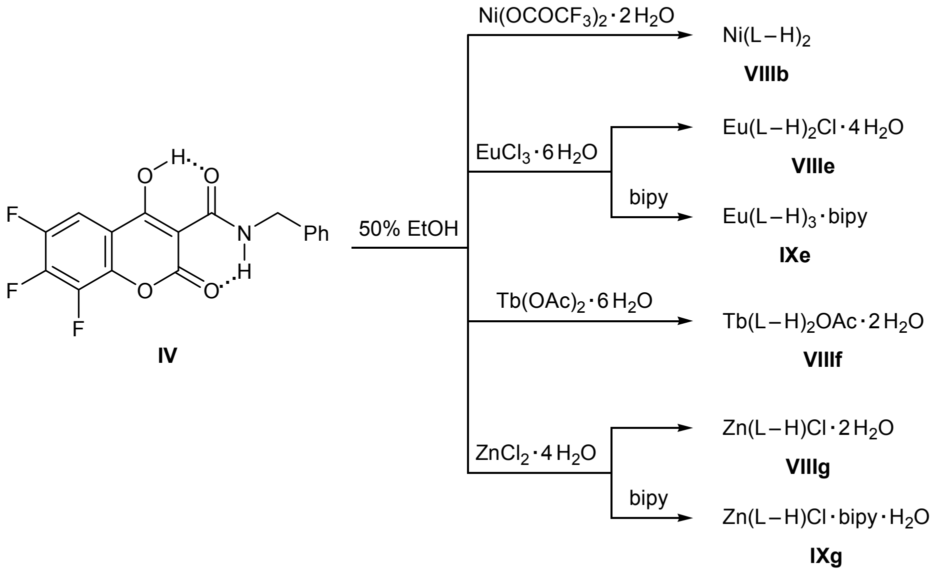
Scheme 2.



VI, R = Me, X = F; **VII**, R = OEt, X = H; M = Cu^{2+} (**a**), Ni^{2+} (**b**), Co^{2+} (**c**), Fe^{3+} (**d**), Eu^{3+} (**e**); Y = OAc, CO_2CF_3, Cl; *n* = 2, 3.

Complexes **V**–**VII** were characterized by the data of elemental analysis and IR spectroscopy, and ^1H and ^{19}F NMR spectra of the nickel complexes were recorded. The complexes had the composition $M(L-H)_2$ or $M(L-H)_3$ where L is the initial ligand (**Ia**, **IIa**, or **IIIb**). Almost all complexes **V–VII** were isolated as crystal hydrates. Presumably, the presence of water molecules is necessary for stabilization of the complexes; attempts to remove crystallization water by heating led to their decomposition. The ^1H NMR spectra of nickel chelates **Vb**, **VIb**, and **VIIb** in DMSO-d_6 displayed broadened signals from all groups of protons, which were displaced upfield relative to the

Scheme 3.



corresponding signals of free ligands **I–III**. In the IR spectra of **V–VII**, characteristic absorption bands were also displaced relative to the corresponding bands in the spectra of free ligands; in addition, strong bands in the region 3463–3260 cm^{-1} were observed due to OH stretching vibrations in water molecules. Unfortunately, we failed to obtain crystals of **V–VII** suitable for X-ray analysis.

Molecules of carboxamide **IV** possess two possible coordination sites, enolized 1,3-diketone and carboxamide fragments. The reaction of **IV** with nickel(II), terbium(III), europium(III), and zinc(II) salts afforded metal complexes **VIIIb** and **VIIIe–VIIIg** (Scheme 3). According to the elemental analyses data, coordination of coumarin **IV** with metal ions involves only one chelating entity, most probably, the diketone fragment. All these complexes, except for nickel complex **VIIIb**, were isolated as crystal hydrates.

When the reactions of **IV** with europium(III) and zinc(II) chlorides were carried out in the presence of 2,2′-bipyridine (bipy), we obtained mixed-ligand complexes **IXe** and **IXg** (Scheme 3) where 2,2′-bipyridine is likely to act as stabilizing ligand. In the IR spectra of **VIII** and **IX**, absorption bands were displaced to lower frequencies as compared to the spectrum of free ligand **IV**. In the ^{1}H NMR spectra of nickel and zinc complexes **VIIIb**, **VIIIg** and **IXg**, signals from the benzylic protons and 5-H appeared in a stronger field, and the amide proton, in a weaker field, relative to the corresponding signals of ligand **IV**. Compound **IXg** displayed in the ^{1}H NMR spectrum signals from protons in the bipy and carboxamide ligands with an intensity ratio of 1 : 1.

Alcoholic solutions of coumarins **I** and **IV** at room temperature showed a weak blue fluorescence (see table). In going from ligand **IV** to zinc complex **VIIIg**

Absorption and photoluminescence spectra of coumarins **I** and **IV** and complexes **VIIIe**–**VIIIg**, **IXe**, and **IXg**

Compound no.	Electronic absorption spectrum, λ_{max}, nm	Photoluminescence spectrum, λ_{em}, nm	Stokes shift $\Delta\lambda$, nm	Quantum yield[a]
I	306, 243	400	94	0.001
IV	310, 293	367	57	0.005
VIIIg	303	389	86	0.020
VIIIe	292, 232	405	113	+ phosphorescence
VIIIf	293, 233	377	84	
IXe	288	387	99	
IXg	305, 294, 233	383	78	0.0022

[a] Relative to anthracene ($\Phi = 0.27$).

the emission maximum shifts by 22 nm toward longer wavelengths, and the fluorescence quantum yield increases by a factor of four. Europium(III) and terbium(III) complexes **VIIIe** and **VIIIf** displayed both fluorescence and phosphorescence with the emission maxima in the red and green regions, respectively.

Thus, polyfluorinated 4-hydroxycoumarins functionalized at the 3-position are capable of forming coordination compounds with transition and rare earth metal ions. Coumarin derivatives with nitrogen-containing substituents and their metal complexes exhibit fluorescence properties.

EXPERIMENTAL

The melting points were determined in open capillaries on a Stuart SMP3 melting point apparatus and were not corrected. The IR spectra were recorded in the range from 4000 to 400 cm^{-1} on a Perkin Elmer Spectrum One spectrometer from samples dispersed in mineral oil. The photoluminescence spectra were measured on an Agilent Cary Eclipse instrument from solutions in ethanol at 293 K. The ^{1}H and ^{19}F NMR spectra were obtained on a Bruker DRX-400 spectrometer at 400 and 376.4 MHz, respectively, using tetramethylsilane (^{1}H) and hexafluorobenzene (^{19}F) as references and DMSO-d_6 as solvent. The mass spectrum (electron impact, 70 eV) of compound **IV** was recorded on an Agilent GC 7890A/MS 5975C instrument. The elemental compositions were determined on a Perkin Elmer 2400 Series II CHNS-O EA 1108 analyzer. Microwave-assisted syntheses were carried out in a Discover SP microwave reactor module (2455 MHz, 300 W, 0–300 psi). The progress of reactions was monitored by TLC on Sorbfil PTSKh-AF-V-UF plates using chloroform and chloroform–methanol (10:1) as eluents.

The X-ray diffraction data for a single crystal of **IV** were acquired on an Xcalibur 3 diffractometer equipped with a CCD detector (λMo$K_α$ 0.71073 Å, graphite monochromator, ω-scanning, scan step 1 deg, frame time 20 s). Analytical absorption correction was applied according to the multifaceted crystal model using CrysAlis RED 1.171.29.9 program. The structure was solved by the direct method followed by Fourier syntheses using SHELXS-97 and was refined by the least-squares procedure in full-matrix anisotropic approximation for all non-hydrogen atoms using SHELXL-97 [13].

Initial coumarins **Ia**, **IIa**, and **IIIb** were synthesized according to the procedures described in [8, 9].

***N*-Benzyl-6,7,8-trifluoro-4-hydroxy-2-oxo-2*H*-chromene-3-carboxamide (IV).** *a*. A mixture of 0.288 g (1 mmol) of compound **IIIb** and 0.107 g (1 mmol) of benzylamine in anhydrous toluene was heated under reflux in a flask equipped with a Dean–Stark trap. The progress of the reaction was monitored by TLC, following disappearance of the initial compounds. When the reaction was complete, the solvent was removed, and the solid residue was recrystallized from diethyl ether. Yield 0.206 g (59%), white powder, mp 174°C.

b. A mixture of 0.288 g (1 mmol) of compound **IIIb** and 0.107 g (1 mmol) of benzylamine in anhydrous toluene was subjected to microwave irradiation in a microwave furnace (100 W, 130°C) over a period of 10 min. The solvent was removed, and the solid residue was recrystallized from diethyl ether. Yield 0.297 g (85%). IR spectrum, ν, cm^{-1}: 3278 (CH, NH), 1692 (C=O), 1643 (δNH), 1569, 1486, 1445 (δNH, C=C), 1265, 1226 (C–N), 1027, 999 (C–F). ^{1}H NMR spectrum, δ, ppm: 4.62 d (2H, C**H**$_2$C$_6$H$_5$, J = 6.0 Hz), 7.32 m (5H, C$_6$H$_5$), 7.87 d.d.d (1H, 5-H, J = 10.0, 8.2, 2.2 Hz), 9.80 t (1H, NH, J = 5.8 Hz). ^{19}F NMR spectrum, δ$_F$, ppm: 9.80 m, 13.19 m, 24.04 m (1F each). Mass spectrum, m/z (I_{rel}, %): 349 (14) $[M]^+$, 243 (1) $[M - NHCH_2C_6H_5]^+$, 174 (7) $[C_7HF_3O_2]^+$, 106 (100) $[NHCH_2C_6H_5]^+$, 91 (27) $[CH_2C_6H_5]^+$. Found, %: C 58.49; H 2.77; F 16.39; N 4.17. $C_{17}H_{10}F_3NO_4$. Calculated, %: C 58.46; H 2.89; F 16.32; N 4.01.

X-Ray diffraction data for compound IV. M 349.26; monoclinic crystal system, space group $P2(1)/n$; unit cell parameters: a = 7.4118(8), b = 7.4493(8), c = 26.175(4) Å; β = 91.341(10); V = 1444.8(3) Å^3; Z = 4; d_{calc} = 1.606 g/cm^3; μ = 0.140 mm^{-1}. Total of 3537 reflection intensities were measured at 295(2) K; 1285 independent reflections; R = 0.0323; 238 variables.

Metal complexes V–IX (*general procedure*). Compound **Ia**, **IIa**, **IIIb**, or **IV**, 1 mmol, was dissolved in ethanol, a solution of 1 mmol of the corresponding metal salt in water was added, and the mixture was heated under reflux and filtered. The filtrate was cooled, and the precipitate was filtered off and recrystallized from ethanol.

Bis[3-(1-aminoethylidene)-5,6,7,8-tetrafluoro-2-oxo-2*H*-chromen-4-olato]copper(II) (Va). Yield 0.260 g (85%), gray powder, mp 239°C. IR spectrum, ν, cm^{-1}: 3329 (N–H), 1729 (C=O), 1654 (C–N), 1586, 1517 (C=C), 1040, 1017 (C–F). Found, %: C 42.89;

H 1.29; F 24.75; N 4.22. $C_{22}H_8CuF_8N_2O_6$. Calculated, %: C 43.19; H 1.32; F 24.84; N 4.58.

Bis[3-(1-aminoethylidene)-5,6,7,8-tetrafluoro-2-oxo-2*H*-chromen-4-olato]nickel(II) dihydrate (Vb). Yield 0.244 g (76%), yellow powder, mp 312°C. IR spectrum, ν, cm^{-1}: 3327, 3060 (O–H, N–H), 1717 (C=O), 1651 (C–N), 1577, 1512, 1461 (C=C), 1040, 1015 (C–F). ^{1}H NMR spectrum, δ, ppm: 2.56 s (3H, CH_3), 10.22 br.s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: –2.83 m, 2.08 m, 11.69 m, 16.54 m (1F each). Found, %: C 41.34; H 1.77; F 23.20; N 4.62. $C_{22}H_8F_8N_2NiO_6 \cdot 2H_2O$. Calculated, %: C 41.09; H 1.88; F 23.64; N 4.36.

Bis(3-acetyl-5,6,7,8-tetrafluoro-2-oxo-2*H*-chromen-4-olato)copper(II) (VIa). Yield 0.295 g (96%), blue powder, mp 250°C. IR spectrum, ν, cm^{-1}: 1747 (C^2=O), 1653, 1630 (C=O), 1575, 1529, 1511 (C=C), 1046, 1014 (C–F). Found, %: C 43.13; H 0.99; F 25.17. $C_{22}H_6CuF_8O_8$. Calculated, %: C 43.05; H 0.99; F 24.76.

Bis(3-acetyl-5,6,7,8-tetrafluoro-2-oxo-2*H*-chromen-4-olato)nickel(II) dihydrate (VIb). Yield 0.258 g (80%), yellow powder, mp 280°C. IR spectrum, ν, cm^{-1}: 3328 (OH), 1696, 1678 (C^2=O), 1645, 1630 (C=O), 1602, 1527 (C=C), 1039, 1017 (C–F). ^{1}H NMR spectrum: δ 2.28 ppm, s (3H, CH_3). ^{19}F NMR spectrum, δ_F, ppm: –2.16 m, 0.58 m, 10.49 m, 16.28 m (1F each). Found, %: C 40.59; H 1.65; F 23.27. $C_{22}H_6F_8NiO_8 \cdot 2H_2O$. Calculated, %: C 40.97; H 1.56; F 23.56.

Bis(3-acetyl-5,6,7,8-tetrafluoro-2-oxo-2*H*-chromen-4-olato)cobalt(II) dihydrate (VIc). Yield 0.219 g (68%), pink powder, mp 218°C. IR spectrum, ν, cm^{-1}: 3460 (O–H), 1702 (C^2=O), 1646, 1630 (C=O), 1601, 1525 (C=C), 1038, 1018 (C–F). Found, %: C 40.58; H 1.57; F 23.27. $C_{22}H_6CoF_8O_8 \cdot 2H_2O$. Calculated, %: C 40.95; H 1.56; F 23.56.

Tris(3-acetyl-5,6,7,8-tetrafluoro-2-oxo-2*H*-chromen-4-olato)iron(III) tetrahydrate (VId). Yield 0.216 g (68%), yellow powder, mp 208°C. IR spectrum, ν, cm^{-1}: 3334 (O–H), 1742 (C^2=O), 1649, 1628 (C=O), 1502, 1460 (C=C), 1038, 1017 (C–F). Found, %: C 41.21; H 1.65; F 23.54. $C_{33}H_9F_{12}FeO_{12} \cdot 4H_2O$. Calculated, %: C 41.58; H 1.80; F 23.91.

Bis(3-ethoxycarbonyl-6,7,8-trifluoro-2-oxo-2*H*-chromen-4-olato)copper(II) (VIIa). Yield 0.258 g (81%), green powder, mp 345°C. IR spectrum, ν, cm^{-1}: 1721 (C^2=O), 1646, 1604 (C=O), 1560, 1493, 1435 (C=C), 1078, 1057 (C–F). Found, %: C 45.87; H 1.92; F 17.85. $C_{24}H_{12}CuF_6O_{10}$. Calculated, %: C 45.19; H 1.90; F 17.87.

Bis(3-ethoxycarbonyl-6,7,8-trifluoro-2-oxo-2*H*-chromen-4-olato)nickel(II) dihydrate (VIIb). Yield 0.271 g (81%), green powder, mp >350°C. IR spectrum, ν, cm^{-1}: 3463 (O–H), 1681 (C^2=O), 1622 (C=O), 1524, 1485, 1421 (C=C), 1056, 1016 (C–F). ^{1}H NMR spectrum, δ, ppm: 1.19 br.s (3H, $CH_2\mathbf{CH_3}$), 4.04 br.s (2H, $\mathbf{CH_2}CH_3$), 7.48 br.s (1H, 5-H). ^{19}F NMR spectrum, δ_F, ppm: 8.58 m, 26.33 m, 34.34 m (1F each). Found, %: C 42.85; H 2.36; F 17.49. $C_{24}H_{12}F_6NiO_{10} \cdot 2H_2O$. Calculated, %: C 43.08; H 2.41; F 17.04.

Tris(3-ethoxycarbonyl-6,7,8-trifluoro-2-oxo-2*H*-chromen-4-olato)europium(III) dihydrate (VIIe). Yield 0.240 g (71%), yellow powder, mp 212°C. IR spectrum, ν, cm^{-1}: 3396 (O–H), 1708 (C^2=O), 1612 (C=O), 1510, 1478, 1424 (C=C), 1054, 985 (C–F). Found, %: C 41.65; H 2.43; F 16.40. $C_{36}H_{18}EuF_9O_{15} \cdot 2H_2O$. Calculated, %: C 41.20; H 2.11; F 16.29.

Bis(3-benzylcarbamoyl-6,7,8-trifluoro-2-oxo-2*H*-chromen-4-olato)nickel(II) (VIIIb). Yield 0.283 g (75%), green powder, mp >350°C. IR spectrum, ν, cm^{-1}: 3075, 3032 (N–H), 1639 (C^2=O), 1596 (C=O), 1553, 1496, 1418 (C=C), 1053, 1016 (C–F). ^{1}H NMR spectrum, δ, ppm: 3.31 br.s (2H, $\mathbf{CH_2}C_6H_5$), 7.19–7.89 m (6H, C_6H_5, 5-H). Found, %: C 54.48; H 2.80; F 14.23; N 4.39. $C_{34}H_{18}F_6N_2NiO_8$. Calculated, %: C 54.07; H 2.40; F 15.09; N 3.71.

Bis(3-benzylcarbamoyl-6,7,8-trifluoro-2-oxo-2*H*-chromen-4-olato)chlorooeuropium(III) tetrahydrate (VIIIe). Yield 0.283 g (55%), white powder, mp 174°C. IR spectrum, ν, cm^{-1}: 3360 (O–H), 3060 (N–H), 1682 (C^2=O), 1643 (C=O), 1619, 1569, 1486, 1445 (C=C), 1060, 1017 (C–F). Found, %: C 43.00; H 2.63; Cl 3.97; F 11.53; N 2.78. $C_{34}H_{26}ClEuF_6N_2O_{12} \cdot 4H_2O$. Calculated, %: C 42.72; H 2.74; Cl 3.71; F 11.92; N 2.93.

Acetatobis(3-benzylcarbamoyl-6,7,8-trifluoro-2-oxo-2*H*-chromen-4-olato)terbium(III) dihydrate (VIIIf). Yield 0.204 g (43%), yellow powder, mp >350°C. IR spectrum, ν, cm^{-1}: 3293 (O–H), 3068 (N–H), 1686 (C^2=O), 1659, 1639 (C=O), 1598, 1559, 1498, 1422 (C=C), 1048, 1011 (C–F). Found, %: C 45.71; H 2.57; F 11.65; N 3.20 $C_{36}H_{21}F_6N_2O_{10}Tb \cdot 2H_2O$. Calculated, %: C 45.49; H 2.65; F 11.99; N 2.95.

(3-Benzylcarbamoyl-6,7,8-trifluoro-2-oxo-2*H*-chromen-4-olato)chlorozinc(II) dihydrate (VIIIg). Yield 0.417 g (86%), white powder, mp 322°C. IR spectrum, ν, cm^{-1}: 3344 (O–H), 3074 (N–H), 1652

(C^2=O), 1638 (C=O), 1599, 1572, 1504, 1498 (C=C), 1049, 1012 (C–F). ^{1}H NMR spectrum, δ, ppm: 4.46 d (2H, C**H**$_2$C$_6$H$_5$, *J* = 5.8 Hz), 7.18–7.26 m (5H, C_6H_5), 7.54 m (1H, 5-H), 10.21 br.s (1H, NH). ^{19}F NMR spectrum, $δ_F$, ppm: 8.51 m, 9.13 m, 22.02 m (1F each). Found, %: C 41.88; H 2.59; Cl 7.43; F 11.57; N 3.26. $C_{17}H_9ClF_3NO_4Zn \cdot 2H_2O$. Calculated, %: C 42.09; H 2.70; Cl 7.31; F 11.75; N 2.89.

Tris(3-benzylcarbamoyl-6,7,8-trifluoro-2-oxo-2*H*-chromen-4-olato)(2,2-bipyridine)europium(III) (IXe). Yield 0.257 g (57%), white powder, mp 238°C. IR spectrum, ν, cm^{-1}: 3078 (N–H), 1679 (C^2=O), 1592 (C=O), 1559, 1495, 1419 (C=C), 1066, 1007 (C–F). Found, %: C 53.72; H 2.54; F 12.79; N 5.10. $C_{51}H_{27}EuF_9N_5O_{12} \cdot$bipy. Calculated, %: C 54.15; H 2.61; F 12.64; N 5.18.

(3-Benzylcarbamoyl-6,7,8-trifluoro-2-oxo-2*H*-chromen-4-olato)(2,2-bipyridine)chlorozinc(II) hydrate (IXg). Yield 0.455 g (73%), white powder, mp 288°C. IR spectrum, ν, cm^{-1}: 3259 (O–H), 3106, 3081 (N–H), 1675 (C^2=O), 1645 (C=O), 1599, 1552, 1492, 1417 (C=C), 1022, 1010 (C–F). ^{1}H NMR spectrum, δ, ppm: 4.42 br.s (2H, C**H**$_2$C$_6$H$_5$), 7.16–7.25 m (5H, C_6H_5), 7.52–8.68 m (9H, $C_{10}H_8N_2$, 5-H), 10.25 br.s (1H, NH). ^{19}F NMR spectrum, $δ_F$, ppm: 8.57 m, 9.23 m, 21.97 m (1F each). Found, %: C 51.84; H 2.72; Cl 5.76; F 9.39; N 6.68. $C_{17}H_9ClF_3N_3O_4Zn \cdot$bipy$\cdot H_2O$. Calculated, %: C 52.03; H 3.07; Cl 5.69; F 9.14; N 6.74.

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