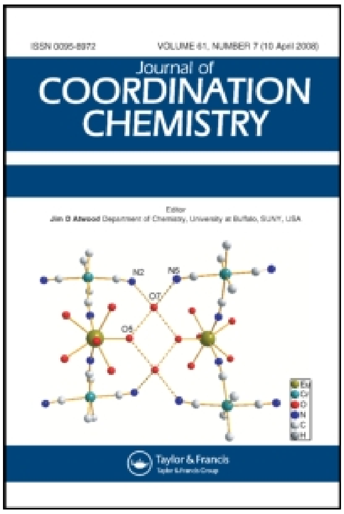

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The novel azomethine ligands for binuclear copper(II) complexes with ferro- and antiferromagnetic properties

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The novel azomethine ligands for binuclear copper(II) complexes with ferro- and antiferromagnetic properties

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A series of novel binuclear ferro- and antiferromagnetic Cu(2+) chelates of structurally broadly varied Schiff bases (derived from *o*-tosylamino(hydroxyl)benzaldehydes and monoalkylated *o*-phenylenediamine, *o*-aminophenol, *o*-aminothiophenol, 1,2-diaminobenzimidazole, 1-aminobenzimidazoline-2-thione) and *β*-diketimines (derived from 2,6-di-i-Pr-aniline) has been prepared. The tautomerism of the ligands and structureof their copper complexes have been studied with the use of IR, ^{1}H NMR EPR and EXAFS spectroscopy. Molecular and crystal structure of a *β*-diketimine copper dimer has been determined by X-ray crystallography. The magnetic measurements (2–300 K) performed for all the complexes showed that the ferro- and antiferromagnetic character of the exchange interaction depends both on the structure of the coordination site (origin of the ligating centers) and the structure of the ligands (in particular, on the type of the cycle annelated to the bridging fragment). Whereas S-binding metal chelates **13** (X = NTs, Y = S, R = H) are diamagnetic, the complexes **15** with annelated azole moieties are ferromagnetic.

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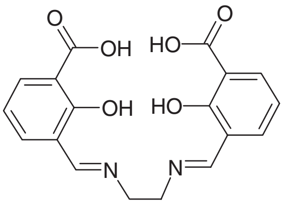
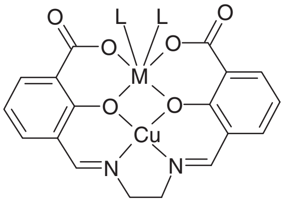
Keywords: Copper; Schiff bases; Binuclear complexes; Ferromagnetic and antiferromagnetic interaction

1. Introduction

Schiff-base chelating ligands are known to form a large family of metal complexes with some of them having been found to behave as molecular magnets [1–8]. O. Kahn synthesized a model azomethine ligand **1** which was used as a basic unit of a variety of the heteronuclear complexes **2** with ferro- and antiferromagnetic interactions [9–11].



1

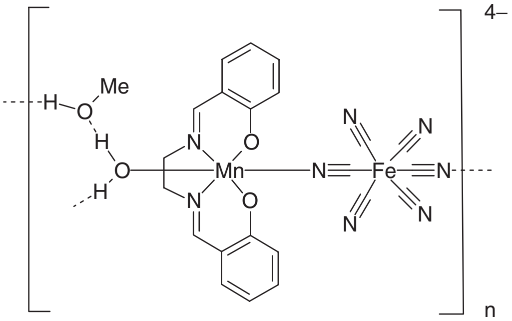


2

$M=Cr, Fe, VO; L=H_2O, MeOH$

Cu-VO	$J=+118\ cm^{-1}$
Cu-Cr	$J=+115\ cm^{-1}$
Cu-Fe	$J=-105\ cm^{-1}$

Kahn's model was later succesfully employed in the synthesis of diverse analogues of **2** [12–18]. Another approach to ferromagnetic heteronuclear azomethine chelates **3** [2, 19] and **4** [20] is based on the use of Schiff-base complexes as "metal-ligands" in their reactions with hexaferricyanide salts or with lanthanoid acetylacetonates.



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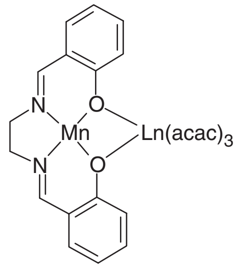
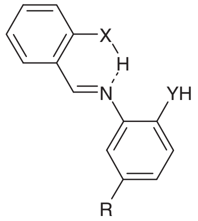


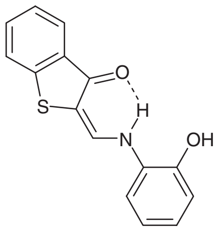
4

The strategy suggested in the present work involves application of dibasic tridentate ligands whose coordination ability (the number of donor centers) is insufficient for full saturation of the coordination requirements of copper(2+). As in the case of dibasic bidentate ligands with sterically hindered donor centers this strategy ensures formation of binuclear complexes and gives rise to dimerization of the CuL moieties via anionic bridges.

We have synthesized a series of ligands **5–8** with various donor centers X, substituents at the nitrogen atom of the C=N group (including electron donor and bulky groups) and aldehyde (ketone) fragments.



5: X = NTs, Y = NMe, R = NO_2 (a);
X = NTs, Y = NEt, R = NO_2 (b);
X = NTs, Y = NBu-*n*, R = NO_2 (c);
X = NTs, Y = O, R = H (d)
X = O, Y = NEt, R = NO_2 (e)



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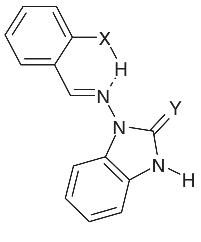
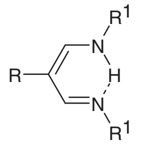


7: X = O, Y = S (a);
X = NTs, Y = S (b);
X = NTs, Y = NH (c);
X = O, Y = NH (d)



8: R = Ph (a);
R = NO2 (b);
R^1 = 2,6-(*i*-Pr)C_6H_3

Copper (2+) was chosen as the metal center due to growing interest in magnetic properties of its complexes [1–3, 8–11, 21–33].

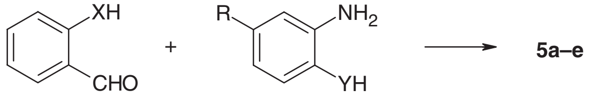
2. Experimental

2.1. *Preparation of ligands*

The Schiff bases **5a–c**, **e** were prepared by coupling 2-tosylaminobenzaldehyde (**9**: X = NTs) [34, 35] or 2-hydroxybenzaldehyde (**9**: X = OH) with 2-alkylamino-5-nitroaniline **10** [36] in toluene (Scheme 1).

2-((E)-{[2-(ethylamino)-5-nitrophenyl]imino}methyl)-N-*p*-toluenesulfoaniline (5b). To the solution of 2.75 g (0.01 mol) of **9** (X = NTs) in 30 mL of ethanol a solution of 1.81 g (0.01 mol) of 2-ethylamino-5-nitroaniline in 100 mL of the same solvent was added and the resultant mixture was refluxed under argon for 3 h. Solid precipitated after cooling to the room temperature, was filtered off, washed with cool ethanol and recrystallized from the same solvent giving orange needles with m.p. 141–142°C. Yield 84%.

Imines **5d** and **6** (Scheme 2) were synthesized by reaction of **9** (X = NTs) or 2-formyl-3-hydroxybenzo[b]thiophene (**11**) [37] with *o*-aminophenol **10** in ethanol.



(1)

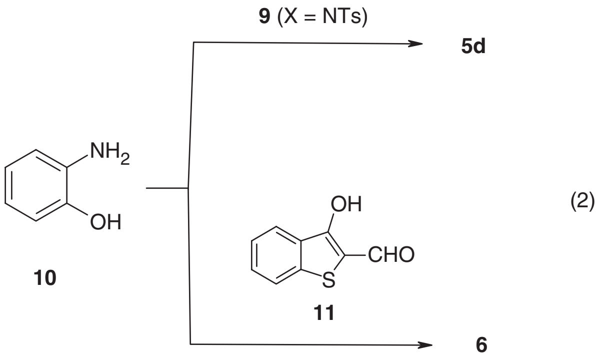
9 **10**

Scheme 1. Synthesis of the ligands **5a–e**.

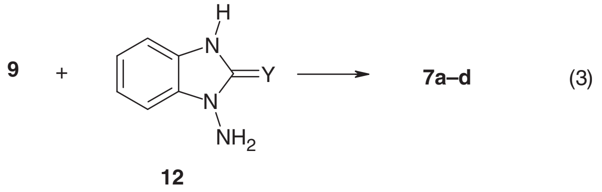
Schiff bases **7** were obtained by reflux of a solution of **9** (X = NTs) or **9** (X = OH) and 1,2-diaminobenzimidazole **12** (Y = NH) [38] or 1-aminobenzimidazoline-2-thione **12** (Y = S) [39] in glacial acetic acid (Scheme 3) for 2 h.

β-Diketoimines **8** were prepared according to the previously described methods [40–44].

The characteristics of the organic compounds are given in table 1 and their ^{1}H NMR data are presented in table 2.



Scheme 2. Synthesis of the ligands **5d** and **6**.



Scheme 3. Synthesis of the ligands **7**.

Table 1. Analytical data for ligands.

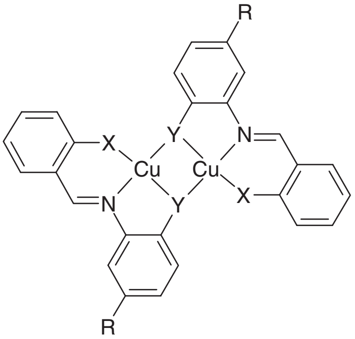
				Anal. found/Calcd (%)			
No	Color	M.p. (°C)	Empirical formula	C	H	N	S
5a	Yellow	195	$C_{21}H_{20}N_4O_4S$	59.52/59.42	4.65/4.75	13.17/13.20	7.65/7.55
5b	Orange	141	$C_{22}H_{22}N_4O_4S$	60.16/60.26	5.16/5.06	12.88/12.78	7.42/7.31
5c	Yellow	140	$C_{24}H_{26}N_4O_4S_2$	57.83/57.81	5.36/5.26	11.32/11.24	12.90/12.86
5d	Orange	142	$C_{20}H_{18}N_2O_3S$	65.56/65.56	5.02/4.95	8.19/7.64	8.90/8.75
5e	Light-yellow	194	$C_{15}H_{15}N_3O_3$	63.25/63.15	5.15/5.30	14.83/14.73	
6	Dark-red	246	$C_{15}H_{11}NO_2S$	66.45/66.93	3.95/4.09	5.23/5.23	10.27/10.81
7a	Colorless	220	$C_{14}H_{11}N_3OS$	62.39/62.44	4.16/4.12	15.47/15.60	12.03/11.90
7b	Colorless	253	$C_{21}H_{18}N_4O_2S_2$	59.37/59.70	4.21/4.29	13.42/13.26	16.24/16.41
7c	Yellow	219–220	$C_{21}H_{19}N_5O_2S$	62.33/62.21	4.77/4.72	17.34/17.27	7.56/7.90
7d	Yellow		$C_{14}H_{12}N_4O$	66.61/66.66	4.71/4.79	22.24/22.21	
8a	Yellow	156	$C_{33}H_{42}N_2$	84.75/84.93	8.89/9.07	5.76/6.00	
8b	Yellow	171	$C_{27}H_{37}N_3O_2$	74.22/74.45	8.23/8.56	9.44/9.65	

Table 2. ^{1}H NMR data of the ligands.

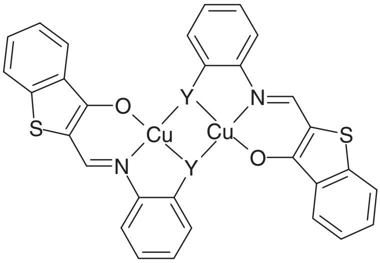
Compound	Solvent	^{1}H NMR data, δ (ppm)
5a	$CDCl_3$	1.43 (3H, s, $ArCH_3$), 2.37 (3H, d, $^3J = 7.2$ Hz, NCH_3), 5.53 (1H, quart, $^3J = 7.2$ Hz, HNMe), 6.68–8.20 (11H, m, Ar–H), 8.70 (1H, s, HC=N), 12.47 (1H, s, TsNH)
5b	$CDCl_3$	1.42 (3H, t, $^3J = 7.2$ Hz, CH_2CH_3), 2.38 (3H, s, $ArCH_3$), 3.41 (2H, q, $^3J_{CH2–NH} = 7.2$ Hz, CH_2CH_3), 5.51 (t, $^3J_{NH–CH2} = 7.2$ Hz, $NH–C_2H_5$), 6.67–8.17 (11H, m, Ar–H), 8.68 (1H, s, HC=N), 12.45 (1H, s, TsNH)
5c	$CDCl_3$	0.99 (3H, t, $^3J = 7.3$ Hz, $CH_2CH_2CH_2CH_3$), 1.49 (2H, sext, $^3J = 7.3$ Hz, $CH_2CH_2CH_2CH_3$), 1.77 (2H, dt, $^3J_{CH2–CH2} = 7.3$ Hz, $^3J_{CH2–NH} = 5.5$ Hz, $CH_2CH_2CH_2CH_3$), 2.39 (3H, s, $ArCH_3$), 3.37 (2H, q, $^3J = 7.3$ Hz, $CH_2CH_2CH_2CH_3$), 5.57 (1H, t, $^3J = 5.5$ Hz, HNBu), 6.60–8.20 (10H, m, Ar–H), 8.68 (1H, s, HC=N), 12.42 (1H, s, TsNH)
5d	$CDCl_3$	2.37 (3H, s, CH_3), 6.07 (1H, s, OH), 6.80–7.90 (12H, m, Ar–H), 8.62 (1H, s, HC=N), 12.33 (1H, s, TsNH)
5e	$CDCl_3$	1.34 (3H, t, $^3J = 7.2$ Hz, CH_2CH_3), 3.35 (2H, q, CH_2CH_3), 5.07 (t, $^3J = 7.2$ Hz, $NH–C_2H_5$), 6.62–8.15 (7H, m, Ar–H), 8.71 (1H, s, HC=N), 12.31 (1H, s, OH)
6	DMSO-d_6	6.75–6.95 (3H, m, Ar–H), 7.20–7.35 (1H, m, Ar–H), 7.40–7.85 (4H, m, Ar–H), 8.35 (0.1H, d, $^3J = 13$ Hz, CH, *Z*-isomer), 8.43 (0.9H, d, $^3J = 12$ Hz, CH, *E*-isomer), 8.80 (0.1H, d, $^3J = 13$ Hz, NH), 9.98 (0.1H, s, OH, *Z*-isomer), 10.08 (0.9H, s, OH, *E*-isomer), 12.39 (0.9H, d, $^3J = 12$ Hz, NH, *E*-isomer)
7a	DMSO-d_6	2.30 (3H, s, CH_3), 7.20–7.80 (12H, m, Ar–H), 10.21 (1H, s, HC=N), 10.82 (1H, s, NH_{Bzm}), 13.02 (1H, s, TsNH)
7b	DMSO-d_6	6.80–7.50 (7H, m, Ar–H), 7.8 (1H, dd, Ar–H), 10.05 (1H, s, HC=N), 10.52 (1H, s, NH), 12.95 (1H, s, OH)
7c	DMSO-d_6	2.21 (3H, s, CH_3), 6.52 (2H, s, NH_2), 6.90–7.60 (11H, m, Ar–H), 8.13 (1H, dd, Ar–H), 8.82 (1H, s, HC=N), 10.01 (1H, s, TsNH)
7d	DMSO-d_6	6.49 (2H, s, NH_2), 6.80–7.40 (6H, m, Ar–H), 7.53 (1H, d, Ar–H), 8.00 (1H, d, Ar–H), 9.21 (1H, s, HC=N), 10.03 (1H, s, OH)
8a	$CDCl_3$	1.22 (24H, d, $^3J_{CH3–CH} = 6.9$ Hz, $8CH_3$), 3.27 (4H, hept, $^3J_{CH3–CH} = 6.9$ Hz, 4CH), 7.00–7.40 (11H, m, $2C_6H_3$, C_6H_5), 7.71 (2H, s, 2CH–NH); 12.06 (1H, br s, NH)
8b	$CDCl_3$	1.21 (24H, d, $^3J_{CH3–CH} = 6.9$ Hz, $8CH_3$), 3.05 (4H, hept, $^3J_{CH3–CH} = 6.9$ Hz, 4CH), 7.16–7.26 (6H, m, $2C_6H_3$), 8.74 (2H, d, $^3J = 4$ Hz, 2CH–NH), 12.79 (1H, br s, NH)

2.2. *Synthesis of complexes*

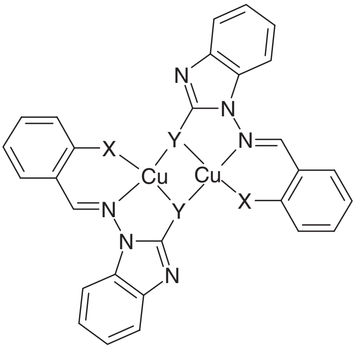
General methods for the synthesis of chelates **13–16** are based on the direct interaction of ligands with copper acetate/chloride (**13a–e, 14a, 15, 16**) or coupling (**13f**, **14b**) of amines **10** and aldehydes **9** (X = O), **11** on Cu(2+) template [45].



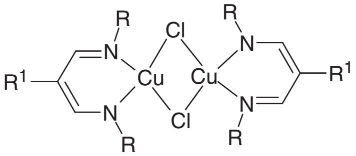
13: X = NTs, Y = NMe, R = NO_2 (a);
X = NTs, Y = NEt, R = NO_2 (b);
X = NTs, Y = NBu-*n*, R = NO_2 (c);
X = NTs, Y = O, R = H (d);
X = O, Y = NEt, R = NO_2 (e);
X = O, Y = NBu-*n*, R = NO_2 (f)



14: Y = O (a); S (b)



15: X = O, Y = S (a);
X = NTs, Y = S (b);
X = NTs, Y = NH (c);
X = O, Y = NH (d)



16: R^1 = Ph (a), NO_2 (b)

Metal complexes **13** and **14a** were obtained by reflux of ethanolic solution of ligands **5** or **6** (LH_2) and dicopper tetraacetate dihydrate [$Cu_2(OAc)_4 \cdot 2H_2O$] (DTD) taken in 2 : 1 molar ratio. For the synthesis of complexes **15** *n*-butanol was employed as the solvent. The chelates **13f** and **14b** were prepared from corresponding Schiff-base precursors and DTD (2 : 2 : 1) by template procedure in ethanol. Chlorine bridged binuclear compounds **16** were isolated from the boiling ethanol solutions of corresponding derivatives **8** and $CuCl_2 \cdot 2H_2O$.

Bis[2-((E)-{[2-(ethylamino)-5-nitrophenyl]imino}methyl)-N-*p*-toluenesulfoanilinato]copper (II) (13b). To a solution of 0.438 g (0.001 mol) of compound **5b** in 50 mL of ethanol a solution of 0.199 g (0.001 mol) of DTD in 10 mL of the same solvent was added. The resulting mixture was refluxed under argon during 4 h. The precipitate was filtered off, triply washed with 5 mL of hot ethanol and dried *in vacuo* at 100°C. Dark-brown crystals, m.p. > 260°C. Yield 78%.

Bis[2-{(E)-[(2-mercaptophenyl)imino]methyl}-1-benzothiophene-3-olato]copper(II) (14b). The solution of 1.25 g (0.01 mol) of *o*-aminothiophenol in 10 mL of methanol was added to a solution containing 1.78 g (0.01 mol) of 3-hydroxybenzo[b]thiophenecarbaldehyde in 10 mL of methanol. The reaction mixture was refluxed during 1 h under argon then 2.49 g (0.03 mol) of sodium acetate in 10 mL of methanol was added. A methanol solution of DTD (2.0 g, 0.01 mol) was added and the reaction mixture left to reflux for 1 h. The precipitate was filtered off and dried *in vacuo*. The complex was recrystallized from chloroform/methanol (2 : 1) solution. m.p. > 260°C. Yield 65%.

Bis{$\mu(Cl_2)$-(2,6-diisopropylphenyl)amino-4-(2,6-diisopropylphenyl)iminatocopper(II)-3-nitro-2-pentene} (16b). A hot solution containing $CuCl_2 \cdot H_2O$ (0.17 g, 0.001 mol) in methanol was added to a hot solution of 2,6-diisopropylphenyl)amino-4-(2,6-diisopropylphenyl)imine-3-nitro-2-pentene ($R^1 = NO_2$) (0.435 g, 0.001 mol) in 10 mL of methanol. The mixture was refluxed for 20–30 min. The precipitated brown crystals were filtered off, washed with ethanol, and dried. m.p. > 200°C. Yield 60%.

The characteristics of coordination compounds are given in table 3.

Table 3. Analytical data for complexes.

				Anal. found/Calcd (%)			
Compound	Colour	M.p. (°C)	Empirical formula	C	H	N	S
13a	Red-brown	>250	$C_{42}H_{36}N_8O_8S_2Cu_2$	51.91/51.89	3.65/3.73	11.48/11.53	6.71/6.60
13b	Dark-brown	>260	$C_{44}H_{40}N_8O_8S_2Cu_2$	52.75/52.84	4.13/4.03	11.32/11.20	6.51/6.41
13c	Red-brown	200	$C_{48}H_{48}N_8O_8S_2Cu_2$	54.62/54.58	4.63/4.59	10.65/10.61	6.18/6.07
13d	Dark-green	>260	$C_{40}H_{32}N_4O_6S_2Cu_2$	56.64/56.13	4.08/3.77	6.75/6.55	8.00/7.49
13e	Dark-brown	234	$C_{30}H_{26}N_6O_6Cu_2$	52.01/51.95	3.72/3.78	12.32/12.12	
13f	Dark-brown	>260	$C_{34}H_{34}N_6O_6Cu_2$	54.66/54.46	4.68/4.57	11.32/11.21	
14a	Brown	>260	$C_{30}H_{18}N_2O_4S_2Cu_2$	54.56/54.45	2.84/2.74	4.13/4.23	9.75/9.69
14b	Red-brown	>260	$C_{30}H_{18}N_2O_4S_4Cu_2$	51.84/51.93	2.65/2.61	4.15/4.04	18.52/18.49
15a	Black	>260	$C_{28}H_{18}N_6O_2S_2Cu_2$	50.73/50.82	2.69/2.74	12.67/12.70	
15b	Black	>260	$C_{42}H_{32}N_8O_4S_4Cu_2$	52.19/52.11	3.36/3.33	11.59/11.57	
15c	Black	>260	$C_{42}H_{34}N_{10}O_4S_2Cu_2$	54.11/54.01	3.57/3.67	15.08/15.00	
15d	Black	>260	$C_{28}H_{20}N_8O_2Cu_2$	53.45/53.59	3.17/3.21	17.82/17.85	
16a	Dark-green	>260	$C_{66}H_{82}N_4Cl_2Cu_2$	70.35/70.19	7.56/7.32	4.89/4.96	
16b	Brown	>260	$C_{54}H_{72}N_6O_4Cl_2Cu_2$	60.47/60.78	6.54/6.80	7.53/7.87	

2.3. *IR and ^{1}H NMR studies*

IR spectra of the ligands and complexes were recorded in KBr pellets or nujol mulls on a Nicolet Impact-400 spectrophotometer in the region 1000–4000 cm^{-1}. ^{1}H NMR spectra were recorded on a Varian Unity-300 spectrometer in $CDCl_3$ or DMSO-d_6 in internal stabilization regime relative to the signal of residual protons of the corresponding deuterated solvent at 20°C.

2.4. *EXAFS spectroscopy*

The EXAFS spectra of the CuK edge for all the samples were obtained at the EXAFS station of the siberian synchrotron radiation center (SSRC). The storage ring VEPP-3 with the electron beam energy of 2 GeV and current of 70–90 mA was used as the source of radiation. All the spectra were recorded in a transmission mode using a double-crystal Si(111) monochromator and two ionization chambers as detectors. EXAFS data were analyzed using the IFEFFIT data analysis package [46]. The radial pair distribution functions around Cu atoms were obtained by the Fourier transformation of the k^3-weighted EXAFS functions over the range of photoelectron wave numbers 2.8–12.0 $Å^{-1}$. The structural parameters (the interatomic distances, the coordination numbers and Debye–Waller factors) were found by non-linear fit of theoretical spectra to experimental ones. Theoretical spectra were simulated by means of FEFF7 [47]. The quality of fit was estimated from discrepancy factors between the experimental and simulated functions (Q-factor).

2.5. *X-Ray crystallography*

Crystallographic data. Crystals of **16b** ($C_{56}H_{80}Cl_2Cu_2N_6O_6$, M = 1131.24) are monoclinic, space group $P2_1/n$, at 120 K: $a = 12.447(2)$ Å, $b = 13.428(2)$ Å, $c = 17.604(3)$ Å, $\beta = 95.933(4)°$, $V = 2926.6(8)$ $Å^3$, $Z = 2$ ($Z' = 0.5$), $d_{calc} = 1.284$ g cm^{-3}, μ(Mo-K_α) = 0.869 cm^{-1}, $F(000) = 1196$. Intensities of 14192 reflections were measured with a SMART APEX2 CCD diffractometer (λ(Mo-K_α) = 0.71072 Å, ω-scans, $2\theta < 52°$) and 5975 independent reflections ($R_{int} = 0.0657$) were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The disorder was resolved using the model in which isopropyl and methyl groups were occupying two positions with 50% contributions.

The hydrogen atoms of methanol were located from the Fourier synthesis while for the rest of hydrogen atoms the positions were calculated geometrically. The refinement converged to $wR_2 = 0.1647$ and GOF = 1.085 for all independent reflections ($R_1 = 0.0791$ was calculated against F for 1750 observed reflections with $I > 2\sigma(I)$). All calculations were performed using the SHELXTL PLUS 5.0 [48].

2.6. *EPR spectroscopy*

EPR spectra were recorded on the Bruker ER 200D-SRC spectrometer equipped with double resonator ER 4102 SDT and temperature equipment ER 4111 VT.

Diphenylpicrylhydrazine (DPPH, $g = 2.0037$) was used as standard for g-factor determination.

2.7. *Magnetic susceptibility measurements*

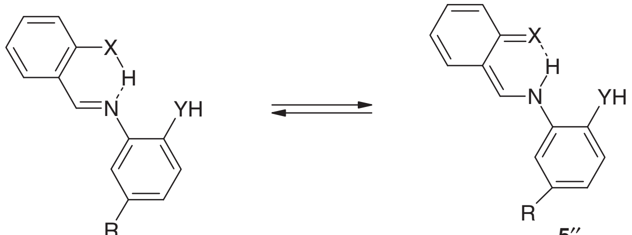
All measurements of complexes **13–16** were carried out on MPMS-5S Quantum Design SQUID magnetometer (2–300 K, magnetic field 5 kOe). The effective magnetic moment depending on temperature were calculated by the equation: $\mu_{\mathrm{eff}}(T) = \sqrt{8\chi T}$, where χ-molar paramagnetic susceptibility corrected by taking into account the diamagnetic contribution calculated based on the Pascal increments.

3. Results and discussion

3.1. *Tautomerism of the Schiff-base ligands*

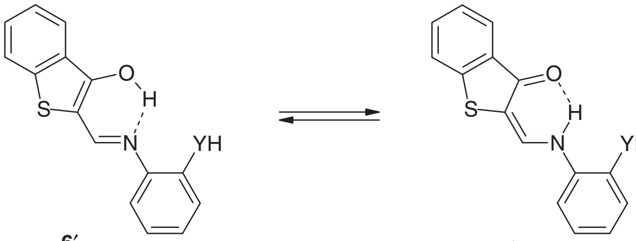
According to our IR and ^{1}H NMR spectral results and literature data [49–55] the tautomeric forms **5′**, **6″**, **7‴a** (Y = S), **7‴b** (Y = S), **7″c** (Y = NH), **7″d** (Y = NH) and **8′** (see Schemes 6–9) represent the major forms of the compounds in the solid state and dominant forms in solutions of $CDCl_3$ and DMSO-d_6 for compounds **5–8**, correspondingly.

The amino-imine (X = NTs) and enole-imine (X = O) tautomeric forms **5′** are typical for Schiff bases **5**. This conclusion is in line with previous findings [54, 56] and is supported by the results of IR and ^{1}H NMR spectral investigation – the presence of the absorbtion bands of C=N groups (1618 and 1615 cm^{-1}) in IR spectra and signals of NH and OH protons (12.45 and 12.31 ppm) in the ^{1}H NMR spectra. By contrast, Schiff base **6**, like other azomethines of 2-formyl-3-hydroxybenzo[b]thiophene [53], exists in keto-amine form **6″** as indicated by the presence of the IR-absorbtion band of the



5′ **5″**

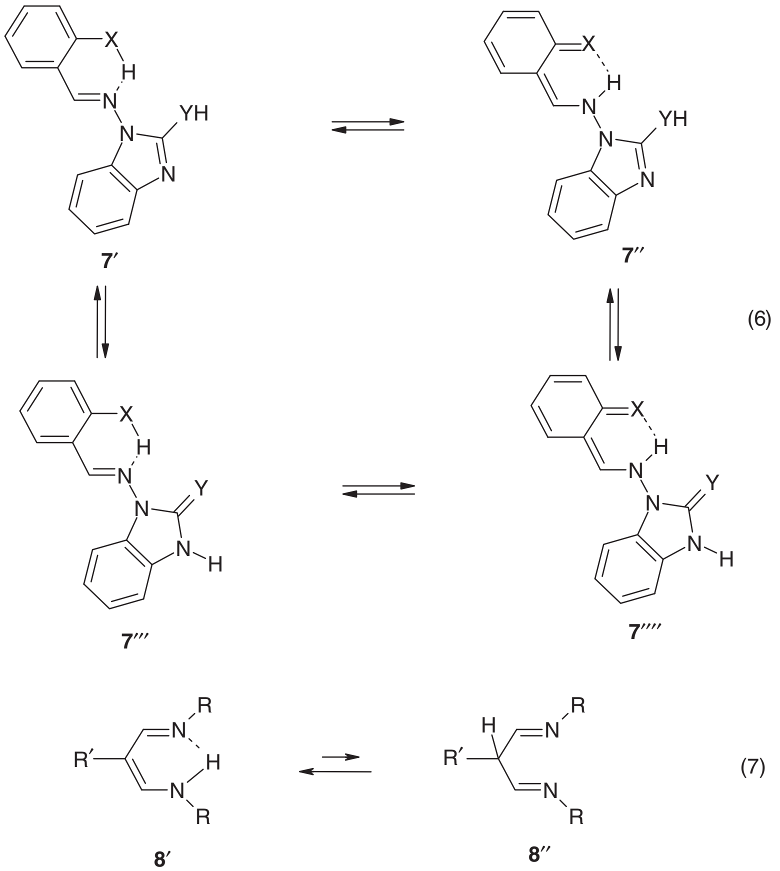
(4)



6′ **6′**

(5)

Schemes 4–5. Possible tautomerism of the ligands **5** and **6**.



Schemes 6–7. Possible tautomerism of the ligands **7** and **8**.

carbonyl group at 1646 cm^{-1} and spin-spin coupling of the amine and methine protons ($J = 12$–14 Hz).

The character of the predominant tautomeric form of imines **7** depends on the nature of a substituent in position 2 of the imidazole ring: with Y = NH they exist in the aminobenzimidazole form **7**′, while with Y = S – in the benzimidazolinethione form **7**‴, which is in good agreement with ^{1}H NMR spectra (see table 2) and literature data [57]. According to the data [54, 55], *β*-diketoimines possess the amino-imine form **8**′ as proved by X-ray crystallography [21].

3.2. *Characterization of the complexes*

Complexes **13–15** have the general formula CuL, where L is the deprotonated ligand H_2L **5–7** (table 3). By analogy with the data [21, 45, 58–60] they may be assigned to the binuclear structures Cu_2L_2. The chelate structure of complexes **13**, **15** is supported by the IR spectral data [61] – disappearance of the absorbtion bands of XH and YH groups (region 3300–3500 cm^{-1}) and low-frequency shift of the C=N bond absorbtion (1600–1620 cm^{-1}), which is in accord with the previous observations [62–64].

Table 4. CuK-edge EXAFS fitting results for copper complexes. Parameters of the nearest coordination shells: coordination numbers (N), interatomic distances (R, Å), Debye–Waller factors (σ^2, $'^2$), type of the nearest neighbors and quality of fit factor (Q, %).

Compound	N	R, Å	σ^2, $'^2$	Atom	Q, %
15a	2	1.98	0.0038	N	7.2
	1	2.19	0.0043	S	
	1	2.32	0.0037	S	
	1	2.66	0.0042	O	
	1	2.85	0.0040	Cu	
15b	2	1.94	0.0024	N/O	8.4
	1	2.24	0.0073	S	
	1	2.30	0.0079	S	
	1	2.92	0.0063	Cu	
15c	2	1.97	0.0031	N	7.4
	2	2.00	0.0031	N	
	4	2.79	0.0044	C/N	
	1	3.01	0.0059	Cu	
16a	2	1.95	0.0049	N	3.5
	2	2.30	0.0054	Cl	
	3	2.94	0.0060	C	
	1	3.01	0.0088	Cu	

3.2.1. EXAFS spectra. The insight into the properties of the nearest environment of copper atoms in chelates **15**, **16** are provided by EXAFS data (see table 4).

For complex **15** (X = NTs, Y = S), the first coordination sphere consists of two nitrogen atoms (of azomethine and tosylamino types) and two sulfur bridging atoms. One of the oxygen atoms of the SO_2 group of tosylamino fragment is located at a distance 2.66 Å from the copper ion. The Cu–Cu distance is equal to 2.85 Å. The central Cu atom in complex **15** (X = O, Y = S) is tetracoordinated by one oxygen atom of phenolic type, one azomethine nitrogen atom and two bridging sulfur atoms with shorter bonds compared to those of **15** (X = NTs, Y = S). The Cu–Cu distance in the complex **15** (X = O, Y = S) is longer by 0.07 Å than that in **15** (X = NTs, Y = S). Four nitrogen atoms are involved into the nearest coordination sphere of the copper ion **15** (X = NTs, Y = NH) with bond distances Cu–N varying in the range 1.97–2.00 Å. No additional coordination of tosyl oxygen atoms in this chelate is observed. The Cu–Cu bond, 3.01 Å, is the longest among discussed complexes.

An alternative structure of the metal chelate **15** (X = O, Y = S) with bridging oxygen atoms of aldehyde fragment is possible [65–68] and the majority of such copper complexes have antiferromagnetic exchange interactions [66–68].

The EXAFS spectrum of **16a** contains two well defined peaks corresponding to the nearest coordination sphere of Cu ion formed by two nitrogen and two chlorine atoms (table 4).

3.2.2. X-ray analysis. The molecular structures of compounds **13d** [21] and **16b** (figures 1 and 2) were determined by X-ray diffraction (XRD) method.

The X-ray diffraction of **16b** show the dinuclear structure of the coordination unit, with two identical five-coordinate Cu(II) ions bridged by two chloride ligands.

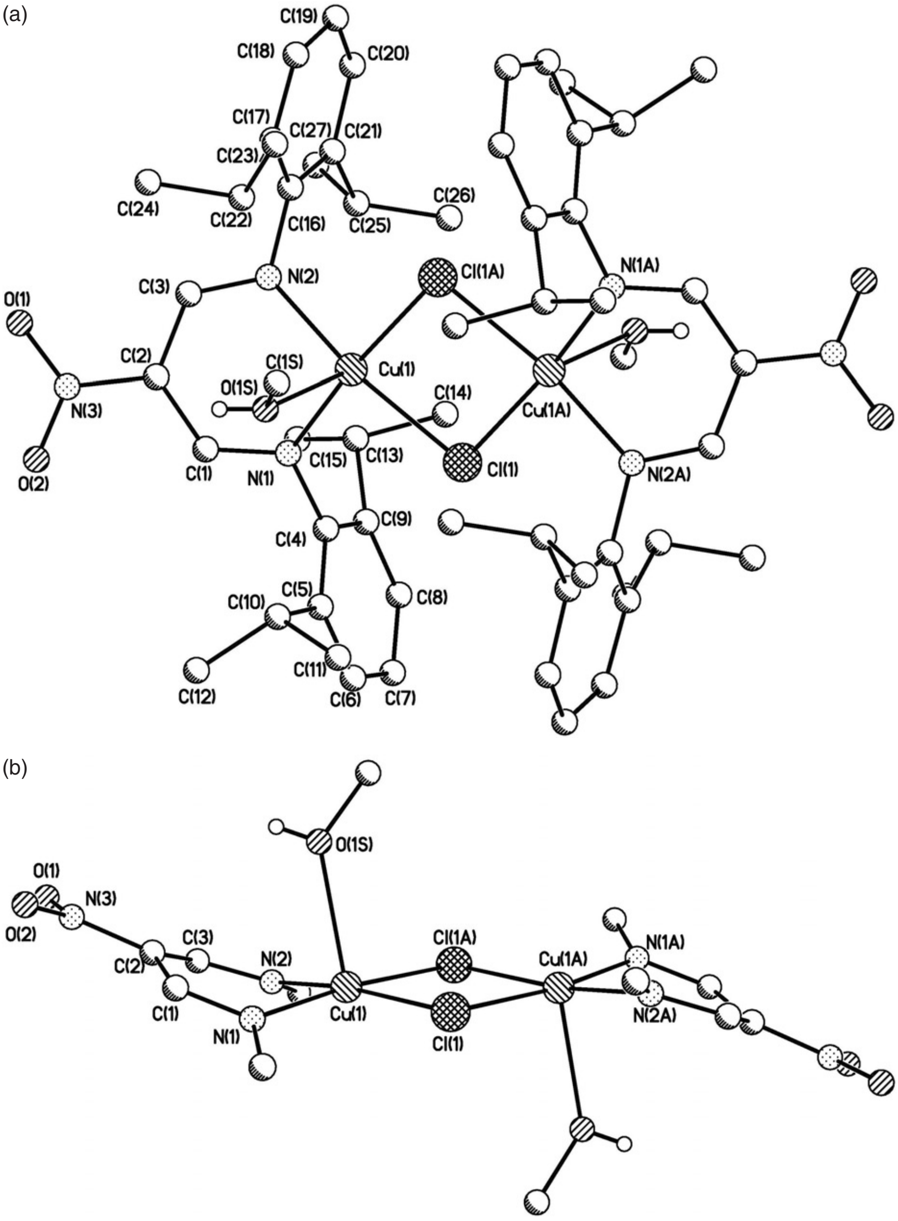


Figure 1. The general view of complex **16b** in two projections. The second position of the disordered *i*-Pr groups and methyl of solvate are omitted for clarity. For (**B**) the aryl groups are omitted for clarity. Selected bond lengths (Å): Cu(1)–N(2) 1.991(5), Cu(1)–N(1) 1.990(4), Cu(1)–Cl(1) 2.2943(17), Cu(1)–Cl(1A) 2.3056(13), Cu(1)–O(1S) 2.398(4), N(1)–C(1) 1.302(7), N(1)–C(4) 1.450(7), N(2)–C(3) 1.300(6), N(2)–C(16) 1.455(7), N(3)–O(2) 1.247(6), N(3)–O(1) 1.251(7), N(3)–C(2) 1.410(7), C(1)–C(2) 1.417(8), C(2)–C(3) 1.414(7); bond angles (°): N(2)–Cu(1)–N(1) 92.22(18), N(2)–Cu(1)–Cl(1) 170.59(13), N(1)–Cu(1)–Cl(1) 91.86(14), N(2)–Cu(1)–Cl(1A) 91.98(13), N(1)–Cu(1)–Cl(1A) 173.50(14), Cl(1)–Cu(1)–Cl(1A) 83.27(6), N(2)–Cu(1)–O(1S) 88.99(18), N(1)–Cu(1)–O(1S) 89.72(15), Cl(1)–Cu(1)–O(1S) 99.50(14), Cl(1A)–Cu(1)–O(1S) 95.31(11), Cu(1)–Cl(1)–Cu(1A) 96.73(6), C(1)–N(1)–C(4) 115.1(4), C(1)–N(1)–Cu(1) 119.8(4), C(4)–N(1)–Cu(1) 124.2(4), C(3)–N(2)–C(16) 115.7(5), C(3)–N(2)–Cu(1) 121.2(4), C(16)–N(2)–Cu(1) 122.8(4), O(2)–N(3)–O(1) 120.6(5), O(2)–N(3)–C(2) 119.3(6), O(1)–N(3)–C(2) 120.2(5), N(1)–C(1)–C(2) 124.8(5), N(3)–C(2)–C(3) 117.6(6), N(3)–C(2)–C(1) 116.6(5), C(3)–C(2)–C(1) 125.2(5), N(2)–C(3)–C(2) 124.0(6).

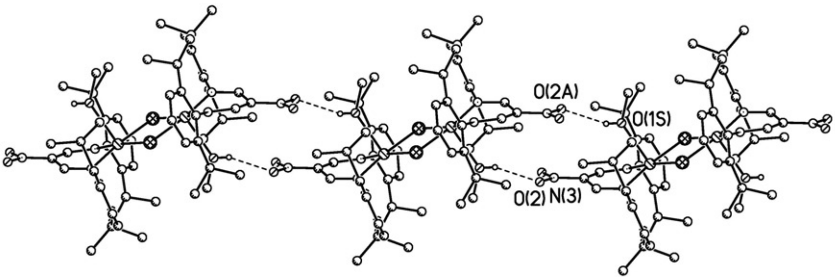


Figure 2. O–H ⋯ O bonded chains in crystal of **16b**.

The copper atoms have slightly distorted square pyramidal coordination polyhedra with chlorine and nitrogen atoms in the basal plane. The Cu(1) atom is deviated from N(1), N(2), Cl(1) and C(1a) atoms towards to the methanol oxygen by 0.12 Å. The conformation of the six-membered metallocycle corresponds to a distorted boat with deviation of C(2) and Cu(1) atoms from the plane of the rest of the atoms by 0.14 and 0.64 Å, respectively. The nitrogen N(1) and N(2) centers have almost planar configuration with the sum of bond angles equal to 359.1–359.7°.

It should be noted that in contrast to the earlier reported β-diketiminate copper complexes [43], the presence of a methanol molecule in the copper coordination sphere substantially planarizes the structure of the coordination site ($N_4Cu_2Cl_2$), the dihedral angle CuN_2/Cu_2Cl_2 being equal to 9.4°. This leads to considerable elongation of the Cu–N (ca. 1.990(4) Å) and shortening of the Cu–Cl (2.294(2)–2.305(2) Å) bond lengths in **16b** compared to the corresponding ones (1.94 and 2.31 Å) in similar dinuclear copper β-diketiminate complexes [43].

Analysis of crystal packing reveals that the intermolecular O(1S)–H(1S) ⋯ O(2) H-bonds (O(1S) ⋯ O(2) 2.917(4) Å) assemble the molecules into an infinite chain directed along crystallographic axis *b*.

3.2.3. EPR spectroscopy. The EPR spectrum of dimer **16b** (powder) contains a broad (linewidth is more than 100 G) band with two centrosymmetrical shoulders. As well as g-factors of other components, g-factor of central line changes under temperature variation (figure 3).

In addition, the "half field" line attributable to a forbidden transition $\Delta M_S = 2$ ($M_S = 1, 0, -1$) is observed. Decreasing of temperature causes hyperfine splitting of low field component. Such spectra are typical for magnetically coupled dicopper systems [43] with weak copper-copper magnetic interaction. It is in accordance with magnetic properties of **16** (figure 7). Zero-field splitting parameter D allows one to evaluate effective distance between the centers of localization of the unpaired electron (copper(II) ions). This distance thus found (D = 1550 G (290 K); $r = 3.3$ Å) is in a good agreement with structural data.

3.2.4. Magnetism. Experimental curves μ_{eff} *versus* T for complexes **13–16** are shown in figures 4–7.

The theoretical curves μ_{eff}/T obtained by simulation of experimental dependences with taking into account the interdimeric exchange interactions (zJ') were calculated by

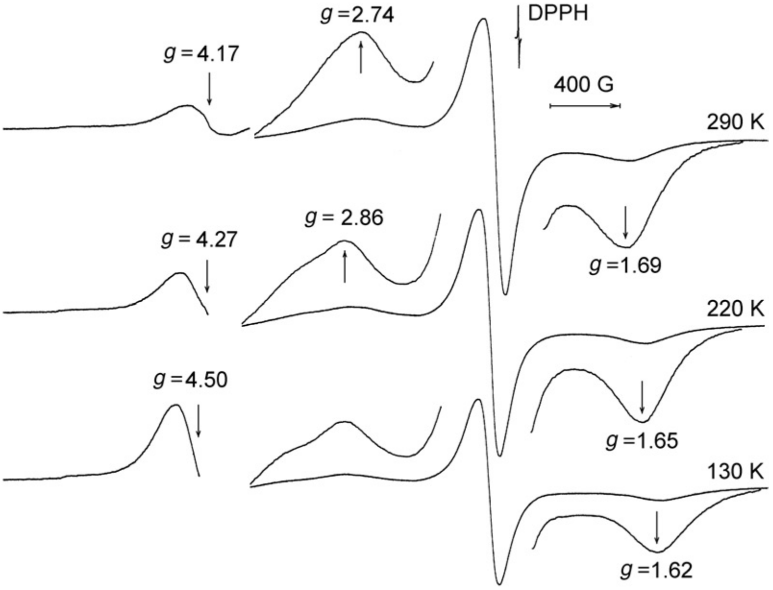


Figure 3. General view of EPR spectra of **16b** at different temperatures (powder).

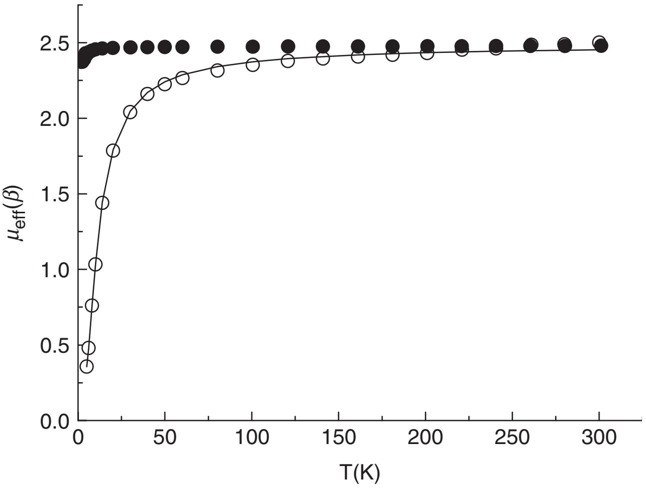


Figure 4. Temperature dependence of effective magnetic moment for **13c** - ●; **13e** - ○.

equation $\chi = \chi_{(Cu-Cu)}/[1 - (2zJ'/Ng^2\beta^2)\chi_{(Cu-Cu)}]$, where $\chi_{(Cu-Cu)}$- the Bleany–Bowers magnetic susceptibility of dimer, g–g-factor of Cu(II), β - Bohr magneton.

$$\chi_{Cu-Cu} = \frac{N\beta^2 g^2}{3kT}\left(1 + \frac{1}{3}\exp\frac{-2J}{kT}\right) - 1 + TIP, \tag{1}$$

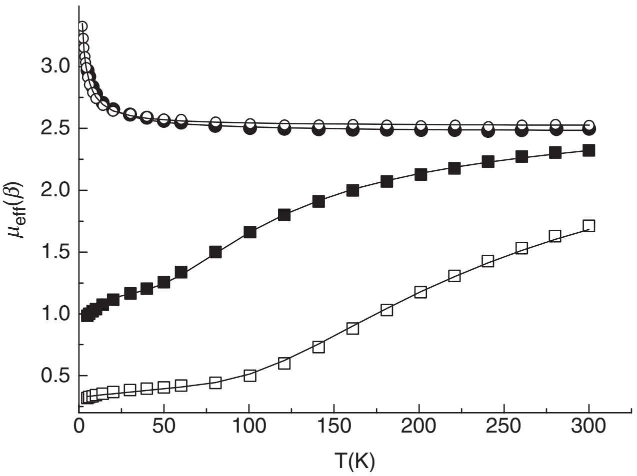


Figure 5. Temperature dependence of effective magnetic moment for **13a** - ○; **13b** - ●; **13d** - □; **13f** - ■.

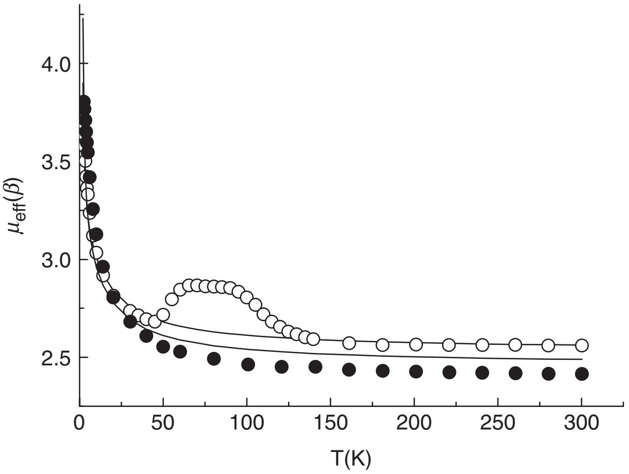


Figure 6. Temperature dependence of effective magnetic moment for **15c** - ●; **15b** - ○; anomaly at 50–120 K is caused by the presence of molecular oxygen in the sample.

$$\chi' = \chi_{\mathrm{Cu-Cu}} \cdot (1 - p) + \frac{0.375}{T} \cdot p, \tag{2}$$

$$\chi = \frac{\chi'}{1 - (2zJ'/Ng^2\beta^2)\chi'}, \tag{3}$$

where N, k, β, J, g, TIP, zJ', p are Avogadro constant, Boltzmann constant, Bohr magneton, exchange interaction parameter, g-factor of Cu(II),

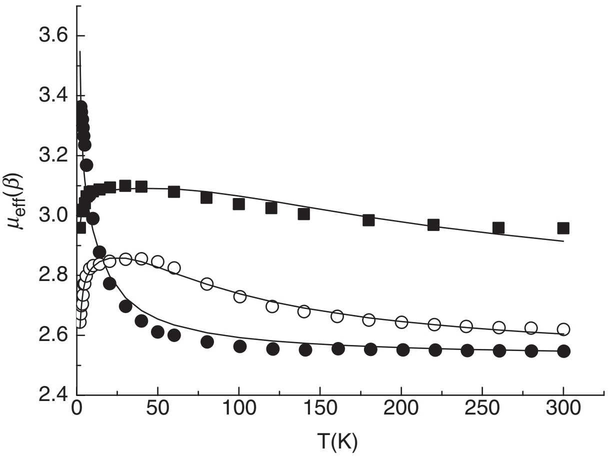


Figure 7. Temperature dependence of effective magnetic moment for **15a** - ●; **16a** - ○; **16b** - ■.

Table 5. Optimal parameters for dimers.

Compound	g	J (cm^{-1})	zJ (cm^{-1})	$TIP \cdot 10^6$ (cm^3 mol^{-1})	p
13a	2.06	+2.3	+0.25		
13b	2.02	+4.0	+0.27	290	
13c	2.02	−0.24			
13d	2.1	−217		130	0.018
13e	2.02	−10.0			
13f	2.1	−89		380	0.176
15a	2.07	+6.8	+0.33		
15b	2.07	+8.2	+0.42		
15c	2.01	+8.3	+0.58		
16a	2.04	+39	−0.21		
16b	2.19	+99	−0.08		

temperature-independent paramagnetism and inter-cluster exchange parameter, and fraction of monomeric impurity with S = 1/2, respectively. Optimal parameters *J*, *g*, *TIP*, *zJ'* and *p* were calculated by approximation of experimental dependence of μ_{eff} by least squares method. Functional$\sum_1^n \left(\mu_{eff}^{exp}(T_i) - \mu_{eff}^{theor}(T_i)\right)^2$, where i – number of experimental points, was minimized. These parameters of equations (1–3) obtained after simulation of experimental dependences are given in table 5. Theoretical curves in the Figures are shown by solid line.

Influence of the nature of donor centers X and Y on the character of exchange interaction is well reflected in the series of complexes **13** and **14**.

The majority of these complexes is characterized by antiferromagnetic exchange interaction - **13c** $J = -0.24\,\mathrm{cm}^{-1}$, **13e** $J = -10\,\mathrm{cm}^{-1}$, **13f** $J = -89\,\mathrm{cm}^{-1}$, **13d** $J = -217\,\mathrm{cm}^{-1}$. Comparison of the J values shows that the exchange parameter increases when Y passing from NR to O.

Such antiferromagnetic interaction of the complexes **13** (X = Y = S, R = H) and **14** (Y = S) results in their diamagnetism reflected by the clear ^{1}H NMR spectrum of **13** (X = NTs; Y = S, R = H) in $CDCl_3$ (see supplements).

It should be noted that introduction of oxygen into the bridging fragment instead of nitrogen (**13**: $Y = NR \rightarrow Y = O$) leads to more significant increase in the magnitude of J (figure 4) than similar O/N replacement in the periphery (**13**: $X = NTs \rightarrow X = O$). Decrease in the volume of the substituent R at bridging nitrogen atom in compounds (**13**: $X = NTs$, $Y = NR$, $R^1 = NO_2$) is accompanied by decrease in the ferromagnetic exchange as seen from comparison of J values for $R = \mathrm{Me}$ ($J = 2.3\,\mathrm{cm}^{-1}$) and $R = Et$ ($J = 4.03\,\mathrm{cm}^{-1}$).

Dependence of magnetic properties on the character of the cycle annelated to the bridging fragment is seen from comparison of **13** and **15**. All studied compounds **15** independent of the nature of X and Y atoms are characterized by ferromagnetic exchange interactions – **15c** $J = 8.3\,\mathrm{cm}^{-1}$ (figure 6), **15b** $J = 8.2\,\mathrm{cm}^{-1}$ (figure 6). This trend is retained even in the presence of sulfur bridges – **15a** $J = 6.8\,\mathrm{cm}^{-1}$ (figure 7). The replacement of periphery donor nitrogen atom by oxygen in sulfur-bridged complexes **15** leads to increase in J-factor.

Ferromagnetic spin–spin interaction is also characteristic for binuclear structures **16** with chlorine bridges. The J values for complexes **16a** and **16b** were found to be positive and equal to 39 and $99\,\mathrm{cm}^{-1}$ correspondingly (figure 7). Weak ferromagnetic exchange was detected earlier for other azomethine complexes containing the $N_4Cu_2Cl_2$ coordination core [17].

It may be noted that the majority of dimers with ferromagnetic exchange interaction possess positive interdimer exchange zJ' (table 5). It means that at temperatures lower than 2 K magnetic phase change to ferromagnetic state for these complexes is possible.

4. Conclusions

A novel type of binuclear ferro-, antiferro- and diamagnetic (strong antiferromagnetic exchange) Cu(2+) chelates of Schiff bases and β-diketimines with N, O, S, Cl bridges and widely varied azomethine ligands (donor atoms (N, O, S), aromatic and heterocyclic aldehyde and amine moieties) were obtained and their magnetic properties were studied. Combined influence of the above factors on the magnetic properties of complexes is most illustrative in the example of S-bridged chelates – dimers with phenyl fragment annelated to the five-membered metallocycles (**13**: $X = NTs$, $Y = S$, $R = H$ [21]; **14b**) are diamagnetic while annelation of an azole fragment leads to the ferromagnetic complexes (**15a, b**).

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited to the Cambridge Crystallographic Data Centre as supplementary no. CCDC 613174. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgments

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