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A New Type of Mixed-Ligand Complex with Nitroxyl Radicals

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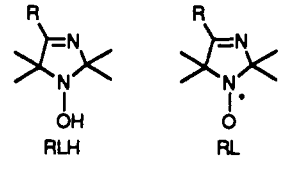
The reaction of $Cu(hfac)_2$ with hydroxylamines RLH (RLH = 1-hydroxy-2,2,5,5-tetramethyl-4-R-3-imidazoline; R = Me, Et, i-Pr, Ph) in inert atmosphere on heating gives rise to the partial reduction of Cu(II) to Cu(I) and yields mixed-ligand mixed-valent complexes of the composition $Cu_2(hfac)_3(RL)_2$ (RL = the 2,2,5,5-tetramethyl-4-R-3-imidazolinyl-1-oxyl nitroxide; R = Me, Et, i-Pr, Ph). The reaction of $Cu(hfac)_2$ with RLH in inert atmosphere at ambient temperature yields $Cu(hfac)_2(RLH)$. $Cu(hfac)_2(MeL)$ and $[Cu(hfac)_2]_3(RL)_2$ (R = Et, i-Pr, Ph) complexes are formed by the reaction of these reagents in air. The X-ray diffraction study of *catena*-poly{[bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II)]-μ-(4-ethyl-2,2,5,5-tetramethyl-3-imidazolinyl-1-oxyl-O:N^3)[(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(I)]-μ-(4-ethyl-2,2,5,5-tetramethyl-3-imidazolinyl-1-oxyl-N^3:O)} (monoclinic, space group $P2_1/c$, a = 9.056 (3) Å, b = 19.622 (6) Å, c = 26.029 (6) Å, β = 100.48 (2)°, V = 4548 (2) Å^3, Z = 4) has shown that the compound has polymeric structure with the alternation of Cu(hfac) and $Cu(hfac)_2$ fragments bridged by EtL. The O atoms of EtL are coordinated to Cu^{2+} ions, while the imine N atoms of EtL are coordinated to Cu^+ ions. Experimental dependence $\mu_{eff}(T)$ analysis for $Cu_2(hfac)_3(RL)_2$ has shown that the exchange interaction in tricentered exchange clusters $N \cdot O - Cu^{2+} - O \cdot N$ is ferromagnetic (J = 7.5–25.5 cm^{-1}), while intercluster exchange interaction is antiferromagnetic ($J'z$ = –0.06 to –2.72 cm^{-1}).

Introduction

Transition-metal complexes with stable nitroxyl radicals are of significant interest today.[2,3] The reason for this, on the one hand, is the possibility of the design of new types of magnetic materials.[4,5] The most promising results have been achieved with nickel, cobalt, and manganese mixed-ligand compounds.[6-9] On the other hand, mixed-ligand copper complexes with nitroxides are widely used as model systems for investigations of exchange interactions between copper and nitroxide odd electrons, providing a good basis for magneto–structural correlations.[10,11] In the course of our investigation of mixed-ligand copper complexes with 3-imidazoline nitroxides it has been revealed that the reaction of bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II), $Cu(hfac)_2$, with sterically hindered 3-imidazoline hydroxylamine derivatives gives a new type of mixed-ligand complex of general composition $Cu_2(hfac)_3(RL)_2$.[12] This contribution describes the synthesis of these compounds and the results of our investigation of their structure and magnetic properties.



RLH RL

R = Me, Et, i-Pr, Ph

Experimental Section

$Cu(hfac)_2 \cdot nH_2O$ (n < 2) was sublimed prior to use. The ligands RLH and RL were prepared by conventional methods.[13] Organic solvents were distilled and dried over $CaCl_2$ before use. The syntheses of $Cu(hfac)_2(RLH)$, $Cu_2(hfac)_3(RL)_2$, and $Cu(hfac)(MeLH)_2$ were carried out in an argon atmosphere.

Synthesis of the Complexes. $Cu_2(hfac)_3(RL)_2$. A 25-mL amount (150 mL in the case of PhLH) of heptane was added to equimolar mixture of $Cu(hfac)_2$ and RLH (1.5–2.0 mmol for both). The mixture was heated with periodical shaking until the reagents dissolved. In the case of the reaction with PhLH, the solution was heated at 80 °C for an additional 1.5 h. The reaction mixture was reduced in volume by argon stream nearly to dryness. After addition of 10 mL of hexane to the residue, the solution was heated to boiling and hexane was added until complete dissolution of the precipitate. The green solution formed was cooled to 0 to –10 °C. After 2 h the mother solution was drained from the yellow crystals formed and they were washed with cold hexane by decantation. The product was recrystallized from hexane in an argon atmosphere and dried in vacuum. The other complexes were dried in the same manner. During the $Cu_2(hfac)_3(PhL)_2$ preparation the concentration of each of the starting reagents must be less than 3×10^{-3} mol/L or $[Cu(hfac)_2]_3(PhL)_2$ will precipitate simultaneously with $Cu_2(hfac)_3(PhL)_2$. $Cu_2(hfac)_3(MeL)_2$: yield 50%; mp 105–107 °C dec. (The synthesis of this compound was reported earlier.[14]) $Cu_2(hfac)_3(EtL)_2$: yield 60%; mp 135–138 °C dec. $Cu_2(hfac)_3(i\text{-}PrL)_2$: yield 70%; mp 99–102 °C dec. $Cu_2(hfac)_3(PhL)_2$: yield 50%; mp 96–98 °C dec.

$Cu(hfac)_2(MeLH)$. The mixture of $Cu(hfac)_2$ (1.2 mmol), MeLH (1.2 mmol), and 50 mL of hexane was stirred at ambient temperature until complete dissolution of the reagents. The solution was filtered, reduced to one-third of its original volume, and cooled to –10 °C. After 1–2 h, a bright green precipitate of the complex was filtered out and washed with cold hexane: yield 70%; mp 80–82 °C dec. The other $Cu(hfac)_2(RLH)$ precipitates were treated in the same manner.

$Cu(hfac)_2(i\text{-}PrLH)$. A mixture of $Cu(hfac)_2$ (0.7 mmol), i-PrLH (0.7 mmol), and 25 mL of hexane was stirred at room temperature until dissolution of the reagents. The solution was filtered and cooled to –15 °C. After 3 h, a dark green complex precipitate was filtered out: yield 70%; mp 71–73.5 °C dec.

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Table I. Crystallographic Data for $Cu_2(hfac)_3(EtL)_2$

chem formula $Cu_2C_{33}H_{37}F_{18}N_4O_8$	space group $P2_1/c$
$a = 9.056\ (3)$ Å	$T = 25$ °C
$b = 19.622\ (6)$ Å	$\lambda = 0.71073$ Å
$c = 26.029\ (6)$ Å	$\rho_{obsvd}{}^{a} = 1.58\ (1)\ g{\cdot}cm^{-3}$
$\beta = 100.48\ (2)°$	$\rho_{calcd} = 1.58\ g{\cdot}cm^{-3}$
$V = 4548\ (2)$ Å^3	$\mu = 10.49\ cm^{-1}$
$Z = 4$	$R(F_o) = 0.076$
fw 1086	$R_w(F_o) = 0.084$

[a] Measured by flotation in KI water solution.

$Cu(hfac)_2(PhLH)$. A mixture of $Cu(hfac)_2$ (1 mmol), PhLH (1 mmol), and 100 mL of hexane was stirred at room temperature for 1 h. Then the reaction mixture was warmed for dissolution of the precipitate formed, and the solution was filtered. The filtrate was reduced in volume nearly to dryness, and a light green precipitate was filtered out: yield 80%; mp 98–100 °C dec.

$[Cu(hfac)_2]_3(RL)_2$ (R = Et, i-Pr). (The analogous compound with PhL was reported earlier.[15]) A mixture of RL (0.6 mmol) and $Cu(hfac)_2$ (1 mmol) was dissolved in an as small as possible volume of boiling hexane; the solution was filtered and cooled to −15 °C. After 2 h (R = Et) or 12 h (R = i-Pr) a green complex precipitate was recrystallized from hexane: yield 50%. $[Cu(hfac)_2]_3(EtL)_2$: mp 108–111 °C. $[Cu(hfac)_2]_3(i\text{-}PrL)_2$: mp 123–125 °C.

$Cu(hfac)(MeLH)_2$. A mixture of $Cu(hfac)_2$ (0.2 mmol), MeLH (0.6 mmol), and 15 mL of hexane was heated to 70 °C, and then hexane was added with periodical shaking until complete dissolution of the reagents. The yellow-green solution formed was cooled to ambient temperature and reduced to one-fourth of its original volume by a stream of argon. The mother solution was drained from the red crystals precipitated, and the precipitate was washed twice with hexane by decantation: yield 50%; mp 68–71 °C dec.

All new compounds give satisfactory elemental analysis (supplementary material, Table 1). $Cu_2(hfac)_3(RL)_2$, $[Cu(hfac)_2]_3(RL)_2$, and $Cu(hfac)_2(PhLH)$ are stable under usual conditions; $Cu(hfac)_2(MeLH)$ and $Cu(hfac)_2(i\text{-}PrLH)$ do not change their properties during several months of being stored in a refrigerator.

Magnetic Susceptibility Measurements. Magnetic susceptibility was measured by Faraday's method in the 4.2–300 K temperature range. Diamagnetic corrections were taken with Pascal's constants. Cu(II) TIP was taken equal to $60 \times 10^{-6}\ cm^3\ mol^{-1}$.

X-ray Data Collection, Structure Solution, and Refinement. Single crystals of $Cu_2(hfac)_3(EtL)_2$, suitable for X-ray investigation, were obtained by slowly passing Ar over a pentane solution of the complex. The X-ray diffraction data for the crystal structure determination were measured by using a single crystal 0.40 × 0.12 × 0.65 mm in size and were collected on an automated Syntex $P2_1$ diffractometer by standard method ($\theta/2\theta$ scanning with varying speed, $v_{min} = 5°/min$, graphite monochromator, $2\theta_{max} = 45°$, absorption correction not performed). The details of the X-ray diffraction study are summarized in Table I. The structure was solved by the heavy-metal method; three independent copper atom coordinates were determined from a three-dimensional Patterson summation ($R = 0.420$), and the other atoms were determined by Fourier and difference Fourier methods. Calculations were performed by using the YANX package[16] to yield $R = 0.076$ ($R_w = 0.084$), atomic scattering factors being taken from ref 17. Atom positional parameters are listed in Table II. Mass spectrometry experiments were performed with an MX-1310 spectrometer.

Results and Discussion

Synthesis and Characterization of the Complexes. The reaction of $Cu(hfac)_2$ with RLH in an argon atmosphere at room temperature in hexane (heptane) yields $Cu(hfac)_2(RLH)$ complexes. The presence of the RLH hydroxylamine group in these compounds is confirmed by the observation of the ν(OH) band in IR spectra of the complexes at 3300 cm^{-1}. Room-temperature magnetic moments of these compounds, equal to 1.78 μ_B (R = Me), 1.75 μ_B (R = i-Pr), and 1.79 μ_B (R = Ph), are in good accord with expected ones for complexes with one electron localized at the Cu(II) ion.

Table II. Positional Parameters ($\times 10^4$) for $Cu_2(hfac)_3(EtL)_2$

atom	*x*	*y*	*z*
Cu(1)	0	0	500
Cu(2)	2607 (2)	753 (1)	2436 (1)
Cu(3)	500	0	0
O(1)	1211 (12)	737 (5)	5355 (4)
O(2)	−1551 (12)	615 (5)	4652 (4)
C(1)	942 (18)	1356 (8)	5250 (7)
C(2)	−278 (19)	1639 (8)	4905 (7)
C(3)	−1388 (16)	1236 (8)	4657 (5)
C(4)	−2679 (23)	1593 (9)	4346 (8)
F(1)	−2548 (16)	2256 (6)	4255 (6)
F(2)	−3884 (14)	1586 (6)	4590 (6)
F(3)	−3245 (16)	1310 (6)	3897 (5)
C(5)	2064 (33)	1853 (12)	5517 (13)
F(4)	3323 (23)	1784 (10)	5303 (11)
F(5)	2756 (24)	1638 (8)	5985 (7)
F(6)	1812 (19)	2449 (6)	5486 (9)
O(3)	4600 (11)	1359 (5)	2526 (4)
O(4)	1389 (12)	1676 (5)	2329 (4)
C(6)	1939 (22)	2270 (9)	2330 (7)
C(7)	3461 (26)	2466 (9)	2395 (7)
C(8)	4631 (19)	1997 (9)	2493 (6)
C(9)	819 (34)	2828 (14)	2261 (14)
C(10)	6171 (25)	2293 (12)	2542 (12)
F(7)	1259 (15)	3433 (6)	2197 (8)
F(8)	49 (19)	2836 (8)	2656 (9)
F(9)	−276 (22)	2710 (8)	1872 (8)
F(10)	7225 (17)	1941 (9)	2689 (13)
F(11)	6447 (19)	2787 (13)	2839 (10)
F(12)	6422 (18)	2618 (14)	2153 (9)
O(5)	4001 (10)	691 (4)	−473 (3)
O(6)	6218 (11)	672 (4)	431 (3)
C(11)	6203 (18)	1306 (7)	318 (6)
C(12)	5354 (18)	1643 (6)	−96 (7)
C(13)	4373 (19)	1303 (7)	−459 (6)
C(14)	7413 (31)	1701 (12)	732 (9)
C(15)	3541 (30)	1720 (10)	−914 (11)
F(13)	6955 (43)	1680 (18)	1167 (12)
F(14)	7595 (43)	2300 (16)	574 (14)
F(15)	8729 (53)	1478 (19)	767 (24)
F(16)	4117 (16)	2266 (7)	−1004 (6)
F(17)	2199 (22)	1886 (10)	−830 (9)
F(18)	3147 (33)	1394 (7)	−1338 (7)
O(7)	1374 (18)	248 (7)	4321 (5)
N(1)	2562 (14)	368 (6)	3133 (4)
N(2)	1932 (16)	161 (7)	3917 (4)
C(16)	3100 (19)	−348 (7)	3869 (5)
C(17)	3343 (18)	−127 (8)	3344 (5)
C(18)	1610 (16)	637 (8)	3485 (5)
C(19)	4462 (23)	−261 (11)	4317 (6)
C(20)	2343 (29)	−1059 (9)	3866 (8)
C(21)	4465 (19)	−538 (8)	3076 (6)
C(22)	6006 (23)	−191 (10)	3151 (10)
C(23)	−69 (17)	625 (11)	3218 (7)
C(24)	2143 (21)	1361 (8)	3641 (6)
C(24)	2143 (21)	1361 (8)	3641 (6)
O(8)	2898 (11)	−40 (6)	480 (4)
N(3)	2287 (12)	280 (5)	1750 (4)
N(4)	2533 (13)	−36 (6)	926 (4)
C(25)	1296 (16)	−468 (6)	1060 (5)
C(26)	1297 (16)	−181 (6)	1593 (5)
C(27)	3211 (16)	428 (6)	1355 (5)
C(28)	1832 (22)	−1226 (8)	1078 (7)
C(29)	−166 (17)	−342 (10)	661 (6)
C(30)	188 (18)	−423 (7)	1915 (6)
C(31)	−1201 (19)	58 (11)	1849 (7)
C(32)	4849 (16)	258 (9)	1553 (6)
C(33)	2934 (18)	1182 (7)	1169 (6)

On heating of the mixture in a stream of argon, the reaction of $Cu(hfac)_2$ with RLH is accompanied by Hhfac evolution. After solvent removal subsequent recrystallization of the product yields $Cu_2(hfac)_3(RL)_2$. $Cu_2(hfac)_3(EtL)_2$ formation takes place so fast even at room temperature that we failed to isolate any individual complex of $Cu(hfac)_2$ with EtLH. $Cu_2(hfac)_3(RL)_2$ compounds are also formed on heating of $Cu(hfac)_2(RLH)$ solutions in hexane (heptane) in argon flow. The stoichiometry of this process was

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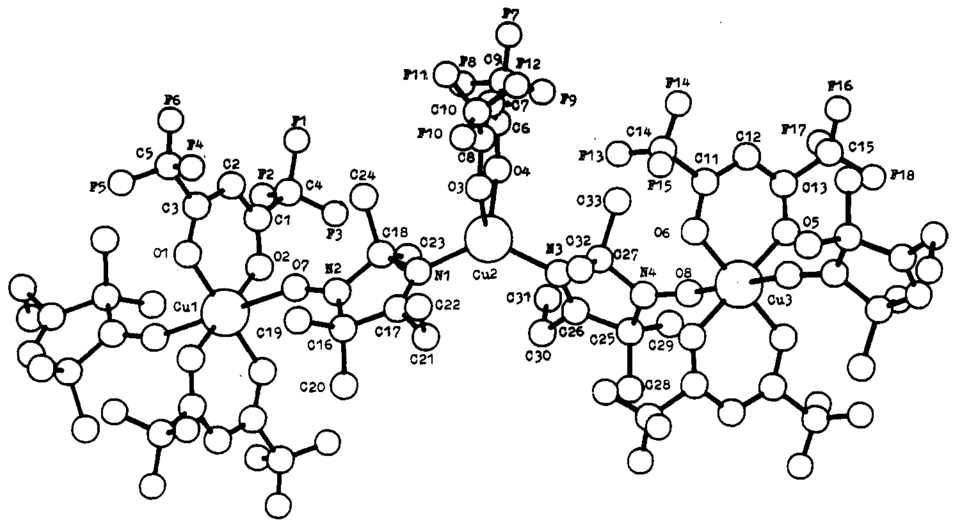


Figure 1. Fragment of the $Cu_2(hfac)_3(EtL)_2$ structure.

investigated with $Cu(hfac)_2(MeLH)$. After heating of $Cu(hfac)_2(MeLH)$ solution and the solvent removal, a yellow crystalline product was obtained, which was identified as somewhat impure $Cu_2(hfac)_3(MeL)_2$ (about 90% purity according to magnetic susceptibility data). Such a high yield provides a good basis to suppose that the reaction may be written as

$$2Cu(hfac)_2(MeLH) = Cu_2(hfac)_3(MeL)_2 + Hhfac + \text{"H"}$$

To check whether Hhfac does evolve, the argon, passing over the reaction mixture, was trapped with a water–ethanol solution of copper(II) acetate. Then the trap solution was extracted with $CHCl_3$, and the extract was evaporated to dryness. The residue contained $Cu(hfac)_2$ according to mass spectrometry data; no ions corresponding to Hhfac reduction products were registered. Thus, Hhfac does evolve and the products of a Hhfac conversion, if any, are not trapped by the described procedure. Without the taking into account of any possible transformation of Hhfac, there must be the weight lost in the course of the reaction, equal to the weight of Hhfac evolved. The measurements have shown that this difference occurs and corresponds rigorously to the value derived from the suggested equation. Thus, this equation is true for the solid products; the question if "H" is molecular hydrogen or whether some Hhfac reduction products are formed needs further investigation.

It is noteworthy that at the early stage of $Cu_2(hfac)_3(RL)_2$ preparation the formation of red crystals is often observed, these crystals disappearing in the course of the reaction. When the reaction of $Cu(hfac)_2$ is carried out with an excess of MeLH, the crystals were successfully isolated. This material is diamagnetic, has an intensive ν(OH) band in the IR spectrum at 3300 cm^{-1}, and according to the elemental analysis has the composition $Cu(hfac)(MeLH)_2$. The IR spectrum of the red crystals forming during $Cu_2(hfac)_3(MeL)_2$ synthesis appeared to be identical with that of $Cu(hfac)(MeLH)_2$. One can assume that the species of $Cu(hfac)L_2$ stoichiometry (L = RLH, RL) are the intermediate products in the process of $Cu_2(hfac)_3(RL)_2$ formation (see also the description of the structure of $Cu_2(hfac)_3(EtL)_2$).

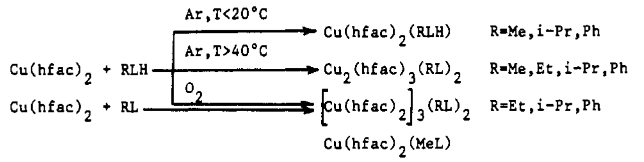
Prolonged heating ($T = 60$ °C) of $Cu(hfac)_2(RLH)$ (R = Me, i-Pr, Ph) in inert atmosphere or under vacuum is accompanied by the transformation $Cu(hfac)_2(RLH) \rightarrow Cu_2(hfac)_3(RL)_2$. Solid-phase transformation of $Cu(hfac)_2(MeLH)$ to $Cu_2(hfac)_3(MeL)_2$ proceeds over a period of months at room temperature in air atmosphere. $Cu_2(hfac)_3(RL)_2$ forming on vacuum heating of $Cu(hfac)_2(RLH)$ is volatile under experimental conditions for R = Me and i-Pr, while $Cu_2(hfac)_3(PhL)_2$ under the same conditions decomposes to form volatile $[Cu(hfac)_2]_3(PhL)_2$.

The reaction of $Cu(hfac)_2$ with RLH in hexane in air atmosphere is accompanied by catalytic oxidation of RLH into RL by oxygen,[14] and $[Cu(hfac)_2]_3(RL)_2$ (R = Et, i-Pr, Ph) and $Cu(hfac)_2(MeL)$ complexes are precipitated. The same compounds are formed on direct reaction of $Cu(hfac)_2$ with RL.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $Cu_2(hfac)_3(EtL)_2$

	Bond Lenghts		
Cu(1)–O(1)	1.944 (9)	Cu(1)–O(2)	1.946 (9)
Cu(1)–O(7)	2.389 (15)	Cu(2)–O(3)	2.138 (10)
Cu(2)–O(4)	2.113 (10)	Cu(2)–N(1)	1.973 (11)
Cu(2)–N(3)	1.986 (10)	Cu(3)–O(5)	1.941 (8)
Cu(3)–O(6)	1.939 (8)	Cu(3)–O(8)	2.461 (11)
N(2)–O(7)	1.26 (2)	N(4)–O(8)	1.26 (2)
	Bond Angles		
O(1)–Cu(1)–O(2)	93.3 (4)	O(1)–Cu(1)–O(7)	82.8 (5)
O(3)–Cu(2)–O(4)	87.0 (4)	O(3)–Cu(2)–N(1)	105.7 (5)
O(3)–Cu(2)–N(3)	109.9 (4)	O(4)–Cu(2)–N(1)	110.6 (5)
O(4)–Cu(2)–N(3)	107.1 (4)	N(1)–Cu(2)–N(3)	128.6 (5)
O(5)–Cu(3)–O(6)	92.4 (3)	O(5)–Cu(3)–O(8)	91.7 (4)
Cu(1)–O(7)–N(2)	159 (1)	Cu(3)–O(8)–N(4)	145 (1)

The following scheme summarizes qualitatively the synthetic conditions of the complexes (hexane or heptane is the solvent):



$Cu_2(hfac)_3(EtL)_2$ Crystal Structure. A fragment of the $Cu_2(hfac)_3(EtL)_2$ structure is shown in Figure 1. The independent structural unit consists of three crystallographically different Cu atoms, two of which—Cu(1) and Cu(3)—lie on different inversion centers ($^1/_2$, 0, 0 and 0, 0, $^1/_2$) and one—Cu(2)—occupies a general position, so that the structural formula of the compound may be depicted as following: $[Cu(1)(hfac)_2\text{-}\mu_2\text{-}EtL\text{-}Cu(2)(hfac)\text{-}\mu_2\text{-}EtL\text{-}Cu(3)(hfac)_2\text{-}\mu_2\text{-}EtL\text{-}Cu(2)(hfac)\text{-}\mu_2\text{-}EtL]_\infty$. This is a repeating fragment of a chain running along the (101) face. The Cu(2) atom is surrounded by two O atoms of the hfac anion and imine N atoms of the imidazoline heterocycles. The coordination polyhedron of Cu(2) (Table III) is a distorted tetrahedron (mean Cu–O = 2.12 (1) Å, Cu–N = 1.96 (2) Å, chelate angle O(3)–Cu(2)–O(4) = 86.5 (5)°, N(1)–Cu(2)–N(3) = 128.7 (7)°; the other Cu(2)-involving angles fall within 107.3 (5)–110.6 (6)°.[18] The structural unit EtL–Cu(2)(hfac)–EtL bridges two centrosymmetrical fragments $Cu(1)(hfac)_2$ and $Cu(3)(hfac)_2$ through

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(18) The existance of the $Cu(hfac)(EtL)_2$ fragment in the structure of $Cu_2(hfac)_3(EtL)_2$ is good evidence for the formation of $Cu(hfac)L_2$ (L = RL, RLH) intermediates on the synthesis of $Cu_2(hfac)_3(RL)_2$, as it was supposed above. It is possible that $Cu(hfac)(RLH)_2$, which probably has a structure similar to that of the $Cu(hfac)(EtL)_2$ fragment, is oxidized to $Cu(hfac)(RL)_2$ in the course of the reaction and reacts with $Cu(hfac)_2$ to form $Cu_2(hfac)_3(RL)_2$.

Table IV. Optimal Parameters of $\mu_{eff}(T)$ Experimental Dependence Fitting for $Cu_2(hfac)_3(RL)_2$[a]

R	g_{Cu}	J, cm^{-1}	$J'z$, cm^{-1}
Me	2.14	9.0	−0.67
i-Pr	2.10	15.6	−0.06
Ph	2.13	7.5	−0.16
Et	2.01	25.5	−2.72

[a] Absolute error for g_{Cu} and J is equal to 1%, and that for $J'z$, 10%.

the O atoms of the N∸O fragments. Thus, the coordination polyhedra of Cu(1) and Cu(3) are the elongated octahedra formed by four atoms of two hfac ligands in an equatorial plane (mean Cu–O = 1.95 (2) and 1.94 (2) Å) and by two O atoms of the N∸O fragments of two EtL ligands in axial positions (Cu–O = 2.38 (2) and 2.46 (1) Å for Cu(1) and Cu(3), respectfully. Bond lengths and bond angles in the hfac fragments (mean C–O = 1.25 (3) Å, C–C = 1.40 (4) Å, O–C–C = 129 (2)°, C–C–C = 121 (2)° are typical for hfac$^-$.[19] The interatomic distances and bond angles in the imidazoline heterocycles also are in accord with the data available.[13] The imidazoline heterocycle is planar with atom deviations from the root-mean-square plane less than 0.03 Å; N(2) and N(4) deviate from the heterocycle plane by −0.02 and −0.004 Å. The O atoms of the N∸O fragments deviate from the planes of the heterocycles by 0.058 and −0.111 Å (O(7) and O(8), respectfully); the N–O bond lengths are equal to 1.26 (2) Å.

These results show that in the solid complex the imidazoline ligand is in the radical form.[13,20] The total data on the coordination surroundings of the Cu(1), Cu(3), and Cu(2) atoms allow different oxidation states to be supposed for the copper ions: +1 for Cu(2) and +2 for Cu(1) and Cu(3). Examples of polymeric complexes where in the solid state a Cu^+ and Cu^{2+} alternation is observed are known,[21] but among mixed-ligand complexes with nitroxides such a type of compound is found for the first time.

Magnetic Properties. The results of the X-ray diffraction study show that the shortest contacts between paramagnetic centers are the ones between Cu^{2+} ions and the N∸O groups of coordinated EtL. These contacts are about 2.4 Å, while all other $Cu^{2+}\cdots Cu^{2+}$ and $Cu^{2+}\cdots$O∸N contacts are more than 7 Å. For this reason the model of tricentered heterospin exchange clusters[22] was used for the fitting of the experimental temperature dependence of the $Cu_2(hfac)_3(EtL)_2$ magnetic susceptibility. In this model an isotropic Hamiltonian is used for the calculation of the energy levels of the cluster in an external magnetic field:

$$\hat{H} = -2J\hat{s}\hat{s}' - \beta(g\hat{S}_z + g'\hat{S}_z)H - 2J'z\hat{S}_z\langle\hat{S}_z\rangle$$

where $\hat{s}$ is the Cu^{2+} spin operator, $\hat{s} = \hat{s}_1 + \hat{s}_2$ is the operator of the total spin of two radicals, g and g' are the g factors of Cu^{2+} and the nitroxide, z is the number of the nearest-neighbour molecules, β is the Bohr magneton, $\hat{S} = \hat{s} + \hat{s}'$ is the operator of the cluster total spin, and $\langle\hat{S}_z\rangle$ is its averaged projection onto the z axis. Magnetic susceptibility per cluster is[11,22]

$$\chi = \chi_{\langle\hat{\mu}_z\rangle,H} + \chi_{\langle\hat{\mu}_z\rangle,\langle\hat{S}_z\rangle}\chi_{\langle\hat{S}_z\rangle,H}/(1 - \chi_{\langle\hat{S}_z\rangle,\langle\hat{S}_z\rangle})$$

The augend is the susceptibility of the isolated exchange cluster N∸O$\cdots Cu^{2+}\cdots$O∸N, equal to

$$\chi_{\langle\hat{\mu}_z\rangle,H} = \frac{\beta^2}{4kT}\left[10\left(\frac{g+2g'}{3}\right)^2\exp(J/kT) + g^2 + \left(\frac{4g'-g}{3}\right)^2\exp(-2J/kT) + \frac{16kT}{27J}(g-g')^2(\exp(J/kT) - \exp(-2J/kT))\right]\Big/(2\exp(J/kT) + 1 + \exp(-2J/kT))$$

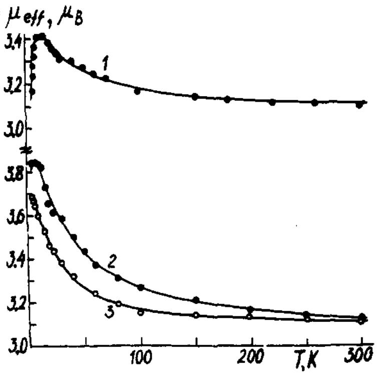

Figure 2. Experimental (heavy dots, circles) and theoretical (curves) μ_{eff} versus T dependences for $Cu_2(hfac)_3(RL)_2$, R = Me (1), i-Pr (2), and Ph (3).

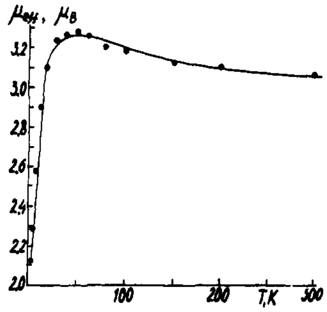

Figure 3. Experimental (heavy dots) and theoretical (curve) μ_{eff} versus T dependences for $Cu_2(hfac)_3(EtL)_2$.

The addend accounts for the intercluster interaction, and corresponding generalized susceptibilities are[11,22]

$$\chi_{\langle\hat{\mu}_z\rangle,\langle\hat{S}_z\rangle} = \frac{\beta(2J'z)}{4kT}\left(10\frac{g+2g'}{3}\exp(J/kT) + g + \frac{4g'-g}{3}\times\exp(-2J/kT)\right)\Big/(2\exp(J/kT) + 1 + \exp(-2J/kT))$$

$$\chi_{\langle\hat{S}_z\rangle,H} = \frac{1}{2J'z}\chi_{\langle\hat{\mu}_z\rangle,\langle\hat{S}_z\rangle}$$

$$\chi_{\langle\hat{S}_z\rangle,\langle\hat{S}_z\rangle} = \frac{2J'z}{4kT}(10\exp(J/kT) + 1 + \exp(-2J/kT))/(2\exp(J/kT) + 1 + \exp(-2J/kT))$$

The optimal J, $J'z$, and g_{Cu} values were obtained by minimization of the $\sum_i[\mu_{eff}^{calcd}(T_i) - \mu_{eff}^{measd}(T_i)]^2$ sum.

This model appeared to fit well the experimental $\mu_{eff}(T)$ dependences for all four $Cu_2(hfac)_3(RL)_2$ compounds. This is the basis to suppose the presence of similar N∸O$\cdots Cu^{2+}\cdots$O∸N exchange clusters in solid $Cu_2(hfac)_3(RL)_2$ and, therefore, some kind of structural similarity of these compounds, although the powder X-ray diffraction patterns of $Cu_2(hfac)_3(RL)_2$ show that all these materials are not isomorphous.

It is noteworthy that the fitting for $Cu_2(hfac)_3(EtL)_2$ is good inspite of the presence of two different exchange clusters, centered on Cu(1) and Cu(3) and differing in the orientation of the nitroxides to the $Cu(hfac)_2$ fragments. This means that J values in these two types of clusters do not differ much.

The fitting results (Table IV and Figures 2 and 3) show that the intracluster exchange in all $Cu_2(hfac)_3(RL)_2$ compounds is ferromagnetic and has approximately the same order of magnitude, while the intercluster exchange is antiferromagnetic and ranges from −0.06 cm^{-1} in $Cu_2(hfac)_3(i\text{-}PrL)_2$ to −2.72 cm^{-1} in $Cu_2(hfac)_3(EtL)_2$. The latter value is rather high and can be explained under assumption that there is an effective exchange pathway along the chain. It is rather probable because 3-imidazoline heterocycles form an effective exchange pathway on coordination by the imine N atom to metal ions.[11] Discussing the exchange parameters obtained, one should keep in mind that the physical

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sense of J and $J'z$ becomes indefinite upon the increase of the $J'z/J$ ratio because the equation used for the fitting is developed under assumption that $J \gg J'z$. It is especially important in the case of $Cu_2(hfac)_3(EtL)_2$, where this ratio exceeds 0.1.

Conclusions

The reaction of $Cu(hfac)_2$ with sterically hindered 3-imidazoline hydroxylamines in inert atmosphere yields new types of mixed-ligand complexes with nitroxides of the composition $Cu_2(hfac)_3(RL)_2$, which are not formed on the direct reaction of $Cu(hfac)_2$ with RL. The polymeric structure of $Cu_2(hfac)_3(EtL)_2$ in solid phase has been determined, this structure being characterized by the Cu^+ and Cu^{2+} ion alternation in the chain manner and also by the coordination of two N∸O fragments to Cu^{2+} ions. In N∸O–Cu^{2+}–O∸N exchange clusters existing in solid $Cu_2(hfac)_3(RL)_2$, ferromagnetic exchange interactions are realized.

In the course of the investigation $[Cu(hfac)_2]_3(EtL)_2$ and $[Cu(hfac)_2]_3(i\text{-}PrL)_2$ were obtained as well, which are representatives of the recently discovered type of mixed-ligand complex with nitroxides.[14,23] The structure and magnetic properties of these compounds are the subject of further investigation and will be reported later.

Acknowledgment. We thank Dr. P. P. Semyannikov for recording the mass spectra.

Registry No. $Cu_2(hfac)_2(PhL)_2$, 131729-29-8; $Cu(hfac)_2$, 14781-45-4; $Cu_2(hfac)_3(EtL)_2$, 131729-30-1; $Cu_2(hfac)_3(i\text{-}PrL)_2$, 131729-31-2; $Cu(hfac)_2(MeLH)$, 120660-34-6; $Cu(hfac)_2(i\text{-}PrLH)$, 131758-59-3; $Cu(hfac)_2(PhLH)$, 131729-32-3; $[Cu(hfac)_2]_3(EtL)_2$, 126913-32-4; $[Cu(hfac)_2]_3(i\text{-}PrL)_2$, 126942-92-5; $Cu(hfac)(MeLH)_2$, 131758-60-6; $Cu_2(hfac)_3(MeL)_2$, 113677-67-1.

Supplementary Material Available: Tables 1–4, listing C, H, N, and Cu analytical data, bond lengths and angles, anisotropic thermal parameter coefficients, and root-mean-square planes (8 pages); Table 5, listing structure factors (41 pages). Ordering information is given on any current masthead page.

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Disubstituted Tungstosilicates. 2. γ- and β-Isomers of $[SiV_2W_{10}O_{40}]^{6-}$: Syntheses and Structure Determinations by ^{183}W, ^{51}V, and ^{29}Si NMR Spectroscopy

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Addition of vanadium to the divacant γ-$[HSiW_{10}O_{36}]^{7-}$ anion gives quantitatively the γ-decatungsto-1,2-divanadosilicate $[SiV_2W_{10}O_{40}]^{6-}$ parent complex. This complex is stable in nonaqueous solution but isomerizes in water. The isomerization was followed by polarography, and depending on the experimental conditions, three geometrical isomers of $[SiV_2W_{10}O_{40}]^{6-}$ were prepared (as pure compounds for two of them). These isomers are characterized by their IR spectra and their ^{183}W, ^{51}V, and ^{29}Si NMR spectra. All have the β-structure with the two vanadium atoms in positions (8,12), (3,12), and (3,8), respectively.

Introduction

The synthesis of polyoxotungstates or molybdates of the Keggin structure in which W or Mo atoms are partially replaced by atoms such as Ti^{IV}, Nb^V, or V^V has attracted increasing attention because of (i) the use of these compounds in oxidation catalysis[1] and (ii) the use of the compounds to link organometallic moieties on the surface oxygen atoms.[2] Important changes of the solution or solid-state properties of these compounds, such as the redox behavior and the strength of the acid, can be expected when the number (usually 1, 2, or 3) and the vicinity of these addenda atoms in the Keggin structure are modified.

A better knowledge of the factors that influence the relative positions of the addenda atoms is required in order to rationalize stereospecific methods for synthesizing such compounds. A possible approach of this problem consists of the preparation of a pure and well-characterized derivative and the study of its isomerization under various conditions (solvent, acidity, temperature, etc.).

This paper deals with the preparation of the divanadium derivative of the γ-12-tungstosilicate obtained from the divacant γ-$[HSiW_{10}O_{36}]^{7-}$ polyanion and its isomerization into three different geometric isomers according to the experimental conditions. Let us be reminded that β- and γ-isomers of the Keggin anion (α-isomer) are derived from the latter by rotation of one or two groups of three edge-sharing WO_6 octahedra, respectively (Figure 1).[3] All the divanadium compounds have been characterized by polarography, ^{29}Si, ^{51}V, and ^{183}W NMR spectroscopy in solution, and infrared spectroscopy in the solid state. A preliminary report of this work has been presented.[4]

Experimental Section

Preparation of Compounds. **Ia, Cs_4H_2-γ(1,2)-$[SiV_2W_{10}O_{40}]\cdot 4H_2O$.**[5] This compound was prepared by using the potassium salt of the γ-10-tungstosilicate obtained as previously described.[6] This salt (10 g, 3.33 × 10^{-3} mol) is dissolved in 1 M HCl (35 mL), 0.5 M sodium metavanadate ($NaVO_3$) (13.5 mL, 6.75 × 10^{-3} mol) is added, and the mixture is gently stirred a few minutes. A small precipitate is filtered off (solution A). Cesium chloride (5 g) is added to the clear solution. The solid is separated by filtration on a fine frit. This crude product is dissolved in 0.5 M HCl (400 mL), and small quantities of insoluble material are

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