New Binuclear Metal Chelate Complexes of Copper(II) Chloride and Acetate with Bis(hetarylhydrazones) Obtained by Condensation of 2,6-Diformyl-4-R-Phenols with 2-Hydrazinoquinoline

V. V. Lukov, I. E. Gevorkyan, E. V. Dontsova, V. A. Kogan, L. D. Popov, and V. V. Dykov

Rostov State University, ul. Zorge 7, Rostov-on-Don, 344104 Russia Received February 19, 2004

Abstract—Bis(hetarylhydrazones) synthesized for the first time were used as ligands to obtain a number of binuclear copper(II) chelates from copper acetate and chloride. The physicochemical and, first of all, magnetic properties of the resulting complexes were studied. Analysis of the calculated exchange parameters showed that they differ significantly from those obtained previously for analogous binuclear metal chelates containing the identical set of donor atoms. Possible reasons for the differences in the magnetochemical behavior of the binuclear complexes obtained are discussed.

In continuation of the study of the complexing ability of bis(hetarylhydrazones) of 2,6-diformyl-4-R-phenols [1-4], we synthesized a number of new ligands I and their complexes with copper(II) acetate and chloride

(II and III, respectively). The compositions and structures of the compounds obtained were confirmed by elemental analysis (Table 1), IR spectroscopy, magnetochemistry, and conductometry.



The IR spectra of complexes II contain no v(OH) (phenol) or v(N-H) absorption bands for the hydrazine

fragment of the quinoline residue, while the IR spectra of ligands I show the respective bands at 3350 and

Type of the complex	R	Empirical formula	Content (found/calculated), %								
			С	Н	Ν	Cu					
II	CH ₃	$C_{28}H_{22}N_6O_2Cu_2$	55.5/55.8	3.3/3.7	13.6/13.9	21.5/21.3					
Π	C_2H_5	$C_{29}H_{24}N_6O_2Cu_2$	56.9/56.5	3.5/3.9	13.3/13.6	20.4/20.6					
II	$C(CH_3)_3$	$C_{30}H_{28}N_6O_2Cu_2$	57.3/57.0	4.6/4.4	13.9/13.3	20.3/20.1					
II	CH ₂ Ph	$C_{34}H_{26}N_6O_2Cu_2$	60.0/60.2	3.7/3.8	12.0/12.4	18.5/18.7					
III	CH ₃	$\mathrm{C}_{27}\mathrm{H}_{21}\mathrm{N}_{6}\mathrm{OCl}_{3}\mathrm{Cu}_{2}$	47.5/47.7	3.4/3.1	12.0/12.4	18.6/18.8					
III	C_2H_5	$\mathrm{C}_{28}\mathrm{H}_{23}\mathrm{N}_{6}\mathrm{OCl}_{3}\mathrm{Cu}_{2}$	48.3/48.5	3.5/3.3	12.3/12.1	18.0/18.3					
III	$C(CH_3)_3$	$\mathrm{C}_{29}\mathrm{H}_{27}\mathrm{N}_{6}\mathrm{OCl}_{3}\mathrm{Cu}_{2}$	49.4/49.0	3.3/3.8	11.6/11.8	18.4/18.0					
III	CH ₂ Ph	$\mathrm{C}_{33}\mathrm{H}_{25}\mathrm{N}_{6}\mathrm{OCl}_{3}\mathrm{Cu}_{2}$	52.0/52.4	3.1/3.3	11.6/11.1	18.9/18.6					

Table 1. Elemental analysis data for complexes II and III

3190 cm⁻¹ [5]. The v(N–H) absorption band is retained in the IR spectra of complexes **III**.

The molar conductivities λ of complexes III in DMF (Table 2) suggest their insignificant dissociation with release of one Cl atom [6]. Apparently, in binuclear complexes III based on 2-hydrazinoquinoline, in contrast to analogous systems containing 2-hydrazinobenzoimidazole [3, 4], both Cl atoms are axially coordinated by copper atoms. The latter circumstance seems to account for some differences in magnetochemical behavior between these complexes and those of copper(II) chloride with ligands I, which were described in [2, 4].

According to the temperature dependence of the magnetic susceptibility of complexes **III**, complexes with $R = CH_3$ and C_2H_5 are trivial paramagnetics, while complexes with $R = CH_2Ph$ and $C(CH_3)_3$ are characterized by antiferromagnetic exchange interactions (2J = -61.6 and -145.2 cm⁻¹, respectively) (Table 3). The antiferromagnetism of complexes **II** is more pronounced than that of complexes **III** (Table 3); this is not surprising because the structural distortion in the

exchanged fragment $Cu \bigvee_{O}^{O} Cu$ is smaller than in

However, it should be noted that the exchange parameters 2J of binuclear metal chelates **II** (Table 3) are, on average, half the absolute values obtained earlier for binuclear copper(II) acetate complexes with 2hydrazinobenzoimidazole [1]. Apparently, their reduced antiferromagnetism is mainly due to more considerable steric hindrances in structure **II** than in benzoimidazole derivatives because of repulsion of the fused aromatic rings of the quinoline fragment. The latter circumstance should make the exchanged fragment $Cu \bigvee_{O}^{O} Cu$ less planar, with the respective reduction of

the contribution from the antiferromagnetic constituent to the resultant exchange interaction [8, 9]. Obviously, replacement of one of the bridging O atoms by a Cl atom and, as noted above, axial coordination of the two other Cl atoms will further distort the exchanged fragment with the corresponding weakening of antiferromagnetism, which is really observed (Table 3).

The totality of our experimental data allows one to state that for the complexes under discussion (obtained from both copper(II) acetate and copper(II) chloride), the geometrical factors determining the structural features of the exchanged fragments have a decisive effect on the character and strength of exchange interactions since there is no noticeable correlation between 2*J* values and the electronic nature of a substituent in the phenol fragment of ligands **I**. Previously, a satisfactory correlation of this type was obtained only for copper(II) complexes with bis(acylhydrazone) derivatives of 2,6-diformyl-4-R-phenols [10, 11].

EXPERIMENTAL

Ligands I were synthesized by refluxing a corresponding 2,6-diformyl-4-R-phenol (0.001 mol) with 2-hydrazinoquinoline (0.002 mol) in 10 ml of ethanol

Table 2. Molar conductivities of complexes III in DMF

R	λ , cm ² Ω^{-1} mol ⁻¹
CH ₃	4.7
C_2H_5	10.8
C(CH ₃) ₃	12.0
CH ₂ Ph	12.7

No. 2

2005

		Comple	x II : R =	CH ₃ , 2 <i>J</i>	= -334 0	cm^{-1}	, <i>g</i> =	2.13,	, <i>f</i> * =	= 0.07,	, <i>r</i> =	= 1.259	%			
Т, К	292		251		225			158				110			83	
$\mu_{eff}^{exp}**, \mu_B$	1.34		1.22		1.16		0.95				0.79		0.70			
μ_{eff}^{calc} , μ_B	1.34		1.24		1.16		0.88			0.63			0.53			
Complex II: $R = C_2H_5$, $2J = -330 \text{ cm}^{-1}$, $g = 2.16$, $f = 0.07$, $r = 0.5\%$																
Т, К	297	275	252	250	240	2	15	17	8 157			138	11	18	102	86
μ_{eff}^{exp},μ_B	1.37	1.33	1.27	1.26	1.23	1.	15	1.0	0	0.90		0.79	0.	69	0.61	0.55
μ_{eff}^{calc} , μ_B	1.37	1.33	1.27	1.26	1.23	1.	15	1.0	0	0.90		0.80	0.0	68	0.60	0.54
Complex II: $R = C(CH_3)_3$, $2J = -309.2 \text{ cm}^{-1}$, $g = 2.04$, $f = 0.06$, $r = 0.46\%$																
Т, К	298	273	250	240	21	5	18	30	1	161		35	120		102	86
μ_{eff}^{exp},μ_B	1.33	1.28	1.22	1.20	1.1	2	0.9	99	0.	.90		.77	0.67	,	0.58	0.50
μ_{eff}^{calc} , μ_B	1.33	1.28	1.23	1.20	1.1	2	0.9	99	9 0.90		0	.77	0.67	,	0.58	0.50
Complex II: $R = CH_2Ph$, $2J = -278.8 \text{ cm}^{-1}$, $g = 2.20$, $f = 0.1$, $r = 0.45\%$																
Т, К	293	274	251	235	207	19	92	166		145	126		11	10	88	82
μ_{eff}^{exp} , μ_B	1.50	1.47	1.42	1.38	1.30	1.	24	1.1	4	1.03		0.92	0.3	83	0.71	0.68
μ_{eff}^{calc} , μ_B	1.50	1.47	1.42	1.38	1.30	1.	24	1.1	4	1.03		0.92	0.3	83	0.71	0.68
		·		Co	omplex I	II: R	R = C	H ₃								·
Т, К	290 243 185 126 99										83					
μ_{eff}^{exp},μ_B	1.79		1.7	1.77		1.79			1.73			1.73			1.78	
				Co	mplex I	II: R	$= C_2$	$_{2}H_{5}$								
<i>Т</i> , К	294	274	263	227	19	5	179		148		1	23	103		91	82
μ_{eff}^{exp},μ_B	1.81	1.81	1.80	1.79	1.7	9	1.78		1.	1.77		.77	1.77	,	1.77	1.76
Complex III: $R = C(CH_3)_3$, $2J = -145.2 \text{ cm}^{-1}$, $g = 2.20$, $r = 0.38\%$																
<i>Т</i> , К	294	263	246	205	18	8 1		73	150		1	23	110		94	82
μ_{eff}^{exp},μ_B	1.70	1.67	1.65	1.59	1.5	55	1.5	51	1.44		1	.31	1.23		1.10	0.97
μ_{eff}^{calc} , μ_B	1.70	1.67	1.65	1.59	1.5	55	1.5	51	1	1.44		.31	1.23		1.10	0.97
Complex III: R = CH ₂ Ph, $2J = -61,6 \text{ cm}^{-1}, g = 2.12, r = 0.27\%$																
Т, К	295	272	254	231	20	9	18	30	150		1	25	99		91	82
μ_{eff}^{exp},μ_B	1.76	1.76	1.75	1.74	1.7	'3	1.7	71	1	.67 1.64		.64 1.58			1.55	1.51
μ_{eff}^{calc} , μ_B	1.76	1.75	1.75	1.74	1.7	'3	1.7	71	1.	.68 1		.64	1.58		1.55	1.51

Table 3. Magnetic properties of binuclear copper complexes II and III

* *f* is the fraction of the paramagnetic admixture in the binuclear sample. **All the μ_{eff} values were calculated per copper atom in the binuclear molecule.

for 3 h. The resulting precipitate was filtered off, washed with hot ethanol, and dried in air.

Complexes II and III were synthesized as follows. A suspension of ligand I (0.001 mol) in methanol was mixed with a hot solution of copper(II) chloride or acetate (0.002 mol) in methanol. The mixture was refluxed for 6 h and then cooled. The resulting precipitate was filtered off, washed with hot methanol, and dried in air. Elemental analysis data for all compounds obtained are given in Table 1.

IR spectra were recorded on a UR20 instrument in the 700–4000 cm⁻¹ range (Nujol).

Magnetic susceptibility was determined by the relative Faraday method in the temperature range from 78 to 300 K on a setup made at the Department of Physical and Colloid Chemistry of the Rostov State University. The setup was calibrated against Hg[Co(CNS)₄]. Exchange parameters were calculated from the temperature dependence of the magnetic susceptibility in terms of the dimeric HDVV model using the modified Bleany–Bauers equation [7] with a program minimizing the mean-square error *r*:

$$r = \left(\frac{1}{n}\sum_{1}^{n} (\chi_{i} - \chi_{i}^{0})^{2} \chi_{i}^{-2}\right)^{\frac{1}{2}},$$

where χ_i and χ_i^0 are the experimental and theoretical molar magnetic susceptibilities at the *i*th point, respectively; *n* is the number of points.

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