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Review

Physico-chemical study of first row transition metal ions coordination compounds with *N*,*N*′-bis(2-tosylaminobenzylidene)-1,3-diaminopropanol. The crystal structure of bis-azomethine and its cobalt(II) complex

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ABSTRACT

The novel Cu(II), Ni(II), Zn(II), Co(II) coordination compounds with Schiff base ligand – *N*,*N*′-bis(2-tosylaminobenzylidene)-1,3-diaminopropanol have been synthesized and studied. The structures of bis-azomethine as well as Co(II) and Zn(II) mononuclear metallochelates have been determined by X-ray analysis. The magnetic properties of all complexes were studied and interpreted in terms of HDVV theory. It was shown that exchange interaction in binuclear copper(II) complexes was affected by tosyl groups.

Leonid Dmitrievich Popov, *was born in 1958, citizen of Russian Federation, in 1996 year he finished postgraduate course of the chemistry faculty of Rostov State University. Now he works as a senior lecturer of physical and colloid chemistry at the chemistry faculty of Southern Federal University. Basic scientific interests: synthesis and physical-chemical study of the polydentate ligands and their mono- and binuclear metal complexes; correlation of a structure and physical and chemical properties of coordination compounds; search of ways of possible application of organic and coordination compounds.*

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Contents

1. Introduction

The metallochelates with Schiff bases produced from condensation of *ortho*-hydroxyaldehydes and β-diketones with 1,3-diaminopropanol-2 have been studied in details [1–35]. The analysis of published data has shown that above-stated azomethines form both mononuclear [1–6] and polynuclear coordination compounds [7–35]. In most cases the paramagnetic centres of bi- and polynuclear complexes exhibit exchange interaction the character of which is determined by the nature of exchange coupled ions and ligand's donor atoms as well as by bridging atoms of acidoligands (Hal, OAc) or heterocycle molecules (pyrazol, azaindol, bipyridyl, etc.). It is also known that presence of tosyl group in the molecules of ligand systems is frequently resulted in essential transformation of complex structure and physical-chemical properties. The latter is caused by both replacement of oxygen donor atom of phenoxide fragment by the nitrogen one of tosylamino group and possible additional coordination of sulpho-group's oxygen atoms to metal ion [36–45].

In this connection it was interesting to synthesize and study the transition metal complexes with Schiff base produced from condensation reaction of ortho- aminotosylbenzaldehyde with 1,3-diaminopropanol-2 (**H_3L**, Fig. 1) in order to elucidate the tosyl group's influence on the structure and properties of obtained metallochelates.

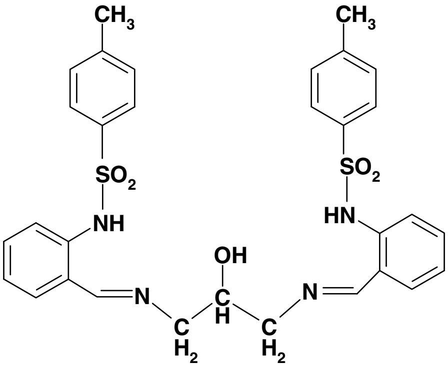

Fig. 1. *N*,*N*′-Bis(2-tosylaminobenzylidene)-1,3-diamino-2-propanol (H_3L).

2. Experimental

2.1. Materials and methods

All chemicals used for the preparative work were of reagent grade. Solvents were dried and distilled before use according to standard procedures. 1,3-Diaminopropan-2-ol, 2-tosylaminobenzaldehyde, pyrazol were purchased from Aldrich and used without further purification. Metal salts $M(CH_3COO)_2 \cdot nH_2O$ were used in their hydrated forms.

Microanalysis on C, H and N was performed on a Perkin–Elmer 240C Analyzer. The infrared spectra were recorded on a Varian Scimitar 1000 infrared spectrophotometer in the range 4000–400 cm^{-1}. ^1H NMR spectra were recorded on a "Unity-300" spectrometer using TMS as internal standard. The UV–Vis spectra were recorded on "Unicam Helios Gamma" spectrometer in the 1100–195 nm range. Magnetic susceptibility of powdered samples of the complexes was measured in the temperature range 300–77.4 K using a Faraday magnetometer employing magnetic field strength 0.9 T. Corrections were made for diamagnetic contributions of the samples according to Pascal's constants [46,47] and for temperature independent paramagnetism. The instrument was calibrated with the use of Hg[Co(CNS)$_4$]. The theoretical interpretation of binuclear complex's magnetic properties was carried out in terms of HDVV theory [48].

2.2. Ligand synthesis

N,N′-Bis(2-tosylaminobenzalidene)-1,3-diamino-2-propanol was synthesized as follows. To a hot solution of 1,3-diaminopropanol-2 (0.003 M) in 10 ml of ethanol 0.006 M *o*-tosylaminobenzaldehyde was added followed by the change of solution colour up to yellow. Four drops of acetic acid were added and the solution was refluxed for 4 h. Next morning the oil deposit was formed at the bottom oh the flask. A day later it transformed into yellow precipitate. The precipitate was left for one day more, after that it was separated, washed with a minimum amount of ethanol and recrystallized from the mixture of DMFA (2 ml) and methanol (6 ml). The recrystallized product was washed with small amount of methanol.

Yellow precipitate. Yield 67%. M.p. 167 °C; lit. 161 °C [45]; ^{1}H NMR (DMSO-d_6): 13.2 (s, 2H, NH), 8.5 (s, 2H, CH$_{\text{azomethene}}$), 5.15 (d, 1H, OH), 7.1–7.7 (m, 16H, Ph-H), 3.7–3.9 (m, 4H, CH$_2$), 4.2 (m, 1H, CH$_{\text{methyn group}}$), 2.2 (s, 6H, CH$_3$). *Anal.* Calc. for $C_{31}H_{32}N_4O_5S_2$: C, 61.56; H, 5.29; N, 9.27. Found: C, 61.23; H, 6.04; N, 9.15%. IR (NaCl, cm^{-1}): *ν*(O–H) 3525 (b), *ν*(N–H) 3278 (b), *ν*(C=N) 1635 (s), *ν*(C–N) 1334 (s), ν_{as}(SO$_2$) 1288 (s), ν_s(SO$_2$) 1157 (s).

2.3. Synthesis of complexes

Caution! It is very important to note that in all cases the molar ratio of reagents M:L was 2:1 during the synthesis of complexes, but in spite of this fact the coordination compounds possessing different structure have been obtained. Cu(CClH$_2$COO)$_2$, Cu(CCl$_3$COO)$_2$, Cu(CF$_3$COO)$_2$ have been obtained by a known method [49].

2.3.1. [MHL] · H$_2$O (M = Zn^{2+}, Co^{2+}, Ni^{2+})

To a hot suspension of ligand (0.0002 M) in 10 ml of absolute methanol a hot solution of corresponding metal acetate (0.0004 M) in 6 ml absolute methanol was added. The colour of solution changed in each case. For the complexes with M = Co(II), Ni(II) the precipitate was formed within 10 min, for Zn(II) complex the precipitate was formed after 6 h of solution's reflux. Complexes were filtered off hot and washed with hot methanol followed by the boiling in a small amount of ethanol for purification.

[ZnHL] · H$_2$O: White solid. Yield 75%. M.p. 240 °C. *Anal.* Calc. for $C_{31}H_{32}N_4O_6S_2Zn$: C, 54.27; H, 4.70; N, 8.17; Zn, 9.53. Found: C, 54.46; H, 4.81; N, 8.31; Zn, 9.37%. IR (NaCl, cm^{-1}): *ν*(O–H) 3523 (b), *ν*(C=N) 1639(s), *ν*(C–N) 1289 (s), ν_{as}(SO$_2$) 1263(s), ν_s(SO$_2$) 1135(s).

[CoHL] · H$_2$O: Pink solid. Yield 71%. M.p. 238 °C. *Anal.* Calc. for $C_{31}H_{32}N_4O_6S_2Co$: C, 54.78; H, 4.75; N, 8.24; Co, 8.67. Found: C, 54.98; H, 4.81; N, 8.39; Co, 8.72%. IR (NaCl, cm^{-1}): *ν*(O–H) 3520 (b), *ν*(C=N) 1581(s), *ν*(C–N) 1342 (s), ν_{as}(SO$_2$) 1249(s), ν_s(SO$_2$) 1139(s).

7*[NiHL] · H$_2$O*: Green solid. Yield 67%. M.p. 228 °C. *Anal.* Calc. for $C_{31}H_{32}N_4O_6S_2Ni$: C, 54.80; H, 4.75; N, 8.25; Ni, 8.64. Found: C, 55.15; H, 5.27; N, 8.76; Ni, 8.41%. IR (NaCl, cm^{-1}): *ν*(O–H) 3522 (b), *ν*(C=N) 1635(s), *ν*(C–N) 1290 (s), ν_{as}(SO$_2$) 1263(s), ν_s(SO$_2$) 1132(s).

2.3.2. [Cu$_2$L(X)], where X = CH$_3$COO$^-$, CH$_2$ClCOO$^-$, CCl$_3$COO$^-$, CF$_3$COO$^-$

To a hot suspension of ligand (0.0002 M) in 10 ml of absolute methanol the copper(II) salt (0.0004 M) solution in methanol was added. For the complexes with X = CH$_3$COO$^-$, CF$_3$COO$^-$, CCl$_3$COO$^-$ the precipitate was formed within 10 min, but for X = CH$_2$ClCOO$^-$ the precipitate was formed after half-hour boiling. The solutions of complexes were refluxed for 3–5 h, then filtered hot, followed by the boiling of complexes with X = CF$_3$COO$^-$, CCl$_3$COO$^-$ in 10 ml ethanol for purification. The compound with X = CH$_2$ClCOO$^-$ is partially soluble in this solvent.

[Cu$_2$L(CH$_3$COO)]: Green solid. Yield 81%. M.p. > 250 °C. *Anal.* Calc. for $C_{33}H_{32}O_7N_4S_2Cu_2$: C, 50.31; H, 4.09; N, 7.11; Cu, 16.13. Found: C, 49.91; H, 3.68; N, 6.65; Cu, 15.81%. IR (NaCl, cm^{-1}): *ν*(C=N) 1636(s), *ν*(C–N) 1294(s), ν_{as}(SO$_2$) 1250(s), ν_s(SO$_2$) 1141(s).

[Cu$_2$L(CH$_2$ClCOO)]: Green solid. Yield 74%. M.p. > 250 °C. *Anal.* Calc. for $C_{33}H_{31}O_7N_4S_2ClCu_2$: C, 48.22; H, 3.81; N, 6.84; Cu, 15.51. Found: C, 48.51; H, 4.23; N, 7.16; Cu, 15.96%. IR (NaCl, cm^{-1}): *ν*(C=N) 1642(s), *ν*(C–N) 1292(s), ν_{as}(SO$_2$) 1255(s), ν_s(SO$_2$) 1135(s).

[Cu$_2$L(CCl$_3$COO)]: Green solid. Yield 72%. M.p. > 250 °C. *Anal.* Calc. for $C_{33}H_{29}O_7N_4S_2Cl_3Cu_2$: C, 44.47; H, 3.35; N, 6.31; Cu, 14.34. Found: C, 44.83; H, 3.92; N, 5.96; Cu, 14.64%. IR (NaCl, cm^{-1}): *ν*(C=N) 1643(s), *ν*(C–N) 1285(s), ν_{as}(SO$_2$) 1264(s), ν_s(SO$_2$) 1137(s).

[Cu$_2$L(CF$_3$COO)]: Green solid. Yield 77%. M.p. > 250 °C. *Anal.* Calc. for $C_{33}H_{29}O_7N_4S_2F_3Cu_2$: C, 47.14; H, 3.46; N, 6.72; Cu, 15.18. Found: C, 46.85; H, 2.90; N, 7.04; Cu, 15.57%. IR (NaCl, cm^{-1}): *ν*(C=N) 1643(s), *ν*(C–N) 1290(s), ν_{as}(SO$_2$) 1250(s), ν_s(SO$_2$) 1137(s).

2.3.3. [Cu$_2$L(Pz)]

To a hot suspension of ligand (0.0002 M) in 10 ml methanol the solution of copper(II) acetate (0.0004 M) in 10 ml methanol was added followed by the addition of pyrazole (0.0004 M). The dark green solution was formed. In 5 min the complex has precipitated. The mixture was refluxed for 5 h, then filtered off and washed with methanol.

Green solid. Yield 71%. M.p. > 250 °C. *Anal.* Calc. for $C_{34}H_{32}O_5N_6S_2Cu_2$: C, 51.38; H, 4.06; N, 10.61; Cu, 16.05. Found: C, 50.93; H, 4.31; N, 10.22; Cu, 15.68%. IR (NaCl, cm^{-1}): *ν*(C=N) 1645(s), *ν*(C–N) 1290(s), ν_{as}(SO$_2$) 1263(s), ν_s(SO$_2$) 1139(s).

2.4. X-ray crystallography

Crystals of bis-azomethine and Co(II), Zn(II) complexes suitable for X-ray diffraction were grown up by slow evaporation of solutions in mixture C$_2$H$_5$OH and CH$_3$Cl (2:1). X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD in case of Zn(II) complex and Bruker SMART APEX II CCD diffractometer in case of Co(II) complex compound and free ligand, using graphite monochromated Mo K*α* radiation (= 0.71073 Å, *ω*-scans). Reflection intensities were integrated using SAINT software and adsorption correction was applied semi-empirically using SADABS program [50]. The structures was solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for not-hydrogen atoms. The OH and NH hydrogen atoms were located from the Fourier density synthesis and refined in isotropic approximation, for all other ones the positions were calculated from geometrical point of view. Analysis of Fourier density synthesis has revealed that in complexes solvate water molecule and OH-group are disordered by two positions with self occupancies factors (s.o.f) equal to 0.8, 0.2 and 0.7, 0.3 for OH and H$_2$O molecules, respectively. In the crystal structure of the ligand one of phenyl groups is disordered by two positions with equal occupancies. The hydrogen atom for disordered OH-group was located only for position with s.o.f. equal to 0.8. The hydrogen atom of OH-group for ¼ of methanol molecule was not located. The positions of all other hydrogen atoms were calculated geometrically. Crystal data and structure refinement parameters for ligand and Co(II) and Zn(II) complexes are given in Table 1. All calculations were performed using the SHELXTL software [51].

3. Results and discussion

3.1. Crystal structure of ligand

The molecular structure of H$_3$L is obtained from single crystal X-ray crystallographic studies. Selected bond distances and angles are listed in Table 2 and the ORTEP views are given in Fig. 2.

Table 1
Selected crystallographic data for [H_3L], [CoHL] · H_2O, [ZnHL] · H_2O

Compound	[H_3L]	[CoHL] · H_2O	[ZnHL] · H_2O
Empirical formula	$C_{31}H_{32}N_4O_5S_2$	$C_{31}H_{32}CoN_4O_6S_2$	$C_{31}H_{32}ZnN_4O_6S_2$
Formula weight	604.73	679.66	686.10
Temperature (K)	100(2)	100(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.0991(6)	8.9953(8)	9.0591(6)
b (Å)	12.0481(8)	16.7289(15)	16.7557(12)
c (Å)	15.9941(11)	20.4180(16)	20.2064(14)
α (°)	79.5800(10)	90	90
β (°)	82.8750(10)	90	90
γ (°)	71.8730(10)	90	90
V (Å^3)	1454.93(18)	3072.5(5)	3067.2(4)
Z	2	4	4
D_{calc} (Mg/m$^{3)}$	1.380	1.469	1.486
Absorption coefficient (mm^{-1})	0.231	0.745	0.988
$F(000)$	636	1412	1424
Crystal size (mm)			
0.40 × 0.20 × 0.20			
0.30 × 0.20 × 0.20			
0.40 × 0.20 × 0.20			
θ Range (°)	1.80–29.00	1.99–29.00.	1.58–27.16
Index ranges	$-10 \leqslant h \leqslant 11$, $-16 \leqslant k \leqslant 16$, $-21 \leqslant l \leqslant 21$	$-12 \leqslant h \leqslant 11$, $-16 \leqslant k \leqslant 22$, $-22 \leqslant l \leqslant 27$	$-11 \leqslant h \leqslant 11$, $-21 \leqslant k \leqslant 21$, $-21 \leqslant l \leqslant 25$
Reflections collected	16711	16457	31704
Independent reflections (R_{int})	7662 (0.0213)	8000 (0.0237)	6805 (0.0806)
Completeness to θ = 29.00° (%)	99.1	99.5	99.9[a]
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Maximum and minimum transmission	0.9552 and 0.9132	0.8653 and 0.8074	0.8269 and 0.6934
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	7662/0/413	8000/2/413	6805/2/413
Goodness-of-fit on F^2	1.030	1.051	1.015
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0497$, $wR_2 = 0.1240$	$R_1 = 0.0361$, $wR_2 = 0.0884$	$R_1 = 0.0427$, $wR_2 = 0.0935$
R indices (all data)	$R_1 = 0.0611$, $wR_2 = 0.1326$	$R_1 = 0.0411$, $wR_2 = 0.0914$	$R_1 = 0.0708$, $wR_2 = 0.1059$
Largest difference in peak and hole (e Å^{-3})	0.534 and −0.468	0.669 and −0.492	0.693 and −0.447

[a] Completeness to $\theta = 27.16°$ (%).

Bis-azomethine crystallizes in an asymmetric conformation due to flexibility of the propanol spacer. *o*-Aminobenzylidene fragments are individually close to planar with the evidence of strong intramolecular hydrogen bond $NH\cdots N_{az}$ (interatomic distances are $d(N(2)H\cdots N(1)) = 1.932$ Å; $d(N(2')H\cdots N(1')) = 1.914$ Å). Aminopropanol fragment have the following structure: one of the azomethine nitrogen atoms is placed close to the plane, formed by carbon atoms of the spacer (dihedral angle 172°), at the same time other one is out of this plane due to rotation along (OH)C–C(N) bond by 60°. OH-group participates in intermolecular hydrogen bong with the oxygen atom of the SO_2-group ($d(OH\cdots O) = 1.818$ Å) of another molecule, resulting in the formation of infinite supramolecular structure. It is worth noting that oxygen atoms of the second tosyl moiety is not involved in the analogous $H\cdots O$ hydrogen bond, but forms short intermolecular contact with proton of the methyl group of the neighbouring molecule. ($d(O\cdots HC) = 2.449$ Å).

Table 2
Selected bond distance (Å) and angles (°) for ligand [**H_3L**]

Bond lengths	
C(1)–C(2)	1.514(3)
C(1)–C(2’)	1.529(2)
C(1)–O(1)	1.428(2)
N(1)–C(3)	1.279(3)
N(1’)–C(3’)	1.278(2)
N(1)–C(2)	1.467(2)
N(1’)–C(2’)	1.460(2)
S(1)–O(2)	1.4362(15)
S(1)–O(3)	1.4351(15)
S(1’)–O(2’)	1.4415(16)
S(1’)–O(3’)	1.4225(15)
S(1)–N(2)	1.6244(17)
S(1’)–N(2’)	1.6218(16)
N(2)–C(5)	1.408(2)
N(2’)–C(5’)	1.407(2)
S(1)–C(10)	1.760(2)
S(1’)–C(10’)	1.757(2)
Bond angles	
O(1)–C(1)–C(2)	106.77(15)
O(1)–C(1)–C(2’)	112.12(15)
C(2)–C(1)–C(2’)	113.01(15)
N(2)–S(1)–C(10)	105.66(9)
C(5)–N(2)–S(1)	126.53(13)
C(6)–C(5)–N(2)	123.15(17)
N(2)–C(5)–C(4)	117.20(17)
C(11)–C(10)–S(1)	120.53(15)
C(15)–C(10)–S(1)	118.80(15)
N(2’)–S(1’)–C(10’)	108.69(9)
C(3’)–N(1’)–C(2’)	117.09(14)
C(5’)–N(2’)–S(1’)	127.43(13)
N(1’)–C(2’)–C(1)	111.92(14)
C(6’)–C(5’)–N(2’)	123.29(16)
N(2’)–C(5’)–C(4’)	116.75(15)
C(11A)–C(10’)–S(1’)	110.2(3)
C(15’)–C(10’)–S(1’)	117.3(2)
C(3)–N(1)–C(2)	118.29(17)
N(1)–C(2)–C(1)	108.10(15)

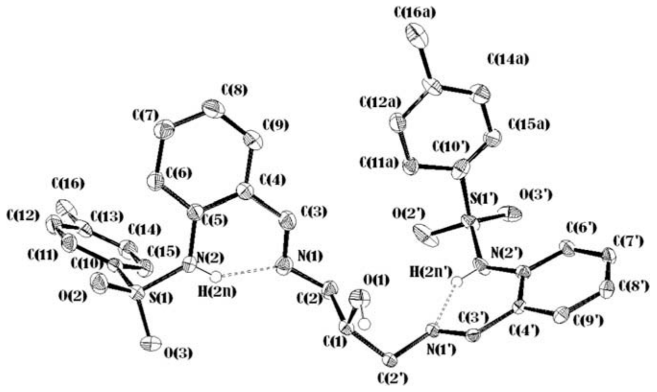

Fig. 2. Molecular structure of ligand H_3L (50% probability).

Planes of the benzylidene fragment and phenyl ring of the tosyl moiety are nearly mutually perpendicular with the angle 97° between them. Configuration of the bonds around amine nitrogen is distorted pyramidal, bonds C–N and N–H lies in the plane of the benzylidene fragment, but N–SO_2 bond is turned from it by the angle 19°. Thus, no conjugation of the benzylidene fragment and S═O bond is observed.

3.2. Mononuclear complexes of Zn(II), Co(II), Ni(II)

The mononuclear type **1** metallochelates (Fig. 3) with the general formula [MHL], where HL^{2-} is the doubly deprotonated ligand

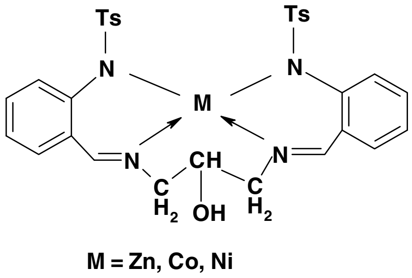

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Fig. 3. Mononuclear Zn(II), Co(II), Ni(II) complexes.

form have been obtained by the reaction between bis-azomethine ligand and Zn(II), Co(II), Ni(II) salts. Similar complexes based on bis-azomethines of hydroxycarbonyl compounds are known to have polynuclear structure [24–28].

3.2.1. Infrared spectroscopy of Zn(II), Co(II), Ni(II) complexes

In IR-spectra of Zn(II), Co(II), Ni(II) complexes the disappearance of absorption band corresponding to bond stretches of NH-groups (3278 cm^{-1} region) is observed in comparison with the spectra of ligand whereas the absorption band corresponding to OH-group stretches (3520–3525 cm^{-1} region) is preserved. The latter allow to conclude that in these coordination compounds the OH-group of diaminopropanol fragment doesn't take part in coordination. The absorption band of ν(C═N) bond stretches is observed in 1639 cm^{-1} region whereas the absorption band ν(C–N) group of diaminopropanol fragment is shifted to low-frequency region (1289 cm^{-1}) that indicates the coordination of nitrogen atom to the metal ion. The symmetric and asymmetric bond stretches of SO_2-group are shifted to low-frequency region on 20 cm^{-1} in comparison with the spectra of ligand and observed at 1135 cm^{-1} and 1263 cm^{-1} correspondingly.

The molecular structures of the Zn(II) and Co(II) complexes are established by X-ray analysis.

3.2.2. X-ray structures determination of [CoHL] · H_2O, [ZnHL] · H_2O

The crystal structure of [CoHL] · H_2O is shown in Fig. 4. Selected bond distances and angles are listed in Table 3.

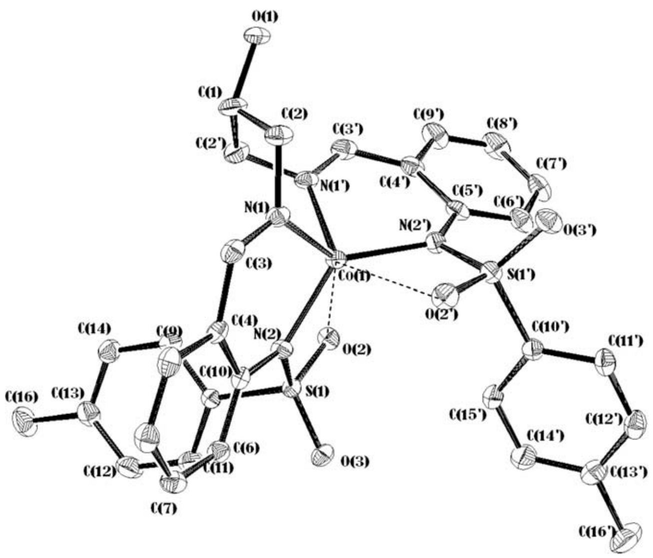


Fig. 4. Molecular structure of Co(II) complex (50% probability).

Table 3
Selected bond distance (Å) and angles (°) for [CoHL] · H_2O, [ZnHL] · H_2O

	[CoHL] · H_2O		[ZnHL] · H_2O
Bond lengths			
Co(1)–N(2')	1.977(2)	Zn(1)–N(2)	1.971(3)
Co(1)–N(2)	1.9797(19)	Zn(1)–N(2')	1.977(3)
Co(1)–N(1')	2.006(2)	Zn(1)–N(1)	2.026(3)
Co(1)–N(1)	2.017(2)	Zn(1)–N(1')	2.036(3)
Bond angles			
N(2')–Co(1)–N(2)	130.78(8)	N(2)–Zn(1)–N(2')	129.70(13)
N(2')–Co(1)–N(1')	91.50(9)	N(2)–Zn(1)–N(1)	91.51(13)
N(2)–Co(1)–N(1')	123.17(8)	N(2')–Zn(1)–N(1)	128.39(13)
N(2')–Co(1)–N(1)	127.68(8)	N(2)–Zn(1)–N(1')	123.16(13)
N(2)–Co(1)–N(1)	90.19(8)	N(2')–Zn(1)–N(1')	91.43(14)
N(1')–Co(1)–N(1)	88.77(9)	N(1)–Zn(1)–N(1')	87.87(14)
C(3')–N(1')–Co(1)	125.58(18)	C(3')–N(1')–Zn(1)	124.8(3)
C(2')–N(1')–Co(1)	114.62(16)	C(2')–N(1')–Zn(1)	114.4(3)
C(5')–N(2')–Co(1)	126.18(16)	C(5')–N(2')–Zn(1)	125.6(3)
S(1')–N(2')–Co(1)	111.47(11)	S(1')–N(2')–Zn(1)	111.16(18)
C(5)–N(2)–Co(1)	128.68(15)	C(5)–N(2)–Zn(1)	127.0(2)
S(1)–N(2)–Co(1)	108.61(10)	S(1)–N(2)–Zn(1)	110.51(17)
C(3)–N(1)–Co(1)	126.21(16)	C(3)–N(1)–Zn(1)	124.6(3)
C(2)–N(1)–Co(1)	114.67(16)	C(2)–N(1)–Zn(1)	115.8(3)

In the Co(II) complex metal ion is surrounded by 4 nitrogen atoms (2 from azomethine and 2 from sulphamide fragments) in a distorted tetrahedral configuration. Angle between planes of chelate rings is 70° Alcoholic hydroxyl group does not participate in coordination. Bond distances between Co(II) and the nearest donor atoms are the following: 2.017 Å and 2.006 Å for azomethine nitrogen atoms, and 1.980 Å and 1.977 Å in case of nitrogens of tosyl moieties. Oxygen atoms of sulpho-group are weakly coordinated to metal ion with rather long not equal interatomic distances Co···O═S (2.608 Å and 2.718 Å). Evidence of this interaction can be also found in the lengthening of the coordinated O═S bond compared to the non coordinated bond of the same group (1.454 Å and 1.445 Å correspondingly) and this bond in free ligand (1.436 Å). Four membered fragment Co–N–S═O is close to planar (folding along N···O line is only 6.3° and 5.6°).

Six membered chelate rings formed with Co(II) ion by benzylidene moieties are not planar and undergo typical distortions. Atoms N(2) and C(3) (N(2′) and C(3′)) lies in the plane of the aromatic ring. Plane of the chelate rings are folded along N(2)···C(3) line by angle 12.6° (7.7°) and along N(2)···N(1) line by 20.0° (16.3°). Chelate ring formed by aminopropanol spacer due to three sp^3-hybridizated carbon atoms adopts distorted bath conformation, with nitrogen atom of one azomethine fragment and carbon atom of the spacer in apical positions.

The crystal structure besides the molecules of the complex compounds is arranged by water molecules with molar ratio 1:1, which due to formation of intermolecular hydrogen bonds with donor centres of the complex molecules build up infinite hydrogen bond supramolecular pattern (Fig. 5). Protons of each water molecule interacts with oxygen atom of tosyl moiety of the first complex molecule (d(HOH···O═S) = 2.013 Å) and with oxygen atom of alcoholic hydroxyl group of the other molecule (d(HOH···OH) = 1.720 Å), at the same time oxygen atom of each water molecule is connected by hydrogen bond with the proton of the hydroxyl group proton of the first molecule of the complex (d(OH···OH_2) = 1.884 Å).

The X-ray analysis of zinc(II) complex has been carried out by our group in order to specify the structure of this complex being synthesized previously [45]. Our data practically coincide completely with the results shown in the cited work. The zinc(II) complex is isostructural with the cobalt(II) complex and has no any peculiarities compared with it. Bond distances between Zn(II) donor atoms are the following: 2.026 Å and 2.036 Å for azomethine

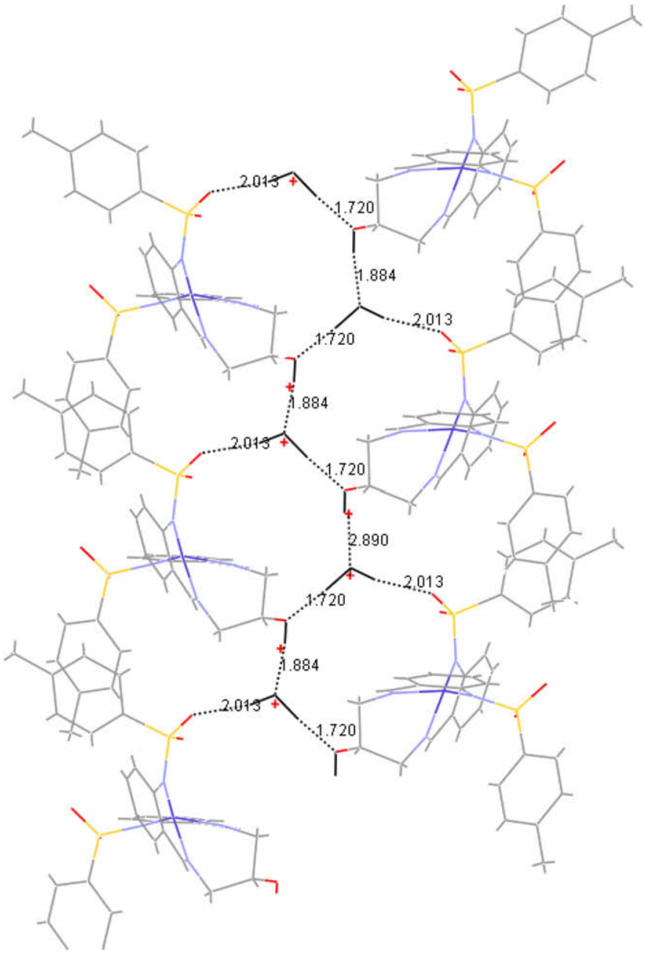


Fig. 5. Infinite hydrogen bond supramolecular structure in the crystal structure of Co(II) complex.

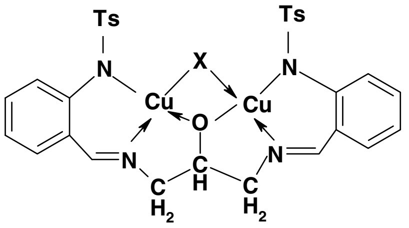
nitrogen atoms, and 1.971 Å and 1.977 Å in case of nitrogens of tosyl moieties. Angle between planes of chelate rings is 69°.

3.2.3. Magnetic properties

The study of magnetic properties of Ni(II) and Co(II) complexes revealed that these compounds exhibit trivial paramagnetism. The values of μ_{eff} at room temperature are 3.1 B.M. and 4.9 B.M. and practically do not change up to the temperature of liquid nitrogen (77.4 K). These values of μ_{eff} support the suggested non-planar structure of coordination unit, and as it is well-known [52] the range of 2.8–3.2 B.M. is characteristic for octahedral environment of nickel(II) ion. The octahedral coordination of nickel ion with **H_3L** ligand is taking place due to additional coordination of tosyl fragment of sulpho-group. This assumption is supported by the data of X-ray analysis of cobalt(II) complex (Fig. 5). In this compound the additional coordination of tosyl group's oxygen atom is observed. The axial coordination to the central ion obviously causes the essential orbital contribution in the resulting magnetic moment of Co^{2+} cation (4.9 B.M.) the spin-only value being equal 3.77 B.M. ($s = 3/2$). It is known that the octahedral Co^{2+} complexes as well as the complexes with tetrahedral-pyramidal configuration are characterized by the values of μ_{eff} in the range 4.7–5.1 B.M.

3.3. Binuclear Cu(II) complexes

The binuclear complexes (type **2**, $[Cu_2LX]$) with an asymmetrical exchange fragment (Fig. 6) have been obtained by the reaction between **H_3L** ligand and copper (II) salts.



X=CH_3COO, CH_2ClCOO, CCl_3COO, CF_3COO, Pz

2

Fig. 6. Binuclear Cu(II) complexes.

3.3.1. Infrared spectroscopy

In IR-spectra of copper (II) complexes the absorption bands of NH- and OH-groups disappear and the bands of C=N group bond stretches are shifted to lower frequencies on 20–30 cm^{-1}. The symmetric and asymmetric bond stretches of SO_2-group are shifted to low-frequency region on 20–40 cm^{-1} in comparison with the spectra of ligand. These bands are observed in the 1135–1141 cm^{-1} and 1250–1264 cm^{-1} region correspondingly.

3.3.2. Magnetic properties

The type **2** binuclear structure of copper (II) complexes is confirmed by the data of magnetic measurements (Table 4). All complexes exhibit the exchange antiferromagnetic interaction the strength of which is determined by the nature of bridging acyl or heterocyclic group included in an asymmetrical exchange fragment. The values of $2J$ exchange parameters calculated in terms of HDVV model [48] are shown in Table 4.

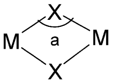
The analysis of these values has shown that for the complexes under discussion there is no strict correlation between $2J$ values and an electronic nature of substituents (halogen atom) in acetate bridge. Recently the similar correlation has been revealed for the Cu(II) binuclear metallochelates with ligands produced from condensation of salicylic aldehyde substituted derivatives with 1,3-diaminopropanol-2 [53]. It should be noted that the absence of similar correlation for the complexes under discussion is not surprising since one should take into account the existence of rather bulky tosyl substituents in the molecules of both ligand and complexes. The possibility of H-bond formation as well as sterical hindrances due to tosyl group with respect to bridging acetate group should result in distortion of exchange fragment's structure. Thus it is well-known that even small changes of bond angles in the exchange fragment  usually results in significant changes of exchange parameter's values [52,54]. In would be interesting to elucidate the influence of tosyl group having based on magneto-structural correlations for these complexes but unfortunately

Table 4
Magnetic properties of copper(II) binuclear complexes

Compound	X	T (K)	μ_{eff}[a] (B.M.)	$-2J$ (cm^{-1})
2	CH_3COO^-	295	1.71	121
		77.4	1.05	
2	CH_2ClCOO^-	296	1.97	76
		77.4	1.42	
2	CCl_3COO^-	294	1.74	153
		77.4	0.84	
2	CF_3COO^-	286	1.73	126
		77.4	1.3	
2	Pz	286	1.47	232
		77.4	0.78	

[a] The effective magnetic moments are calculated per one metal ion.

it is impossible to obtain them as monocrystals due to their poor solubility in the most organic solvents.

Thus, as well as for previously studied complexes the replacement of acetate bridge on heterocyclic (pyrazol) molecule leads to significant increase of antiferromagnetic exchange interaction. This phenomenon can be explained by increase in overlap integrals of copper(II) ion magnetic orbitals with molecular orbitals of heterocyclic fragment that usually results in strengthening of antiferromagnetism [52,54].

4. Supplementary material

CCDC 673858, 673859 and 673860 contain the supplementary crystallographic data for ligand, Co(II) and Zn(II) complexes. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] J. Sanmartin, M.R. Bermejo, A.M. Garia-Deibe, M. Maneiro, Polyhedron 19 (2000) 185.
[2] K. Bertoncello, G.D. Fallon, K.S. Murray, E.R.T. Tiekink, Inorg. Chem. 30 (1991) 3562.
[3] M. Mikuriya, K. Minowa, J.W. Lim, Bull. Chem. Soc. Jpn. 74 (2001) 331.
[4] J. Lisowski, P. Starynowicz, Polyhedron 18 (1999) 443.
[5] F. Averseng, P.G. Lacroix, I. Malfant, N. Perisse, C. Lepetit, K. Nakatani, Inorg. Chem. 40 (2001) 3797.
[6] B.B. Trivedi, P.K. Bhattacharya, J. Chem, Soc. Res. Synop. (1992) 300.
[7] V.V. Lukov, V.A. Kogan, Yu.P. Tupolova, L.D. Popov, I.E. Gevorkyan, V.V. Tkachev, G.V. Shilov, D.D. Makitova, Russ. J. Inorg. Chem. 49 (2004) 1993.
[8] L. Stelzig, A. Steiner, B. Chansou, J.-P. Tuchagues, Chem. Commun. (1998) 771.
[9] Y.-C. Chou, S.-F. Huang, R. Koner, G.-H. Lee, Y. Wang, S. Mohanta, H.-H. Wei, Inorg. Chem. 43 (2004) 2759.
[10] Y. Nishida, S. Kida, Chem. Soc. Dalton Trans. (1986) 2633.
[11] B. Mabad, P. Cassoux, J.-P. Tuchagues, D.N. Hendrickson, Inorg. Chem. 25 (1986) 1420.
[12] M. Mikuriya, T. Sasaki, A. Anjiki, S. Ikenoue, T. Tokii, Bull. Chem. Soc. Jpn. 65 (1992) 334.
[13] M. Mikuriya, Y. Yamato, T. Tokii, Bull. Chem. Soc. Jpn. 65 (1992) 2624.
[14] M. Mikuriya, K. Minowa, N. Nagao, Bull. Chem. Soc. Jpn. 74 (2001) 871.
[15] H. Kara, Y. Elerman, A. Elmali, Z. Naturforsch., B: Chem. Sci. 58 (2003) 955.
[16] V.A. Kogan, V.V. Lukov, V.M. Novotorsev, I.L. Eremenko, G.G. Alexandrov, Russ. Chem. Bull., Int. Ed. 54 (2005) 600.
[17] Y. Nishida, S. Kida, Inorg. Chem. 27 (1988) 447.
[18] A. Elmali, C.T. Zeyrek, Y. Elerman, J. Mol. Struct. 693 (2004) 225.
[19] A. Mukherjee, M.K. Saha, M. Nethaji, A.R. Chakravarty, Polyhedron 23 (2004) 2177.
[20] A. Mukherjee, M.K. Saha, M. Nethaji, A.R. Chakravarty, Chem. Commun. (2004) 716.
[21] S.-F. Huang, Y.-C. Chou, P. Misra, C.-J. Lee, S. Mohanta, H.-H. Wei, Inorg. Chim. Acta 357 (2004) 1627.
[22] E. Kavlakoglu, A. Elmali, Y. Elerman, I. Svoboda, Polyhedron 21 (2002) 1539.
[23] A. Mukherjee, R. Raghunathan, M.K. Saha, M. Nethaji, S. Ramasesha, A.R. Chakravarty, Chem. Eur. J. 11 (2005) 3087.
[24] P.E. Kruger, B. Moubaraki, G.D. Fallon, K.S. Murray, J. Chem. Soc., Dalton. Trans. (2000) 713.
[25] S. Uhlenbrock, R. Wegner, B. Krebs, J. Chem. Soc., Dalton Trans. (1996) 3731.
[26] M. Mikuriya, K. Minowa, Inorg. Chem. Commun. 3 (2000) 227.
[27] M. Mikuriya, K. Minowa, N. Nagao, Inorg. Chem. Commun. 4 (2001) 441.
[28] M. Mikuriya, N. Nagao, K. Kondo, Chem. Lett. 29 (2000) 516.
[29] M. Mikuriya, K. Majima, Y. Yamato, Chem. Lett. 21 (1992) 1929.
[30] C.-J. Lee, S.-C. Cheng, H.-H. Lin, H.-H. Wei, Inorg. Chem. Commun. 8 (2005) 235.
[31] A. Mukherjee, I. Rudra, M. Nethaji, S. Ramasesha, A.R. Chakravarty, Inorg. Chem. 42 (2003) 463.
[32] Y. Song, C. Massera, O. Roubear, P. Gamez, A.M.M. Lanfredi, J. Reedijk, Inorg. Chem. 43 (2004) 6842.
[33] A. Mukherjee, I. Rudra, S.G. Naik, M. Nethaji, S. Ramasesha, A.R. Chakravarty, Inorg. Chem. 42 (2003) 5660.
[34] A. Gelasco, M.L. Kirk, J.W. Kampf, V.L. Pecoraro, Inorg. Chem. 36 (1997) 1829.
[35] Yu.P. Tupolova, V.A. Kogan, V.V. Lukov, L.D. Popov, I.E. Gevorkyan, Transition Met. Chem. 32 (2007) 656.
[36] V.A. Alekseenko, A.S. Burlov, B.M. Bolotin, O.A. Lukova, B.C. Nedzveckiy, A.D. Garnovskii, Russ. J. Coord. Chem. 17 (1991) 76.
[37] D.A. Garnovskii, M.F.C. Guedes da Silva, M.N. Kopylovich, A.D. Garnovskii, J.J.R. Frausto da Silva, Polyhedron 22 (2003) 1335.
[38] A.S. Burlov, V.N. Ikorskii, A.I. Uraev, Yu.V. Koshchienko, I.V. Vasil'chenko, D.A. Garnovskii, G.S. Borodkin, S.A. Nikolaevskii, A.D. Garnovskii, Russ. J. Inorg. Chem. 76 (2006) 1337.
[39] A.S. Burlov, D.A. Garnovskii, L.I. Kuznecova, N.V. Volobyshko, O.Yu. Korshunov, O.T. Asmaev, B.I. Xarisov, L.M. Blanko, A.D. Garnovskii, Russ. J. Coord. Chem. 24 (1998) 915.
[40] M. Vazquez, M.R. Bermejo, J. Sanmartin, A.M. Garcia-Deibe, C. Lodeiro, J. Mahia, J. Chem. Soc., Dalton Trans. (2002) 870.
[41] M.R. Bermejo, J. Sanmartin, A.M. Garcia-Deibe, M. Fondo, F. Novio, D. Navarro, Inorg. Chim. Acta 347 (2003) 53.
[42] A.M. Garcia-Deibe, J.S. Matalobos, M. Fondo, M. Vazquez, M.R. Bermejo, Inorg. Chim. Acta 357 (2004) 2561.
[43] A.S. Burlov, D.A. Garnovskii, V.A. Alekseenko, A.E. Mistryukov, V.S. Sergienko, V.G. Zaletov, V.V. Lukov, A.V. Xoxlov, M.A. Poray-Koshic, Russ. J. Coord. Chem. 18 (1992) 859.
[44] A.S. Burlov, L.I. Kuznecova, S.I. Adamova, V.P. Kurbatov, G.I. Bondarenko, A.D. Garnovskii, Russ. J. Gen. Chem. 79 (2000) 804.
[45] M.R. Bermejo, M. Vazquez, J. Sanmartin, A.M. Garcia-Deibe, M. Fondo, C. Lodeiro, New J. Chem. 26 (2002) 1365.
[46] R.L. Carlin, Magnetochemistry, Springer-Verlag, Berlin, Heidelberg, 1986.
[47] O. Kahn, Molecular Magnetism, VCH Publishers, Inc., New York, 1983.
[48] B. Bleaney, K.D. Bowers, Proc. Roy. Soc. London, Ser. A 214 (1952) 451.
[49] M.D. Judd, B.A. Plunkett, M.J. Pope, J. Therm. Anal. 9 (1976) 83.
[50] G.M. Sheldrick, SADABS, Bruker AXS Inc., Madison, WI-53719, USA, 1997.
[51] G.M. Sheldrick, SHELXTL-97, Version 5.10, Bruker AXS Inc., Madison, WI-53719, USA.
[52] V.T. Kalinnikov, Yu.V. Rakitin, Modern Magnetochemistry, Science, St-Petrsburg, 1994.
[53] V.A. Kogan, V.V. Lukov, V.M. Novotorsev, Yu.P. Tupolova, I.E. Gevorkyan, Russ. J. Coord. Chem. 31 (2005) 376.
[54] Yu.V. Rakitin, The Molecular Structure and Chemical Bond, VINITI, Moscow, 1986.