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Synthesis, Structure, and Complexing Ability of Fluoroalkyl-Containing 2,2′-(Biphenyl-4,4′-diyldihydrazono)bis(1,3-dicarbonyl) Compounds

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Abstract—New fluoroalkyl-containing 2,2′-(biphenyl-4,4′-diyldihydrazono)bis(1,3-diketones) and 2,2′-(biphenyl-4,4′-diyldihydrazono)bis(3-oxopropionates) were synthesized by azo coupling of the corresponding 1,3-dicarbonyl compounds with biphenyl-4,4′-bis(diazonium) dichloride. Complexing ability of the obtained bis-hydrazones was studied, and new coordination compounds of the general formula M_2L_2 [where M = Ni(II), Cu(II); L = fluoroalkyl-containing 2,2′-(biphenyl-4,4′-diyldihydrazono)bis(1,3-diketone)] were obtained.

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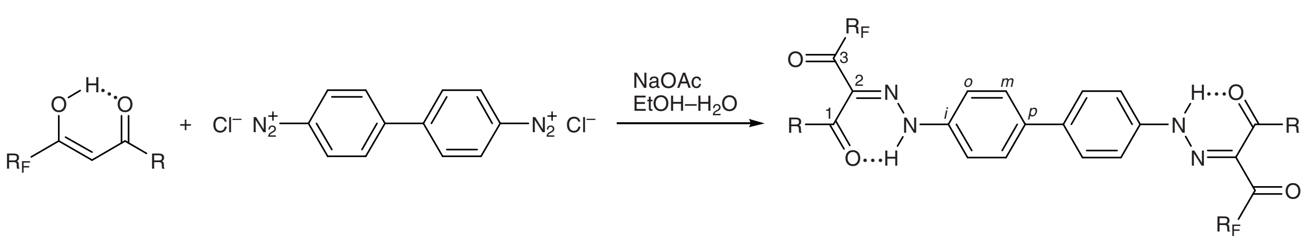
In the recent years, strong interest in transition metal chelates has arisen due to prospects in their application for the preparation of polyfunctional magnetoactive materials [1]. We previously [2] synthesized fluoroalkyl-substituted 2-arylhydrazono-1,3-dicarbonyl compounds which were converted into fluorinated ligands via reactions with nucleophiles. While continuing studies in this line, we examined reactions of fluorinated 1,3-diketones **Ia**–**If** and 3-oxoalkanoates **IIa**–**IId** with biphenyl-4,4′-bis(diazonium) dichloride in aqueous alcohol in the presence of sodium acetate (Scheme 1). Compounds **IIIa**–**IIIf** and **IVa**–**IVd** thus obtained may exist as three symmetric isomers **A**, **C**, and **D** and three asymmetric isomers **E**–**G** due to keto–enol and azo–hydrazone tautomerism (Scheme 2). In addition, isomerism related to different orientation of substituents with respect to the C=N bond is possible (e.g., isomers **A** and **B** in Scheme 2).

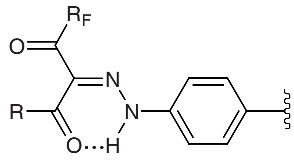
The ^{1}H and ^{19}F NMR spectral patterns of compounds **IIIa**–**IIIf** and **IVa**–**IVd** in $CDCl_3$ cannot be interpreted unambiguously. Hydrazones **IIIb**, **IIIc**, and **IIIe** having a bulky benzoyl group and even bulkier pivaloyl substituent in $CDCl_3$ solution exist as two isomers, as follows from the presence of double sets of signals in their ^{1}H and ^{19}F NMR spectra. Compounds **IIIa**, **IIId**, **IIIf**, and **IVa**–**IVd** with smaller acyl and alkoxycarbonyl groups displayed in the NMR spectra only one set of signals (see Experimental).

Scheme 1.

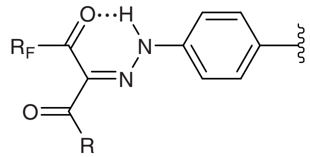


Ia–**If**, **IIa**–**IId** **IIIa**–**IIIf**, **IVa**–**IVd**

I, **III**, R = Me (**a**, **f**), Ph (**b**, **e**), *t*-Bu (**c**), Bu (**d**); R_F = CF_3 (**a**–**c**), HCF_2CF_2 (**b**, **d**), C_3F_7 (**e**), C_4F_9 (**f**); **II**, **IV**, R = EtO (**a**, **c**), MeO (**b**, **d**); R_F = CF_3 (**a**), HCF_2CF_2 (**b**), C_3F_7 (**c**), C_4F_9 (**d**).



A



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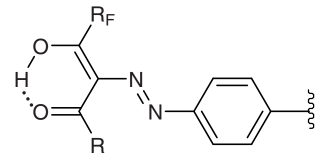

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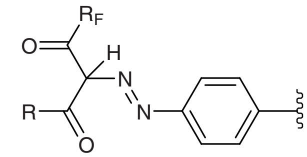
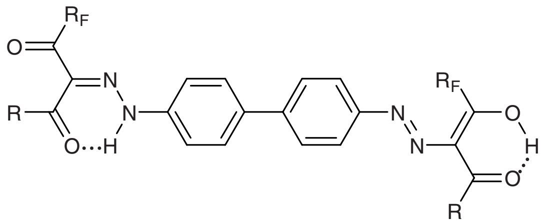
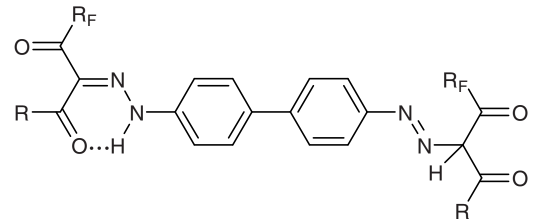


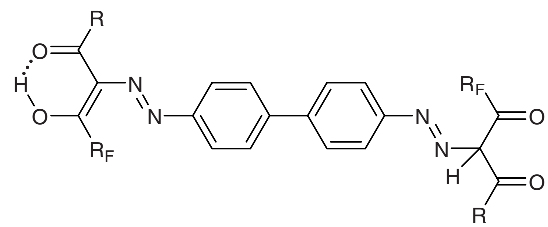
D



E



F



G

The absence of a signal assignable to CH=N proton in the ^{1}H NMR spectra of these compounds rules out symmetric and asymmetric tautomers **D**, **F**, and **G**. Moreover, the NMR spectra lacked two sets of signals with equal intensities; therefore, asymmetric structures **E**–**G** should be excluded. The IR spectra of solutions of **IIIc**–**IIIf** and **IVa** in chloroform and crystalline samples of the same compounds contained two strong absorption bands in the region 1670–1725 cm^{-1}. This may be due to the presence of two nonequivalent carbonyl groups in their molecules, as in symmetric bis-hydrazone structures **A** and **B**. The low-frequency shift of the carbonyl bands, as compared to the data given in [3], results from conjugation with the C=N bond and aromatic fragments, as well as from intramolecular hydrogen bonding with participation of the carbonyl oxygen atom. Thus it remained to distinguish between isomers **A** and **B** with different orientations of substituents at the double C=N bond.

We previously [4] defined some ^{19}F and ^{13}C NMR parameters typical of isomers **A** and **B** of trifluoromethyl-containing 1,2,3-trione 2-arylhydrazones. These are δ_F ~91–92 ppm, $^{1}J_{CF} \approx 292$, and $^{2}J_{CF} \approx 31$–34 Hz for the free CF_3C=O group (isomer **A**, $CDCl_3$) and δ_F ~87–88 ppm, $^{1}J_{CF} \approx 287$, and $^{2}J_{CF} \approx 40$ Hz for the CF_3C=O group involved in intramolecular hydrogen bond (isomer **B**, $CDCl_3$). We tried to use the above parameters to determine the structure of new isomeric bis-hydrazones **IIIa**–**IIIc** and **IVa** ($R_F = CF_3$, R = Me, Ph, *t*-Bu, OEt). Compounds **IIIa** (R = Me) and **IVa** (R = OEt) in $CDCl_3$ were thus assigned structure **A** (δ_F ~91–92 ppm, $^{1}J_{CF} = 292.7$, $^{2}J_{CF} = 32.7$, $^{4}J_{CF} = 1$ Hz), while bis-hydrazone **IIIb** having bulky benzoyl groups was found to exist in $CDCl_3$ and DMF-d_7 as a mixture of isomers **A** (δ_F 93.92 ppm in DMF-d_7) and **B** (δ_F 87.87 ppm in DMF-d_7), the former strongly prevailing (**A**:**B** ≈ 10:1). The presence of a *tert*-butyl group, which creates considerable steric hindrances to intramolecular hydrogen bonding with participation of the neighboring carbonyl group in **IIIc**, favors increased fraction of isomer **A** (**A**: δ_F 92.03 ppm, $^{1}J_{CF} = 292.6$, $^{2}J_{CF} = 32.1$ Hz; **B**: δ_F 89.19 ppm, $^{1}J_{CF} = 288$, $^{2}J_{CF} = 37.1$ Hz; **A**:**B** ≈ 6:5; $CDCl_3$).

Compound **IIIe** possessing heptafluoroacyl and benzoyl substituents exists in $CDCl_3$ as a mixture of two isomers. As we showed previously [4], the formation of intramolecular hydrogen bond between the CF_3CO carbonyl oxygen atom and proton of the arylhydrazone fragment in CF_3-containing hydrazones and bis-hydrazones induces a diamagnetic shift of the CF_3 fluorine nuclei in the ^{19}F NMR spectra. Comparison of the chemical shifts of fluorine nuclei in the α-CF_2 group (neighboring to the carbonyl group) of two isomers of **IIIe** indicated prevalence of isomer **A** in chloroform-*d* (**A**: 91%, $\delta_{\alpha\text{-F}}$ 49.27 ppm; **B**: 9%, $\delta_{\alpha\text{-F}}$ 48.06 ppm; cf. the data given above for CF_3-containing bis-hydrazone **IIIb**).

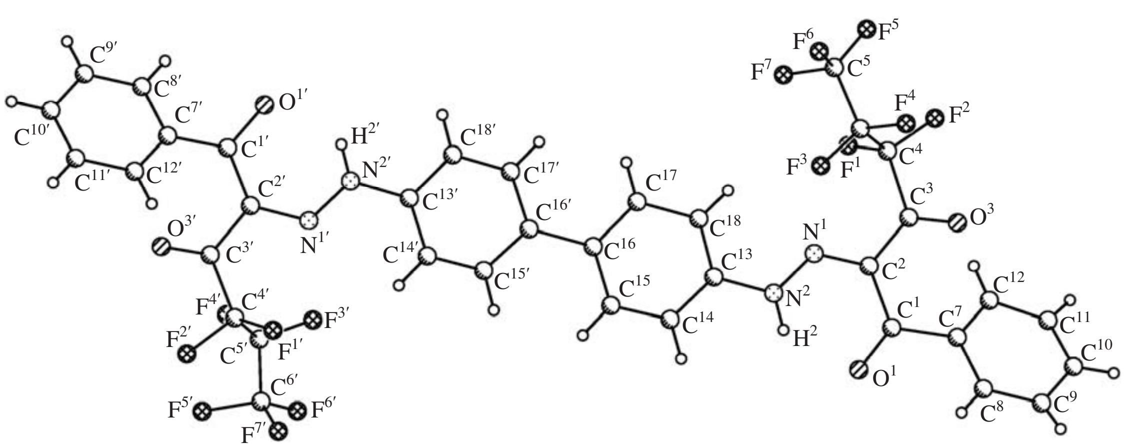
On the other hand, the X-ray diffraction data showed that bis-hydrazone **IIIe** in crystal exists only as isomer **A** (see figure). Presumably, crystallization of **IIIe** from a solution in $CHCl_3$ is accompanied by complete transformation of isomer **B** into sterically more favorable isomer **A**. The X-ray diffraction data unambiguously indicated formation of intramolecular hydrogen bond between the NH protons of the arylhydrazone fragments and benzoyl carbonyl oxygen atoms. The distances $O^1\cdots H^2$ and $O^{1'}\cdots H^{2'}$ are 1.97(2) and 1.92(4) Å, and the bond angles $N^2H^2O^1$ and $C^1O^1H^2$ are 131(1) and 104(9)°, respectively [$\angle N^{2'}H^{2'}O^{1'}$ 134(1)°, $\angle C^{1'}O^{1'}H^{2'}$ 99(4)°]. Molecule **IIIe** is characterized by *trans* orientation of the triketone hydrazone fragments with respect to the biphenyl moiety.

Likewise, diethyl 2,2′-(biphenyl-4,4′-diyldihydrazono)bis(4,4,5,5,6,6,6-heptafluoro-3-oxopropionate) (**IVc**) and bis-hydrazones **IIIf** and **IVd** having nonafluorobutyl substituents at the carbonyl groups are likely to have structure **A** ($CDCl_3$). The chemical shifts of the α-CF_2 fluorine nuclei ($\delta_{\alpha\text{-F}}$ 49.43–50.25 ppm) are comparable with that found for the predominant isomer of **IIIe** (**A**: δ_F 49.27 ppm); a paramagnetic shift is observed relative to the corresponding signal of isomer **B** of **IIIe** ($\delta_{\alpha\text{-F}}$ 48.06 ppm). The chemical shifts of the α-fluorine nuclei in the ^{19}F NMR spectra of bis-hydrazones **IIId** and **IVb** containing tetrafluoroethyl groups ($CDCl_3$; δ_F 42.28–42.59 ppm) are similar to those reported for isomers **A** of tetrafluoroethyl-substituted 1,2,3-trione 2-arylhydrazones (δ_F 42.05–44.26 ppm) [4].

We can conclude that isomeric composition of compounds **IIIa**–**IIIf** and **IVa**–**IVd** is determined mainly by steric factor. If steric hindrances are absent (compounds **IIIa**, **IIId**, **IIIf**, and **IVa**–**IVd**), the bis-hydrazones in $CDCl_3$ exist exclusively as isomers **A**; bis-hydrazones **IIIb**, **IIIc**, and **IIIe** having bulky substituents (such as phenyl or *tert*-butyl group) give rise to mixtures of isomers **A** and **B**.

Using the MOPS algorithm [5] we have searched for most favorable isomers of trifluoromethyl-containing hydrazones **IIIa**–**IIIc** and ester **IVa**, and the energy, charge, and orbital parameters of the isomers found have been calculated *ab initio* using 6-31G basis set (see table). It is seen that isomers **A** of compounds **IIIa**–**IIIc** and **IVa** are more stable than the corresponding isomers **B**, which is consistent with the experimental data for solutions in $CDCl_3$ and DMF-d_7 and crystalline state, obtained by NMR and IR spectroscopy and X-ray analysis. The energy difference between isomers **A** and **B** ranges from 33 to 50 kJ/mol. For all these compounds, the oxygen atom involved in intramolecular hydrogen bonding in isomer **A** have a smaller charge (q_O) than the corresponding oxygen atom in isomer **B**. For example, q_O = –0.635 and –0.634 in **A** and q_O = –0.569 and –0.568 in **B** (**IIIa**). Charges on the NH hydrogen atoms in both isomers are approximately equal. Thus the calculation results showed that the formation of isomer **A** is more favorable from the energy viewpoint and that it is more stable than **B** due to formation of a stronger intramolecular hydrogen bond.

Using compound **IIIe** as an example, we showed that newly synthesized bis-hydrazones **III** are capable of forming complexes with metals. By treatment of



Structure of the molecule of 2,2′-(biphenyl-4,4′-diyldihydrazono)bis(4,4,5,5,6,6,6-heptafluoro-1-phenylhexane-1,3-dione) (**IIIe**) according to the X-ray diffraction data.

Calculated total energies, charges on the carbonyl carbon and oxygen atoms, and the corresponding frontier orbital Fukui indices of isomers **A** and **B** of bis-hydrazones **IIIa–IIIc** and **IVa**

Comp. no., isomer	E_{tot}, kJ/mol	Charges on atoms (Fukui indices for HOMO/LUMO)							
		C^1=O	C^1=**O**	**C**$^{1'}$=O	C$^{1'}$=**O**	**C**^{3}=O	C^3=**O**	**C**$^{3'}$=O	C$^{3'}$=**O**
IIIa, **A**	–5153612.89	0.5545 (0.0018/ 0.03)	–0.6354 (0.0064/ 0.0274)	0.5527 (0.0021/ 0.0322)	–0.6339 (0.0064/ 0.0286)	0.3747 (0.0008/ 0.0415)	–0.4603 (0.0078/ 0.0393)	0.3723 (0.0009/ 0.0444)	–0.4578 (0.0077/ 0.0404)
IIIa, **B**	–5153579.41	0.5274 (0.0004/ 0.0075)	–0.5305 (0.0062/ 0.0049)	0.5271 (0.0005/ 0.0091)	–0.5294 (0.0062/ 0.0052)	0.3773 (0.003/ 0.0765)	–0.5686 (0.0097/ 0.0755)	0.3764 (0.0031/ 0.0850)	–0.568 (0.0097/ 0.0834)
IIIb, **A**	–6157461.58	0.5054 (0.0029/ 0.055)	–0.6181 (0.0051/ 0.0448)	0.5054 (0.0029/ 0.0551)	–0.6172 (0.0051/ 0.0448)	0.3526 (0.0015/ 0.0450)	–0.4563 (0.0067/ 0.0307)	0.3525 (0.0015/ 0.0456)	–0.4568 (0.0068/ 0.0313)
IIIb, **B**	–6157411.77	0.4991 (0.0007/ 0.0220)	–0.5255 (0.0056/ 0.0083)	0.4991 (0.0007/ 0.0219)	–0.5256 (0.0056/ 0.0083)	0.3553 (0.0039/ 0.0845)	–0.5530 (0.0087/ 0.0816)	0.3553 (0.0039/ 0.0841)	–0.5529 (0.0087/ 0.0812)
IIIc, **A**	–5770493.38	0.6085 (0.0011/ 0.0278)	–0.6497 (0.0057/ 0.0285)	0.5812 (0.0034/ 0.0314)	–0.6304 (0.0053/ 0.0219)	0.3877 (0.0004/ 0.0572)	–0.4807 (0.0080/ 0.0595)	0.3781 (0.0014/ 0.0368)	–0.4527 (0.0059/ 0.0259)
IIIc, **B**	–5770452	0.5873 (0.0001/ 0.0029)	–0.5404 (0.0057/ 0.0025)	0.5577 (0.0006/ 0.0152)	–0.5405 (0.0056/ 0.0051)	0.3695 (0.003/ .0662)	–0.6009 (0.0102/ 0.0627)	0.3604 (0.0041/ 0.1047)	–0.5744 (0.0098/ 0.0993)
IVa, **A**	–5753761.38	0.9084 (0.0009/ 0.0178)	–0.6527 (0.0039/ 0.0173)	0.9102 (0.0012/ 0.0206)	–0.651 (0.0038/ 0.0183)	0.3728 (0.0002/ 0.032)	–0.465 (0.0079/ 0.0403)	0.3723 (0.0003/ 0.0357)	–0.4631 (0.0079/ 0.043)
IVa, **B**	–5753718.95	0.8643 (0.0001/ 0.0053)	–0.5594 (0.0048/ 0.006)	0.8754 (0.0002/ 0.006)	–0.5679 (0.0047/ 0.0057)	0.3749 (0.0012/ 0.0701)	–0.5429 (0.0077/ 0.074)	0.3785 (0.0012/ 0.0683)	–0.543 (0.0075/ 0.0714)

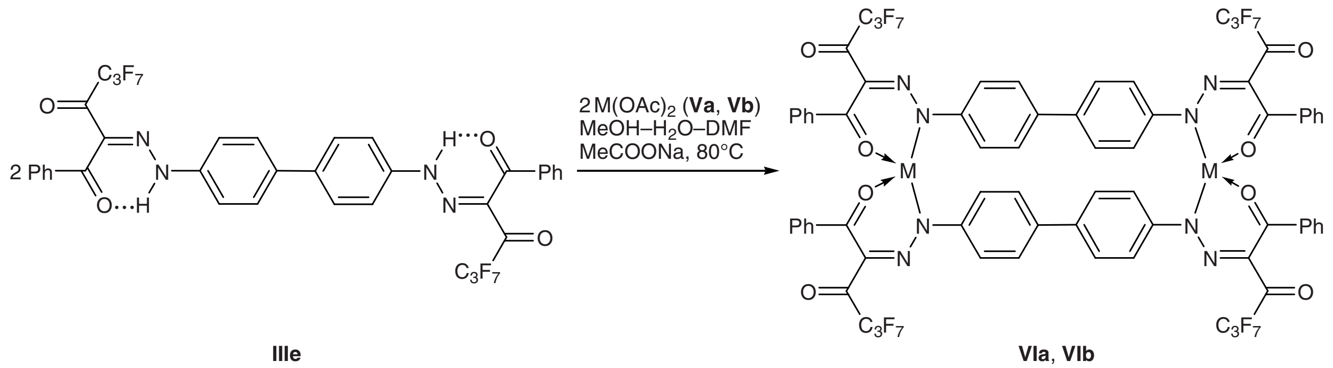
bis-hydrazone **IIIe** with nickel(II) or copper(II) acetate we obtained coordination compounds **VIa** and **VIb**. According to the elemental analysis data, complexes **VIa** and **VIb** have a composition of 2:2 [M_2L_2, where M = Ni(II) or Cu(II) and L = **IIIe** – $2H^+$] (Scheme 3). Unfortunately, complexes **VIa** and **VIb** turned out to decompose in ethanol, $CHCl_3$, pyridine, and DMSO to give the initial ligand; therefore, it was difficult to examine them by NMR spectroscopy and grow crystals suitable for X-ray analysis. Taking into account that the carbonyl oxygen atoms involved in intramolecular hydrogen bonding (in benzoyl or pivaloyl groups) possess smaller negative charges (see table), we presumed that nonfluorinated carbonyl fragments also participate in coordination with metals. Analogous complexes derived from fluorine-free 2,2′-(biphenyl-4,4′-diyldihydrazono)bis(cyclohexane-1,3-dione) and 3,3′-(biphenyl-4,4′-diyldihydrazono)bis(pentane-2,4-dione) [6] were more stable, and they were studied by UV spectroscopy (in alcohol) and mass spectrometry. The presence of molecular ion peaks in the mass spectra confirmed binuclear nature of such chelates.

Thus we have synthesized new fluoroalkyl-containing ligands, 2,2′-(biphenyl-4,4′-diyldihydrazono)bis-(1,3-ketones) and 2,2′-(biphenyl-4,4′-diyldihydrazono)-bis(3-oxoalkanoates), and Ni(II) and Cu(II) chelates derived therefrom. The new ligands are polyfunctional compounds which may be used as synthons for design of various open-chain and heterocyclic ligands.

EXPERIMENTAL

The melting points were determined using open capillaries and were not corrected. The IR spectra (400–4000 cm^{-1}) were recorded on a Perkin–Elmer Spectrum One spectrometer with Fourier transform from samples dispersed in mineral oil (**IIIa–IIIf**, **IVa–IVd**) and 0.1 M solutions in chloroform (**IIIc**, **IIId**, **IIIf**, **IVa**). The ^1H, ^{13}C, and ^{19}F NMR spectra were measured on a Bruker DRX-400 spectrometer (400,

Scheme 2.



M = Ni (**a**), Cu (**b**).

100.6, and 376 MHz, respectively) using tetramethylsilane (internal; ^{1}H, ^{13}C) and C_6F_6 (^{19}F) as reference. The elemental compositions were determined on a Perkin–Elmer PE 2400 Series II analyzer.

Quantum-chemical calculations (SCF MO LCAO, *ab initio* 6-31G) of compounds **IIIa**–**IIIc** and **IVa** were performed at the SKIF Cluster of the United State of Russia and Byelorussia.

The X-ray diffraction study of a single crystal of compound **IIIe** was performed at room temperature on a KM-4 Kuma Diffraction diffractometer (MoK_α irradiation, graphite monochromator, ω/2θ scanning, temperature 100±2 K). The structure was solved by the direct methods, followed by Fourier syntheses, using SHELXS-97 software package [7] and was then refined by the least-squares procedure in full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [7]. The coordinates of hydrogen atoms were determined experimentally and refined in isotropic approximation.

Crystallographic data for compound IIIe. $C_{36}H_{20}F_{14}N_4O_4$, *M* 838.56, space group *Pbc*2$_1$, orthorhombic crystals with the following unit cell parameters: $a = 6.354(4)$, $b = 18.932(2)$, $c = 28.775(3)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 3461.7(8)$ Å^3; $Z = 4$; $\lambda = 0.71073$ Å; $d_{calc} = 1.609$ g/cm^3; $\mu = 0.157$ mm^{-1}. Total of 49650 reflections were measured, 11488 of which were independent and 3017 had $I > 2\sigma(I)$; 513 parameters were calculated; $2\theta_{max} = 52°$, spherical segment $-9 \le h \le 9$, $-28 \le k \le 28$, $-43 \le l \le 42$; $R_1 = 0.0801$ from reflections with $I > 2\sigma(I)$. The complete set of crystallographic data for compound **IIIe** was deposited to the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk/conts/retrieving.html; CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk; entry no. CCDC 624129).

General procedure for the synthesis of bis-hydrazones IIIa–IIIf and IVa–IVd. A solution of 514 mg (2 mmol) of biphenyl-4,4′-diamine in dilute hydrochloric acid (prepared by diluting 6.7 ml of concentrated hydrochloric acid with 21 ml of water) was cooled to 0°C, and a solution of 276 mg of sodium nitrite in 1.2 ml of water was added under vigorous stirring. Solutions of 1.82 g of sodium acetate in 16 ml of water and of 4 mmol of 1,3-dicarbonyl compound **Ia**–**If** or **IIa**–**IId** in 13 ml of ethanol were mixed separately, and the above diazonium salt solution was slowly added under stirring, maintaining the temperature at 10°C. The precipitate was filtered off, recrystallized from ethanol (unless otherwise stated), and dried.

3,3′-(Biphenyl-4,4′-diyldihydrazono)bis(1,1,1-trifluoropentane-2,4-dione) (IIIa). Yield 54%, orange powder, sublimes above 250°C (from ethanol). IR spectrum, ν, cm^{-1}: 3060, 1580 (N–H); 1695 (C=O); 1625, 1505, 1495 (C=N, C=C); 1145–1160 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.67 s (6H, CH_3), 7.58 m (4H, *m*-H), 7.70 m (4H, *o*-H). ^{19}F NMR spectrum ($CDCl_3$): δ_F 91.54 ppm, s. Found, %: C 51.20; H 3.31; F 22.10; N 10.71. $C_{22}H_{16}F_6N_4O_4$. Calculated, %: C 51.37; H 3.14; F 22.16; N 10.89.

2,2′-(Biphenyl-4,4′-diyldihydrazono)bis(4,4,4-trifluoro-1-phenylbutane-1,3-dione) (IIIb). Yield 59%, mixture of isomers **A** and **B** (~10:1), orange powder, mp >250°C (from ethanol). IR spectrum, ν, cm^{-1}: 3200, 1575 (N–H); 1700 (C=O); 1620, 1600, 1520 (C=N, C=C); 1150–1240 (C–F). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: isomer **A**: 7.48–7.74 m (18H, H_{arom}), 14.08 br.s (2H, NH); isomer **B**: 7.91–8.17 m (18H, H_{arom}), 14.03 br.s (2H, NH); in DMF-d_7: isomer **A**: 7.59–8.03 m (18H, H_{arom}), 12.75 br.s (2H, NH); isomer **B**: 7.74–8.2 m (18H, H_{arom}), 11.69 br.s (2H, NH). ^{19}F NMR spectrum (DMF-d_7), δ_F, ppm: isomer **A**:

93.92 s (CF_3); isomer **B**: 87.87 s (CF_3). Found, %: C 60.32; H 3.17; F 17.62; N 8.43. $C_{32}H_{20}F_6N_4O_4$. Calculated, %: C 60.19; H 3.16; F 17.85; N 8.77.

3,3′-(Biphenyl-4,4′-diyldihydrazono)bis(1,1,1-trifluoro-5,5-dimethylhexane-2,4-dione) (IIIc). The product was washed with ethanol. Yield 57%, mixture of isomers **A** and **B** (~6 : 5), brown–red powder, mp 143–145°C. IR spectrum, ν, cm^{-1}: 3120, 1580 (N–H); 1710, 1680 (C=O); 1625, 1515 (C=N, C=C); 1155–1190 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: isomer **A**: 1.34 s (18H, *t*-Bu), 7.53 m (4H, *m*-H), 7.69 m (4H, *o*-H), 14.08 br.s (2H, NH); isomer **B**: 1.43 s (18H, *t*-Bu), 7.48 m (4H, *m*-H), 7.67 m (4H, *o*-H), 13.78 d (2H, NH, *J* = 1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm, **A**: 26.19 [C(**C**H$_3$)$_3$], 44.73 [**C**(CH$_3$)$_3$], 117.4 (C^m), 117.5 q (**C**F$_3$, $^1J_{CF}$ = 292.6 Hz), 128.18 (C^o), 129.3 (C^2), 138.31 (C^i), 140.40 (C^p), 176.95 q (**C**OCF$_3$, $^2J_{CF}$ = 32.1 Hz), 206.41 (**C**OBu-*t*); isomer **B**: 27.83 [C(**C**H$_3$)$_3$], 43.9 [**C**(CH$_3$)$_3$], 115.66 q (CF$_3$, $^1J_{CF}$ = 288 Hz), 117.2 (C^m), 128.32 (C^o), 130.67 (C^2), 138.14 (C^i), 140.27 (C^p), 178.04 q (**C**OCF$_3$, $^2J_{CF}$ = 37.1 Hz), 203.14 (**C**OBu-*t*). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: isomer **A**: 92.03 d.d (CF_3, *J* = 2.2, 0.7 Hz); isomer **B**: 89.19 d (CF_3, *J* = 1 Hz). Found, %: C 56.45; H 4.65; F 18.67; N 9.39. $C_{28}H_{28}F_6N_4O_4$. Calculated, %: C 56.19; H 4.72; F 19.04; N 9.36.

4,4′-(Biphenyl-4,4′-diyldihydrazono)bis(1,1,2,2-tetrafluorononane-3,5-dione) (IIId). Yield 68%, yellow powder, mp 120–121°C (from ethanol). IR spectrum, ν, cm^{-1}: 3040, 1575 (N–H); 1705, 1695 (C=O); 1640, 1510 (C=N, C=C); 1070–1125 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.96 t (6H, CH_3, *J* = 7.3 Hz), 1.42 m and 1.64 m (8H, 7-H, 8-H), 3.02 t (4H, 6-H, *J* = 7.3 Hz), 6.38 t.t (2H, CHF_2, ^2J = 53.3, ^3J = 5.5 Hz), 7.54 m (4H, *m*-H), 7.71 m (4H, *o*-H), 15.32 s (2H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 24.92 d.t (4F, HCF_2, ^2J = 53.2, ^3J = 7.6 Hz), 42.59 m (4F, CF_2). Found, %: C 54.79; H 4.53; F 22.68; N 8.41. $C_{30}H_{30}F_8N_4O_4$. Calculated, %: C 54.38; H 4.56; F 22.94; N 8.46.

2,2′-(Biphenyl-4,4′-diyldihydrazono)bis(4,4,5,5,-6,6,6-heptafluoro-1-phenylhexane-1,3-dione) (IIIe). Yield 74%, mixture of isomers **A** and **B** (~10:1), orange powder, mp 180–181°C (from ethanol). IR spectrum, ν, cm^{-1}: 3080, 1575 (N–H); 1700, 1680 sh (C=O); 1615, 1600, 1515 (C=N, C=C); 1165–1240 (C–F). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3440, 3050, 1575 (N–H); 1725, 1700, 1680 sh (C=O); 1620, 1600 (C=N, C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: isomer **A**: 7.47 m (4H, *m*-H), 7.56–7.62 m (10H, Ph), 7.73 m (4H, *o*-H), 14.05 br.s (2H, NH); isomer **B**: 7.40 m (4H, *m*-H), 7.52–7.69 m (10H, Ph), 8.01 m (4H, *o*-H), 14.02 br.s (2H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: isomer **A**: 37.64 m (4F, 5-F), 49.27 m (4F, 4-F), 81.45 t (6F, 6-F, *J* = 9.5 Hz); isomer **B**: 37.90 m (4F, 5-F), 48.06 m (4F, 4-F), 81.36 t (6F, 6-F, *J* = 9.5 Hz). Found, %: C 51.68; H 2.21; F 31.76; N 6.92. $C_{36}H_{20}F_{14}N_4O_4$. Calculated, %: C 51.56; H 2.40; F 31.72; N 6.68.

3,3′-(Biphenyl-4,4′-diyldihydrazono)bis(5,5,6,6,-7,7,8,8,8-nonafluorooctane-2,4-trione) (IIIf). Yield 77%, yellow powder, mp 185–187°C (from ethanol). IR spectrum, ν, cm^{-1}: 3060, 1580 (N–H); 1705 (C=O); 1630, 1515 (C=N, C=C); 1130–1260 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.64 s (6H, CH_3), 7.56 m (4H, *m*-H), 7.71 m (4H, *o*-H), 15.33 s (2H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 36.46 m (4F, 7-F), 40.97 m (4F, 6-F), 50.25 m (4F, 5-F), 81.92 t.t (6F, 8-F, ^3J = 10, ^4J = 2.4 Hz). Found, %: C 41.19; H 1.75; F 41.96; N 6.57. $C_{28}H_{16}F_{18}N_4O_4$. Calculated, %: C 41.29; H 1.98; F 41.99; N 6.88.

Diethyl 2,2′-(biphenyl-4,4′-diyldihydrazono)bis-(4,4,4-trifluoro-3-oxobutanoate) (IVa). Yield 51%, orange powder, mp 210–212°C (from ethanol). IR spectrum, ν, cm^{-1}: 3140, 1595 (N–H); 1715 (C=O); 1670 (CO, ester); 1535 (C=N, C=C); 1140–1200 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.44 t (6H, CH$_2$C**H**$_3$, *J* = 7.1 Hz), 4.43 q (4H, OCH_2, *J* = 7.1 Hz), 7.51 m (4H, *m*-H), 7.68 m (4H, *o*-H), 13.56 br.s (2H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.03 (CH$_2$**C**H$_3$), 61.98 (OCH_2), 117.12 (C^m), 117.13 q (CF_3, $^1J_{CF}$ = 292.7 Hz), 121.55 (C^2), 128.17 (C^o), 138.17 (C^i), 140.32 (C^p), 163.74 q (**C**O$_2$Et, $^4J_{CF}$ = 1 Hz), 174.57 q (**C**OCF$_3$, $^2J_{CF}$ = 32.7 Hz). ^{19}F NMR spectrum ($CDCl_3$): δ_F 91.3 ppm, d (*J* = 0.9 Hz). Found, %: C 50.23; H 3.37; F 19.79; N 9.70. $C_{24}H_{20}F_6N_4O_6$. Calculated, %: C 50.18; H 3.51; F 19.84; N 9.75.

Dimethyl 2,2′-(biphenyl-4,4′-diyldihydrazono)-bis(4,4,5,5-tetrafluoro-3-oxopentanoate) (IVb). The product was washed with ethanol. Yield 66%, yellow powder, mp 200–201°C. IR spectrum, ν, cm^{-1}: 3130, 1580 (N–H); 1715 (C=O); 1670 (C=O, ester); 1610, 1525 (C=N, C=C); 1220–1250 (C–F). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.97 s (6H, OCH_3), 6.36 t.t (2H, CHF_2, ^2J = 53, ^3J = 5.5 Hz), 7.50 m (4H, *m*-H), 7.69 m (4H, *o*-H), 13.55 s (2H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 24.35 d.t (4F, HCF_2, ^2J = 53, ^3J = 7.3 Hz), 42.28 m (4F, CF_2). Found, %: C 47.31;

H 2.87; F 24.84; N 9.20. $C_{24}H_{18}F_8N_4O_6$. Calculated, %: C 47.22; H 2.97; F 24.90; N 9.18.

Diethyl 2,2′-(biphenyl-4,4′-diyldihydrazono)bis-(4,4,5,5,6,6,6-heptafluoro-3-oxohexanoate) (IVc). Yield 71%, yellow powder, mp 144–146°C (from ethanol). IR spectrum, ν, cm^{-1}: 3120, 1580 (N–H); 1710 (C=O); 1670 (C=O, ester); 1615, 1595, 1530 (C=N, C=C); 1210–1240 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.44 t (6H, $CH_2C\mathbf{H}_3$, J = 7.1 Hz), 4.42 q (4H, OCH_2, J = 7.1 Hz), 7.49 m (4H, *m*-H), 7.68 m (4H, *o*-H), 13.60 s (2H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 37.52 m (4F, 5-F), 49.43 m (4F, 4-F), 81.41 t (6F, 6-F, J = 9.5 Hz). Found, %: C 43.45; H 2.42; F 34.32; N 7.28. $C_{28}H_{20}F_{14}N_4O_6$. Calculated, %: C 43.42; H 2.60; F 34.34; N 7.23.

Dimethyl 2,2′-(biphenyl-4,4′-diyldihydrazono)-bis(4,4,5,5,6,6,7,7,7-nonafluoro-3-oxoheptanoate) (IVd). The product was washed with ethanol. Yield 73%, yellow powder, mp 190–192°C. IR spectrum, ν, cm^{-1}: 3150, 1580 (N–H); 1700 (C=O); 1680 (C=O, ester); 1615, 1515 (C=N, C=C); 1135–1230 (C–F). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.96 s (6H, OCH_3), 7.50 m (4H, *m*-H), 7.69 m (4H, *o*-H), 13.58 s (2H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 36.47 m (4F, 6-F), 40.86 m (4F, 5-F), 50.02 t (4F, 4-F, J = 12 Hz), 80.88 t.t (6F, 7-F_3, ^3J = 9.5, ^4J = 2.3 Hz). Found, %: C 39.75; H 2.04; F 40.65; N 6.64. $C_{28}H_{16}F_{18}N_4O_6$. Calculated, %: C 39.73; H 1.91; F 40.4; N 6.62.

2,2′-(Biphenyl-4,4′-diyldihydrazono)bis(4,4,5,5,-6,6,6-heptafluoro-1-phenylhexane-1,3-dione) (IIIe) nickel and copper complexes VIa and VIb (*general procedure*). A solution of 1 mmol of ligand **IIIe** in 4 ml of DMF was heated to 60°C, a solution of 1 mmol of nickel(II) or copper(II) acetate (**Va** or **Vb**) in 16 ml of methanol was added, and a solution of 10 mg of sodium acetate in 2 ml of water was then added dropwise. The mixture was stirred for 8 h at 80–90°C, and the precipitate was filtered off and washed with water.

Bis[2,2′-(biphenyl-4,4′-diyldihydrazono)bis-(4,4,5,5,6,6,6-heptafluoro-1-phenylhexane-1,3-dionato)-*O*,*N*]dinickel(II) (VIa). Yield 91%, yellow–brown powder, mp >360°C (from methanol). IR spectrum, ν, cm^{-1}: 1665 sh, 1650 (C=O); 1600, 1580, 1530 (C=N, C=C); 1180–1230 (C–F). Found, %: C 48.70; H 2.31; F 29.44; N 6.50. $C_{72}H_{36}F_{28}N_8Ni_2O_8$. Calculated, %: C 48.30; H 2.03; F 29.71; N 6.26.

Bis[2,2′-(biphenyl-4,4′-diyldihydrazono)bis-(4,4,5,5,6,6,6-heptafluoro-1-phenylhexane-1,3-dionato-*O*,*N*)]dicopper(II) (VIb). The product was washed with hot ethanol. Yield 84%, dark green powder, mp 342–343°C. IR spectrum, ν, cm^{-1}: 1685 sh, 1670 (C=O); 1600, 1580, 1510, 1490 (C=N, C=C); 1190–1230 (C–F). Found, %: C 47.99; H 2.24; F 28.98; N 6.19. $C_{72}H_{36}Cu_2F_{28}N_8O_8$. Calculated, %: C 48.04; H 2.02; F 29.55; N 6.22.

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