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Bis(1,1,1,3,5,5,5-heptafluoro-4-iminopent-2-ene-2-aminato)copper(II) — a new metal-containing matrix in the design of heterospin systems

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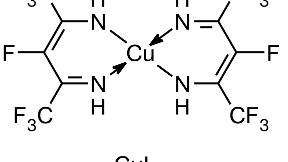
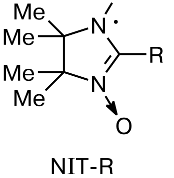
The first heterospin compounds based on bis(1,1,1,3,5,5,5-heptafluoro-4-iminopent-2-ene-2-aminato)copper(II) (CuL_2) and nitronyl nitroxide radicals, 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyls (NIT-R, where R = H, Me, Ph, and 1-methylpyrazol-4-yl), were synthesized and structurally characterized. An important peculiarity of the structure of synthesized solid phases is the formation of a supramolecular structure due to hydrogen bonds between the oxygen atoms of the nitronyl nitroxide fragments of NIT-R and the hydrogen atoms of the NH groups of CuL_2.

Key words: copper(II), copper(II) bischelates, nitroxides, X-ray diffraction analysis, magnetic properties.

Fluorinated metal-containing matrices are widely used in the design of heterospin systems due to the high acceptor properties of the central atom favoring the coordination of weak donors, groups >N—O of nitroxyl radicals.[1,2] However, the scope of these acceptor matrices is restricted: metal hexafluoroacetylacetonates[3] and perfluorocarboxylates[3,4] usually act as such matrices. Therefore, the introduction of new metal-containing acceptors into the design of molecular magnetics is a topical problem. It has recently been shown that bis(μ_2-1,1,2,2,8,8,9,9-octafluorononane-3,5,7-trionato)dicopper(II) ($[Cu_2L'_2]$) and bis(1,1,1,5,5,5-hexafluoro-4-iminopent-2-en-2-olato)copper(II) can be used as acceptor matrices in the reactions with nitroxyl radicals.[5,6] In the present work, we synthesized the first heterospin compounds based on bis(1,1,1,3,5,5,5-heptafluoro-4-iminopent-2-ene-2-aminato)copper(II) (CuL_2) and nitroxyl radicals NIT-R (R = H, Me, Ph, and 1-methylpyrazol-4-yl (MePz)) and studied their structures and magnetic properties.



CuL_2



NIT-R

R = H, Me, Ph, MePz

Results and Discussion

Solutions of the studied compounds are kinetically rather stable; unlike similar solutions of Cu^{II} hexafluoroacetylacetonate, no formation of decomposition products is detected in these solutions on storage under normal conditions for several days. The ratio CuL_2 : NIT-R (R = Me, Ph, MePz) in the isolated solid phases coincides with the ratio of reactants introduced into the synthesis (1 : 1). However, in the case of NIT-H, $CuL_2(NIT\text{-}H)_2$ is isolated from an ether—hexane mixture at ratios of both 1 : 1 and 1 : 2. Only the recrystallization of this compound from toluene gave CuL_2(NIT-H).

The choice of a mixture of solvents for the synthesis of heterospin compounds was determined by the solubility of the reactants and products formed. For instance, the use of hexane and toluene turned out inefficient because of the very low solubility of the starting CuL_2 in these solvents. At the same time, the use of pure ether gave no satisfactory results because of the high solubility of the products.

The procedures of synthesis proposed by us (see Experimental) make it possible to obtain heterospin compounds of CuL_2 with NIT-R as qualitative single crystals in good yield.

The X-ray diffraction study of CuL_2(NIT-R) (R = Me, Ph, MePz) showed that hydrogen bonds of the NH groups with the NO groups of NIT-R play the determining role in

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structure formation. In bischelate CuL_2, the environment of the central atom is close to square, and the distances Cu—N in all the structures range from 1.920(9) to 1.981(9) Å. Molecules of the bischelates linked by hydrogen bonds N—H...O_{NO} with NIT-R are bound into chains in the structures CuL_2(NIT-Me) and CuL_2(NIT-Ph) (Fig. 1).

In the case of NIT-MePz, on of the NO groups of nitroxide and the N atom of the pyrazole cycle are involved in hydrogen bonding, *i.e.*, NIT-MePz performs the bridging function and forms a chain with the motif "head-to-tail" (Fig. 2). In the structure CuL_2(NIT-Me) • C_6H_{14}, the chains almost linear: the Cu atoms lie on the same straight line and hexane molecules are arranged between them perpendicularly to the axis of the chain (see Fig. 1, *c*). The chain is bent in structure CuL_2(NIT-Ph) with the larger bridge NIT-R (see Fig. 1, *b* and *d*). The structure reaches the maximum zigzag character in CuL_2(NIT-MePz) • C_7H_8; in this case, toluene molecules are located in the loops of the structure. A specific feature of structure CuL_2(NIT-MePz) • C_7H_8 is that the O atoms of the uncoordinated group NO form short contacts O...F (3.162(6) and 3.327(6) Å) with the atoms F of the fragments F—C< of the adjacent chains.

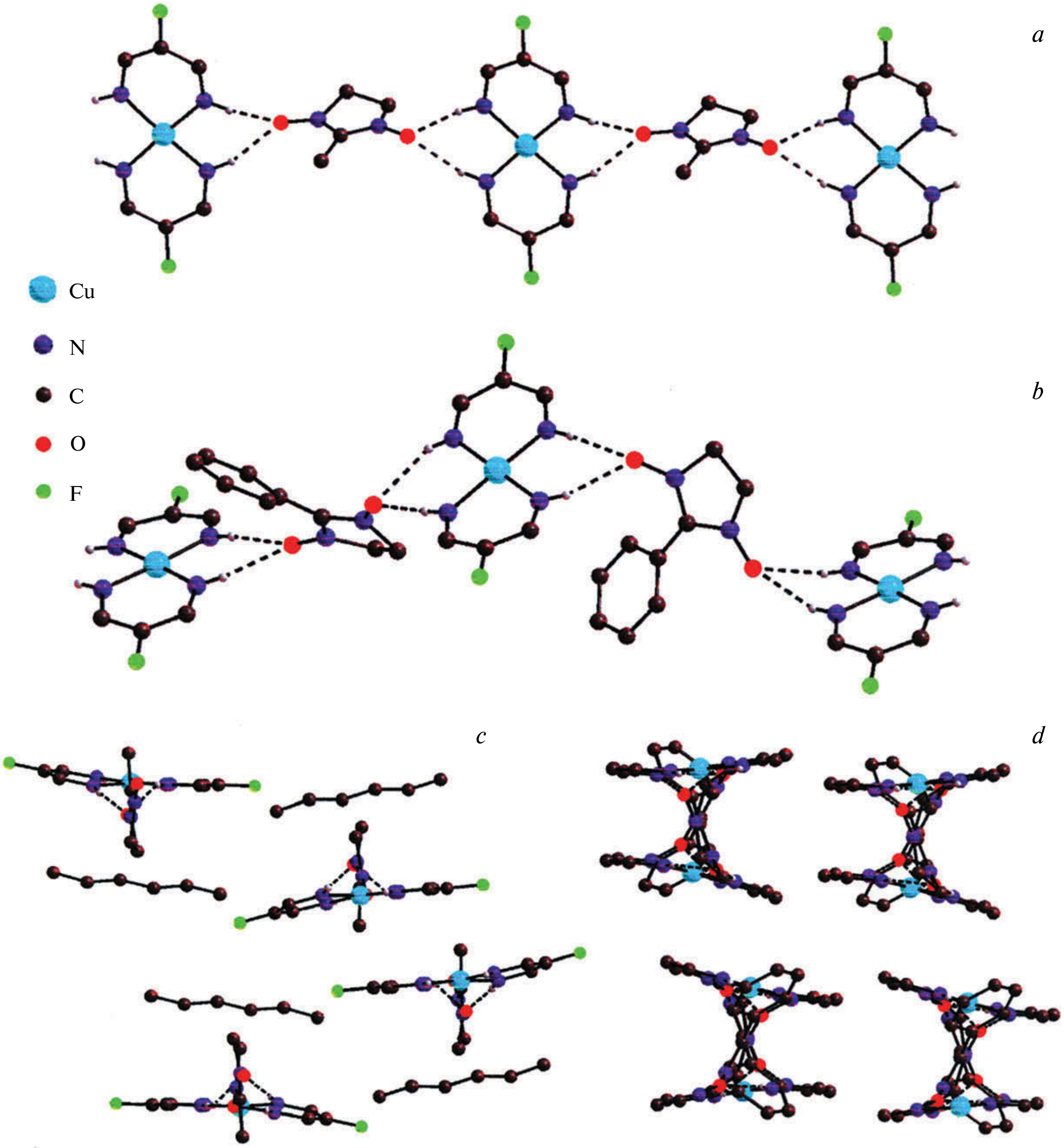

Fig. 1. Structure of chains (*a*, *b*) and their packing (*c*, *d*) in CuL_2(NIT-Me) • C_6H_{14} (*a*, *c*) and CuL_2(NIT-Ph) (*b*, *d*).
Note. Fig. 1 is available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

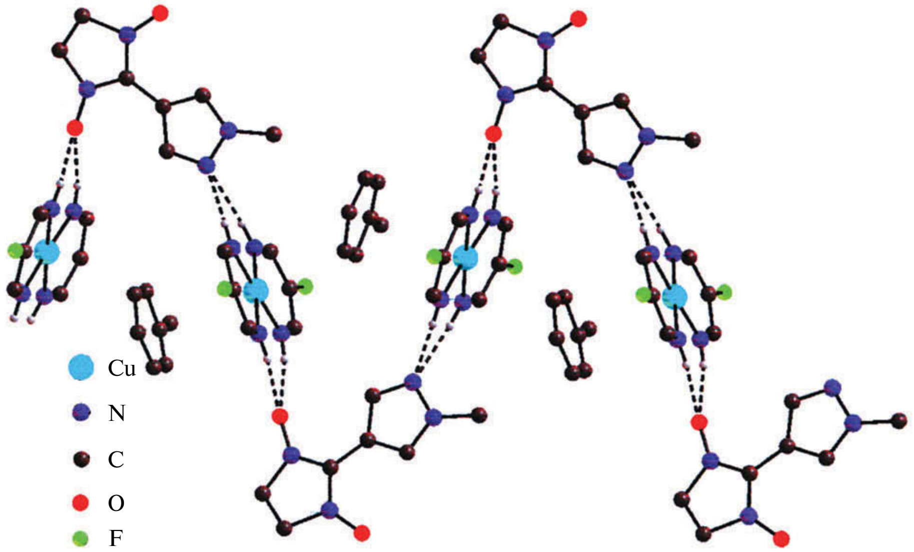

Fig. 2. Structure of the chain in $CuL_2(NIT\text{-}MePz) \cdot C_7H_8$.*

Only one NO group participates in hydrogen bonding in the solid phase of $CuL_2(NIT\text{-}H)_2$, whereas the second group "supplements" the environment of the copper atom to square-pyramidal (Fig. 3, *a*) at a considerable Cu—O distance of 2.657(2) Å. This results in the formation of ribbons. In addition, the formation of hydrogen bonds of the C—H...O type between the molecules NIT-H was observed inside the ribbons. Similar hydrogen bonds in the

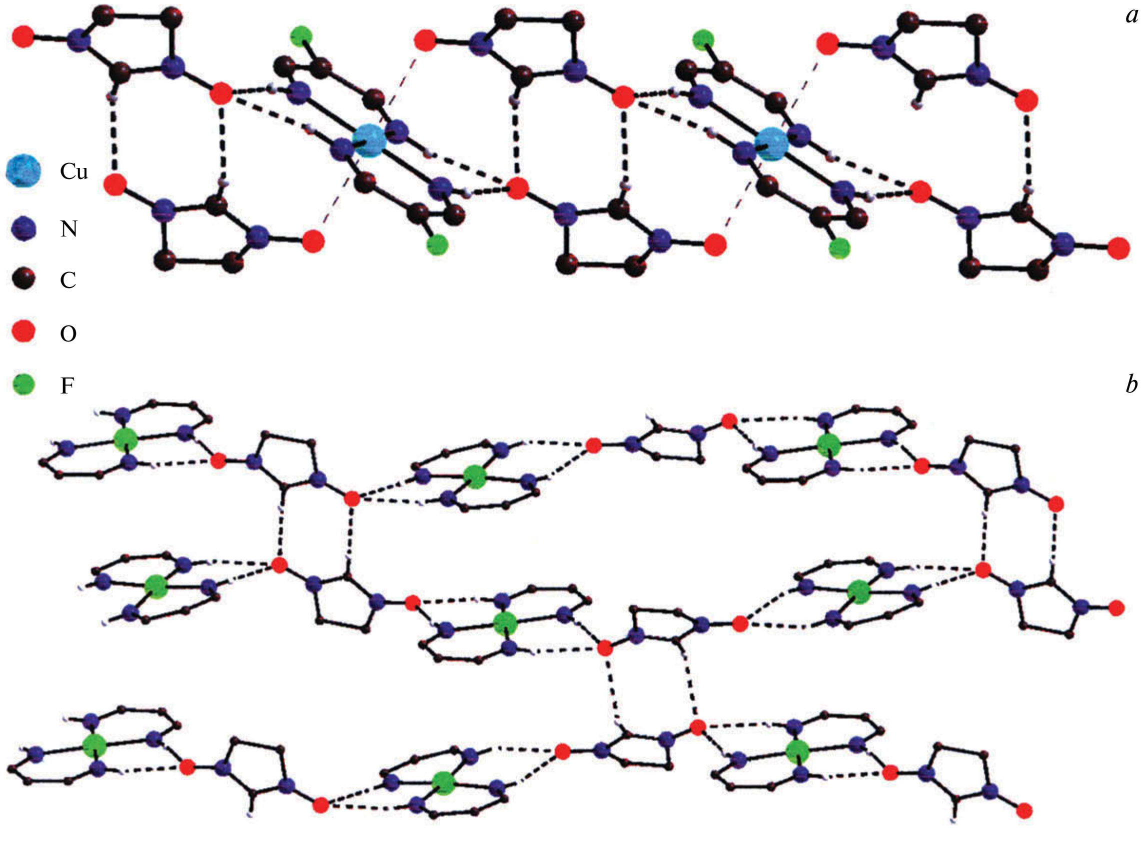

Fig. 3. Structures of the chain in $CuL_2(NIT\text{-}H)_2$ (*a*) and the layer in $CuL_2(NIT\text{-}H)$ (*b*).*

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* Figs 2 and 3 are available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

solid phase of CuL_2(NIT-H) result in joining of the chains into layers (Fig. 3, *b*).

Thus, four variants of hydrogen bonds between CuL_2 and NIT-R caused by the functions of nitroxyl groups are observed in the structures studied: (a) only one NO group of NIT-R acts as an acceptor of the H atoms of two NH groups; (b) each nitroxyl groups form hydrogen bonds with two NH groups from different molecules CuL_2; (c) one NO group of NIT-R serves as an acceptor of H atoms of two NH groups, and another group participates in supplementing of the environment of the copper atom; and (d) one NO group of NIT-R acts simultaneously as an acceptor of hydrogen atoms of two NH groups and the C—H group of the nitroxyl.

The temperature plots of the effective magnetic moment (μ_{eff}) and magnetic susceptibility (χ) for CuL_2(NIT-Me) are presented in Fig. 4. The high-temperature value of μ_{eff} equal to 2.49 μ_B (μ_B is Bohr magneton) for CuL_2(NIT-Me)$\cdot C_6H_{14}$ (see Fig. 4) agrees well with the theoretical purely spin value of 2.45 μ_B for two non-interacting paramagnetic centers with spins $S = 1/2$ at $g = 2$. A decrease in μ_{eff} with the temperature decrease indicates exchange interactions of the antiferromagnetic character. The approximation of the experimental data by the model of uniform chain, whose choice was based on the X-ray diffraction results (see Fig. 1), gave the following optimal values of the parameters for the antiferromagnetically bound paramagnetic centers with the spins $S = 1/2$ ($H = -2J\Sigma S_iS_{i+1}$)^7: $g = 2.17$ (±0.01), $J/k = -45.8$ (±0.5) K.

The plots $\mu_{eff}(T)$ and $\chi(T)$ for CuL_2(NIT-Ph) are presented in Fig. 5. The high-temperature value of μ_{eff} equal to 2.50 μ_B is close to the theoretical value of 2.45 μ_B for two non-interacting paramagnetic centers with the spins $S = 1/2$ at $g = 2$. The value of μ_{eff} decreases with the temperature decrease, indicating exchange interactions of the antiferromagnetic character. The chain structure is similar to CuL_2(NIT-Me) in which molecules of bischelate and nitronyl nitroxide connected by hydrogen bonds alternate. However, an analysis of the magnetic properties using the model for uniform chain of antiferromagnetically bound paramagnetic centers with the spins $S = 1/2$ gave no satisfactory results (see Fig. 5). The best agreement with the experimental data was achieved using the model for alternant chains ($H = -2J\Sigma(S_iS_{i+1} + \alpha S_iS_{i+1})$)^8; the approximation of the experimental data gave the following optimal parameters: $g = 2.137$ (±0.002), $J/k = -36.2$ (±0.2) K, $\alpha = 0.892$ (±0.002). Note that this description better corresponds to the X-ray diffraction data as well. In structure CuL_2(NIT-Ph) slight differences in lengths of the hydrogen bonds and in the angles between molecules CuL_2 and linked molecules NIT-Ph were obtained (Table 1).

For CuL_2(NIT-MePz)$\cdot C_7H_8$, the high-temperature value of μ_{eff} (Fig. 6) equal to 2.57 μ_B is also well consistent with the theoretical purely spin value of 2.45 μ_B. Structure CuL_2(NIT-MePz)$\cdot C_7H_8$ is formed by chains with the motif "head-to-tail" in which the fragments CuL_2 alternate, being linked by hydrogen bonds to the NO group of the paramagnetic ligand from one side, and from another side they are linked with the imine N atom of the pyrazole cycle, *i.e.*, only one of the NO groups participates in hydrogen bonding. Taking into account the short contacts O...F, for the description of the system of exchange channels we chose the model of alternant chain {Cu—N—H...O_{NO}...F...Cu—N—H...O_{NO}...F...} $H = -2J\Sigma(S_iS_{i+1} + \alpha S_iS_{i+1})$.^{8} The following optimal values of the parameters were obtained by the approximation of the experimental data: $g = 2.20$ (±0.01), $J/k = -44.2$ (±0.5) K, $\alpha = 0.73$ (±0.01).

The temperature plots of μ_{eff} and inverse magnetic susceptibility $1/\chi$ for CuL_2(NIT-H)$_2$ are presented in Fig. 7.

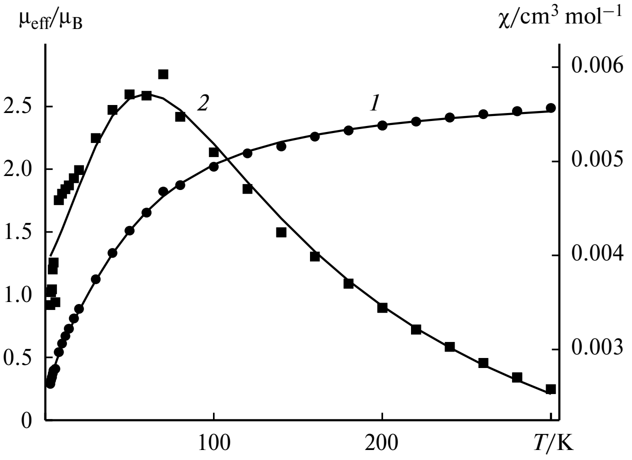

Fig. 4. Temperature plots of the effective magnetic moment (*1*) and magnetic susceptibility (*2*) for CuL_2(NIT-Me)$\cdot C_6H_{14}$. Points are experimental data, and solid lines are theoretical curves.

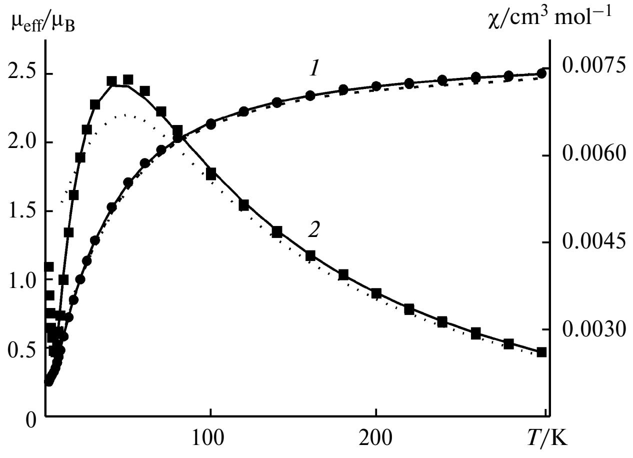

Fig. 5. Temperature plots of the effective magnetic moment (*1*) and magnetic susceptibility (*2*) for CuL_2(NIT-Ph). Points are experimental data, and lines are theoretical curves (solid line is the model of alternant chain, and dotted line is the model of uniform chain).

Table 1. Hydrogen bond lengths (*d*) and the corresponding bond angles (φ) in the structures of the synthesized complexes

Compound (*T*/K)	Bond	*d*(N—H), *d*(C—H)/Å	*d*(H...O$_{NO}$)/Å	*d*(N...O$_{NO}$), *d*(C...O$_{NO}$)/Å	φ(N—H...O$_{NO}$), φ(C—H...O$_{NO}$)/deg
CuL_2(NIT-Me)•C_6H_{14}	N(1)—H(1A)...O(02′)	0.88	2.17	2.938(12)	145.2
	N(2)—H(2A)...O(01)	0.88	2.05	2.911(10)	166.6
	N(3)—H(3A)...O(02′)	0.88	2.06	2.916(12)	163.2
	N(4)—H(4A)...O(01)	0.88	2.15	3.004(11)	165.3
CuL_2(NIT-Ph)	N(1)—H(1A)...O(02′)	0.79(2)	2.27(2)	3.023(2)	161(2)
	N(2)—H(2A)...O(01)	0.76(2)	2.28(2)	3.011(3)	161(2)
	N(3)—H(3A)...O(01)	0.77(2)	2.28(2)	3.004(3)	157(2)
	N(4)—H(4A)...O(02′)	0.74(2)	2.20(2)	2.927(3)	169(2)
CuL_2(NIT-MePz)•C_7H_8	N(1)—H(1A)...N(3R′)	0.86	2.28	3.130(7)	169.6
	N(2)—H(2A)...O(1R	0.86	2.10	2.932(6)	163.0
	N(3)—H(3A)...N(3R′)	0.86	2.27	3.120(7)	169.4
	N(4)—H(4A)...O(1R)	0.86	2.08	2.917(7)	165.1
$CuL_2(NIT\text{-}H)_2$ (70)	N(1)—H(1A)...O(01′)	0.88	2.07	2.931(3)	166.6
	N(2)—H(2A)...O(01′)	0.88	2.15	2.974(3)	156.7
	C(07)—H(07A)...O(01′)	0.95	2.39	3.289(3)	157.6
$CuL_2(NIT\text{-}H)_2$ (150)	N(1)—H(1A)...O(01′)	0.88	2.08	2.945(2)	167.2
	N(2)—H(2A)...O(01′)	0.88	2.15	2.990(2)	158.4
	C(07)—H(07A)...O(01′)	0.95	2.43	3.330(3)	157.0
$CuL_2(NIT\text{-}H)_2$ (290)	N(1)—H(1A)...O(01′)	0.88	2.12	2.962(3)	168.0
	N(2)—H(2A)...O(01′)	0.88	2.19	3.015(3)	161.5
	C(07)—H(07A)...O(01′)	0.95	2.56	3.435(3)	156.9
CuL_2(NIT-H)	N(1)—H(12)...O(2R)	0.87	2.25	3.086(4)	162.6
	N(2)—H(22)...O(2S)	0.87	2.32	3.169(4)	166.6
	N(4)—H(42)...O(2R)	0.87	2.25	3.071(4)	157.9
	N(6)—H(62)...O(1S′)	0.87	2.12	2.981(4)	169.8
	N(7)—H(72)...O(1S′)	0.87	2.16	3.016(4)	167.5
	N(8)—H(82)...O(1R′)	0.87	2.25	3.117(5)	171.2
	C(7R)—H(7R)...O(1R′)	0.94	2.45	3.022(6)	119.6
	C(7S)—H(7S)...O(2S′)	0.94	2.27	3.199(5)	170.0

The high-temperature value of μ_{eff} for $CuL_2(NIT\text{-}H)_2$ equal to 3.12 μ_B agrees well with the theoretical purely spin value of 3.0 μ_B for three non-interacting paramagnetic centers with the spins $S = 1/2$ at $g = 2$. The complicated system of exchange channels in the chain $CuL_2(NIT\text{-}H)_2$ has no appropriate models for the description of the mag-

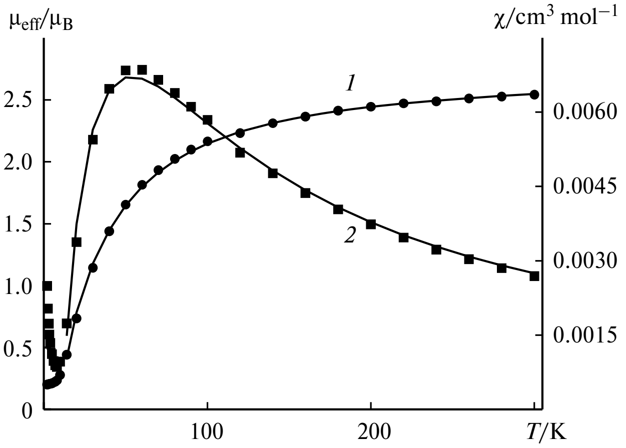

Fig. 6. Temperature plots of the effective magnetic moment (*1*) and magnetic susceptibility (*2*) for CuL_2(NIT-MePz)•C_7H_8. Points are experimental data, and solid lines are theoretical curves.

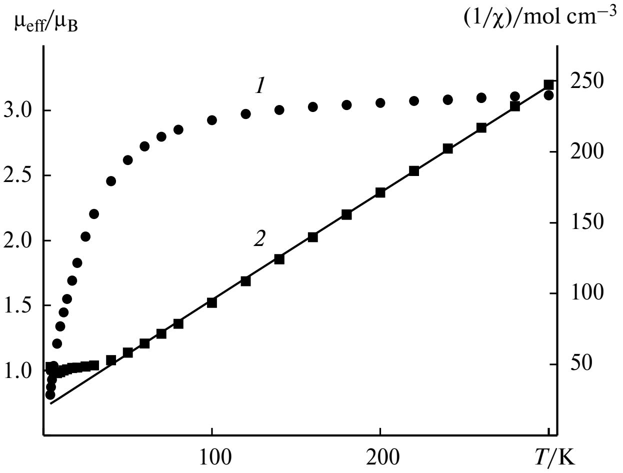

Fig. 7. Temperature plots of the effective magnetic moment (*1*) and inverse magnetic susceptibility (*2*) for $CuL_2(NIT\text{-}H)_2$. Points are experimental data, and solid line is the theoretical curve.

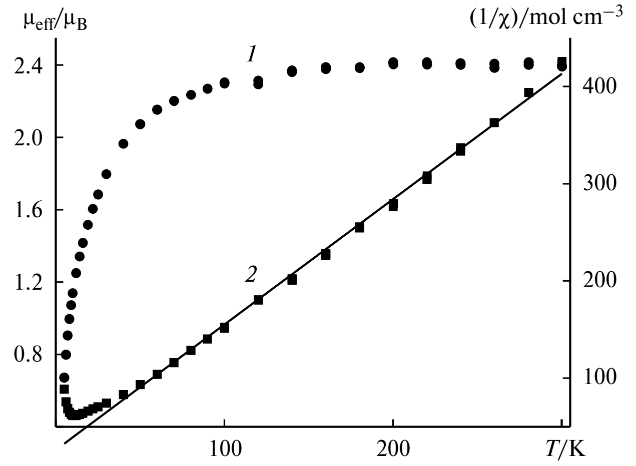

Fig. 8. Temperature plots of the effective magnetic moment (*1*) and inverse magnetic susceptibility (*2*) for CuL_2(NIT-H). Points are experimental data, and solid line is the theoretical curve.

netic properties. At temperatures higher 50 K, the temperature dependence of the inverse magnetic susceptibility is well described by the Curie—Weiss equation with the parameters $C = 1.3$ cm^3 mol^{-1} and $\theta = -25$ K. The negative value of the Weiss constant indicates the presence of antiferromagnetic interactions comparable in value with the exchange interactions in the compounds described above.

The temperature plots of μ_{eff} and inverse magnetic susceptibility $1/\chi$ for CuL_2(NIT-H) are presented in Fig. 8. The value of μ_{eff} at 300 K is equal to 2.40 μ_B and remains almost unchanged with the temperature increase to 100 K, after which it decreases smoothly reaching 0.67 μ_B at 5 K. The value of μ_{eff} in the temperature region 100—300 K agrees well with the theoretical purely spin value of 2.45 μ_B for two non-interacting paramagnetic centers with the spins $S = 1/2$ at $g = 2$. The decrease in μ_{eff} below 100 K is caused by the antiferromagnetic exchange interactions between unpaired electrons of the paramagnetic centers, which is indicated by the negative value of the Weiss constant θ. At temperatures above 50 K, the temperature dependence of the inverse magnetic susceptibility is described by the Curie—Weiss equation with the parameters $C = 0.776$ cm^3 K mol^{-1} and $\theta = -20$ K.

Thus, we synthesized and structurally characterized the first heterospin compounds based on bis(1,1,1,3,5,5,5-heptafluoro-4-iminopent-2-ene-2-aminato)copper(II) and stable nitronyl nitroxide radicals of the 2-imidazoline series. According to the X-ray diffraction data, hydrogen bonds of the NH groups with the NO groups of NIT-R play the determining role in the formation of the supramolecular structure of these compounds.

Experimental

Nitroxyl radicals were synthesized according to the known procedures.[9,10] Bis(4-imino-1,1,1,3,5,5,5-heptafluoropent-2-ene-2-aminato)copper(II) (CuL_2) was synthesized according to a procedure described previously.[11] Microanalyses of the compounds were carried out on a Carlo Erba 1106 analyzer at the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry (Siberian Branch of the Russian Academy of Sciences).

1-Methyl-4-(4,4,5,5-tetramethyl-3-oxide-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)-1*H*-pyrazolebis(4-imino-1,1,1,3,5,5,5-heptafluoropent-2-ene-2-aminato)copper(II) toluene solvate, CuL_2(NIT-MePz)·C_7H_8. A solution of NIT-MePz (0.0233 g, 0.1 mmol) in toluene (4 mL) was added to a solution of CuL_2 (0.0500 g, 0.1 mmol) in ether (3 mL). The solution volume was decreased to ~3 mL by passing a weak argon flow above the surface of the reaction mixture. After 1 h dark blue crystals were formed, filtered off, washed with cold toluene, and dried in air. The yield was 75%. Found (%): C, 33.3; H, 2.4; N, 15.1;

Table 2. Selected bond lengths (*d*) in the structures of the synthesized complexes

Bond	CuL_2(NIT-Me)·C_6H_{14}	CuL_2(NIT-Ph)	CuL_2(NIT-MePz)·C_7H_8	CuL_2(NIT-H)$_2$			CuL_2(NIT-H)
	d/Å			70 K	150 K	290 K	
Cu—N	1.920(9), 1.938(9), 1.968(10), 1.981(9)	1.932(2), 1.933(2), 1.940(2), 1.945(2)	1.946(5), 1.952(5), 1.955(5), 1.963(5)	1.978(2), 1.981(2)	1.976(2), 1.976(2)	1.973(2), 1.973(2)	1.940(3), 1.941(3), 1.946(3), 1.949(3), 1.934(3), 1.938(3), 1.941(3), 1.941(3)
Cu—O	—	—	—	2.637(2)	2.657(2)	2.710(2)	—
O—N	1.302(10), 1.241(10)	1.281(2), 1.281(2)	1.268(5), 1.294(5)	1.294(2), 1.284(3)	1.285(2), 1.280(2)	1.290(3), 1.281(3)	1.275(4), 1.278(4), 1.281(4), 1.270(4)

Table 3. Crystallographic characteristics of the compounds and details of X-ray diffraction experiments

Parameter	CuL_2(NIT-MePz)· ·C_7H_8	CuL_2(NIT-Ph)	CuL_2(NIT-Me)· ·C_6H_{14}	$CuL_2(NIT\text{-}H)_2$			CuL_2(NIT-H)
Empirical formula	$C_{28}H_{29}CuF_{14}N_8O_2$	$C_{23}H_{21}CuF_{14}N_6O_2$	$C_{24}H_{33}CuF_{14}N_6O_2$	$C_{24}H_{30}CuF_{14}N_8O_4$			$C_{17}H_{17}CuF_{14}N_6O_2$
Molecular weight	839.13	743.00	767.10	824.10			666.91
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$C2/c$			$P1$
Z	4	4	4	4			4
T/K	293	240	173	70	150	290	245
a/Å	15.357(5)	12.6561(11)	12.078(3)	17.7807(12)	17.8435(9)	18.0736(11)	10.253(3)
b/Å	17.452(6)	16.1375(14)	15.992(4)	9.1354(9)	9.1348(5)	9.1338(4)	10.780(4)
c/Å	13.189(5)	15.0469(13)	17.155(5)	20.7911(19)	20.9440(12)	21.2430(12)	23.395(6)
α/deg	—	—	—	—	—	—	90.437(18)
β/deg	90.032(7)	106.789(5)	90.289(9)	105.441(6)	105.689(2)	106.072(7)	98.468(16)
γ/deg	—	—	—	—	—	—	103.80(2)
V/Å^3	3535(2)	2942.2(4)	3313.5(16)	3255.3(5)	3255.3(5)	3369.7(3)	2481.3(13)
d_{calc}/g cm^{-3}	1.577	1.677	1.538	1.682	1.665	1.624	1.785
μ/mm^{-1}	0.731	0.865	0.770	0.797	0.789	0.769	1.014
θ Range/deg	1.17—26.50	1.86—28.27	1.19—25.00	4.76—28.02	2.02—26.37	2.02—28.27	1.76—28.18
I_{hkl}, measured/ independent	23041/7299	23671/7190	18303/5821	9583/ 3829	10807/ 3366	11235/ 4085	40884/ 11629
($I_{hkl} > 2\sigma(I)$)/N*	3652/503	3610/487	4801/425	3043/232	2542/232	2145/232	4915/722
R_1/wR_2 ($I > 2\sigma(I)$)	0.0652/0.1040	0.0381/0.0680	0.0959/0.2494	0.0390/ 0.1004	0.0350/ 0.0787	0.0451/ 0.0886	0.0529/ 0.1350

* Number of refined parameters.

F, 35.3. $C_{21}H_{21}N_8O_2F_{14}Cu$. Calculated (%): C, 33.8; H, 2.8; N, 15.0; F, 35.6.

2-Phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxylbis(4-imino-1,1,1,3,5,5,5-heptafluoropent-2-ene-2-aminato)copper(II), CuL_2(NIT-Ph). A solution of NIT-Ph (0.0229 g, 0.1 mmol) in ether (3 mL) and hexane (5 mL) were added to a solution of CuL_2 (0.0500 g, 0.1 mmol) in ether (3 mL). The obtained reaction mixture was stored in the open flask at ~5 °C. After 24 h large dark blue prismatic crystals were formed, filtered off, washed with cold hexane, and dried in air. The yield was 80%. Found (%): C, 37.7; H, 3.0; N, 10.9; F, 35.0. $C_{23}H_{21}N_6O_2F_{14}Cu$. Calculated (%): C, 37.2; H, 2.9; N, 11.3; F, 35.8.

2,4,4,5,5-Pentamethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-octylbis(4-imino-1,1,1,3,5,5,5-heptafluoropent-2-ene-2-aminato)copper(II) hexane solvate, CuL_2(NIT-Me)·C_6H_{14}. A mixture of CuL_2 (0.0500 g, 0.1 mmol) and NIT-Me (0.0168 g, 0.1 mmol) was dissolved in ether (5 mL), hexane (5 mL) was added, and the solution was stored in the open flask at ~5 °C. After 10 h large brown crystals that formed were filtered off, washed with a cold ether—hexane (1 : 5) mixture, and dried in air within 1 min. The yield was 35%. Found (%): C, 31.9; H, 3.3; N, 12.2; F, 39.3. $C_{18}H_{19}N_6O_2F_{14}Cu$. Calculated (%): C, 31.8; H, 2.8; N, 12.3; F, 39.1. A similar procedure was used to synthesize **bis(4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl)-bis(4-imino-1,1,1,3,5,5,5-heptafluoropent-2-ene-2-aminato)-copper(II), $CuL_2(NIT\text{-}H)_2$**, which was isolated as large brown crystals. The yield was 45%. Found (%): C, 34.4; H, 3.8; N, 13.2; F, 32.1. $C_{24}H_{30}N_8O_4F_{14}Cu$. Calculated (%): C, 35.0; H, 3.7; N, 13.6; F, 32.3.

4,4,5,5-Tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxylbis(4-imino-1,1,1,3,5,5,5-heptafluoropent-2-ene-2-aminato)copper(II), CuL_2(NIT-H). $CuL_2(NIT\text{-}H)_2$ (0.081 g, 0.1 mmol) was dissolved in toluene (5 mL), and the solution was left to stay at ~5 °C for 48 h. The brown crystals that formed were filtered off, washed with hexane, and dried in air. The yield was 31%. Found (%): C, 30.9; H, 2.7; N, 12.5; F, 39.7. $C_{17}H_{17}N_6O_2F_{14}Cu$. Calculated (%): C, 30.6; H, 2.6; N, 12.6; F, 39.9.

X-ray diffraction study. X-ray diffraction experiments were carried out on a SMART APEX CCD diffractometer (Bruker AXS) (Mo-Kα radiation, λ = 0.71073 Å, T = 295 K, an absorption correction was applied by the Bruker SADABS program, version 2.10). The structures were solved by direct methods and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms. In most cases, the positions of H atoms were calculated theoretically. The H atoms of the methyl groups were refined isotropically in the rigid group approximation. All calculations on structure determination and refinement were performed using the Bruker Shelxtl Version 6.14 program package. Selected bond lengths in the structures are listed in Table 2, and hydrogen bonding parameters are given in Table 1. The crystallographic characteristics of the compounds and experimental details are presented in Table 3.

The magnetic properties of the complexes were measured on a SQUID magnetometer in the temperature range 2—300 K in a magnetic field of 5 kOe. The paramagnetic components of magnetic susceptibility (χ) were determined with allowance for the diamagnetic contribution estimated from Pascal´s constants and temperature-independent paramagnetism for Cu^{2+} ions, which was accepted to be $60 \cdot 10^{-6}$ cm^3 mol^{-1}. The effective magnetic moment was calculated by the formula

$$\mu_{eff} = [3k/(N_A\beta^2) \cdot \chi T]^{1/2} \approx (8\chi T)^{1/2},$$

where N_A, β, and k are Avogadro´s number, Bohr magneton, and the Boltzmann constant, respectively.

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