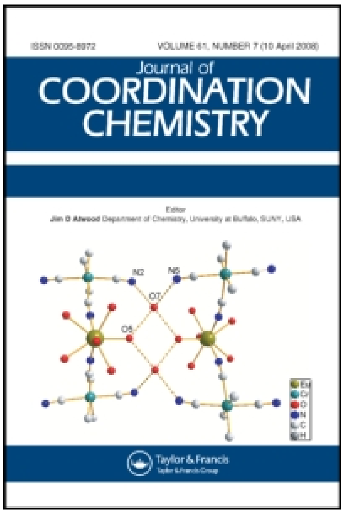

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CONVENTIONAL CHEMICAL AND DIRECT ELECTROCHEMICAL SYNTHESIS OF THE CHELATES OF 2-(N-TOSYLAMINE)BENZALDOXIME AND 2-(N-TOSYLAMINE)BENZAL-O-METHYLOXIME

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CONVENTIONAL CHEMICAL AND DIRECT ELECTROCHEMICAL SYNTHESIS OF THE CHELATES OF 2-(N-TOSYLAMINE)BENZALDOXIME AND 2-(N-TOSYLAMINE)BENZAL-O-METHYLOXIME

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The chemical and direct electrochemical syntheses of copper, cobalt, nickel and zinc chelates of 2-[N-tosylamine)benzaldoxime (L^1H_2) and 2-[N-tosylamine)benzal-O-methyloxime (L^2H) are reported. On the basis of the elemental analyse IR and EPR spectra and magnetic properties, dimeric structures ML are suggested from L^1H_2 under the conditions of the chemical synthesis, while electrosynthesis leads to the monomeric complexes $M(L^1H)_2$. Using L^2H as a ligand, only the chelates ML^2_2 are formed, regardless of the method of synthesis.

The copper dimers CuL^1 have antiferromagnetic properties, while the chelates $M(L^1H)_2$ and ML^2_2 have normal magnetic moments. In agreement with the magnetic properties and literature data on structures of four-coordinate complexes a tetrahedral structure is assigned.

Keywords: Chemical synthesis; electrochemical synthesis; 2-[N-tosylamine)benzaldoxime; 2-[N-tosylamine)benzal-O-methyloxime; IR and EPR spectra; magnetochemistry

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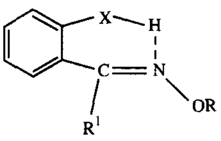
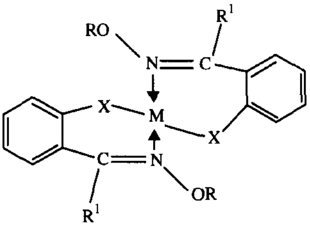
INTRODUCTION

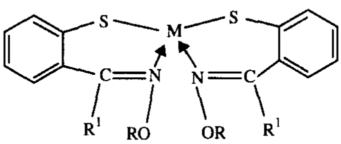
Among the metal complexes of oximes **1**,[1–8] only the chelates of 2-[N-tosylamine)benzaldoxime (**1**, X = NTs, R = R^1 = H) and its O-methyl derivative (**1**, X = NTs, R = CH$_3$, R^1 = H), have not been studied.



1
X=NTs, O, S
R,R^1 = H, Alk, Ar



2
X = NTs, O



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Although complexes with different localization of the coordination bonds could be formed with oxime ligands,[1,6,8] the monomeric *trans*-planar **2** (X = O)[2] and *cis*-planar **3** (X = S) structures[5] are most typical for the ligands **1**. In addition to *trans*-planar (M = Pd) structures,[9] distorted octahedral could be formed in the complexes **2** at the expense of the intermolecular M–O coordination (M = Cu).[10,11]

In order to study more deeply the complexes obtained from the ligands **1**, the ligand system (X = NTs; R = H, Me; R^1 = H) has been examined.

EXPERIMENTAL

Synthesis of the Ligands

2-[N-Tosylamine)benzaldoxime (L^1H_2) Sodium acetate (1.37 g, 0.01 mol) is added to a methanol solution (50 mL) of 2-(N-tosylamino)-benzaldehyde (2.75 g, 0.01 mol) and hydroxylamine hydrochloride (2.1 g, 0.01 mol). The reaction mixture is refluxed 10 min, then cooled and diluted with water

(1 : 1). The obtained solid is filtered and recrystallized from benzene. *Physical properties*: colorless crystals, m.p. 136–137°C. *Elemental analysis*: Found, %: C, 58.22; H, 4.84; N, 9.68. Calculated for $C_{14}H_{14}N_2O_3S$, %: C, 57.92; H, 4.86; N, 9.45.

2-[*N-Tosylamine)benzal-O-methyloxime* (*L^2H*) It is obtained from the same synthetic conditions. *Physical properties*: colorless crystals (recrystallized from benzene), m.p. 125–126°C. *Elemental analysis*: Found, %: C, 59.35; H, 5.21; N, 9.46. Calculated for $C_{15}H_{16}N_2O_3S$, %: C, 59.19; H, 5.30; N, 9.20.

Conventional Synthesis of the Complexes

Copper, nickel, cobalt or zinc acetates (0.01 mol) are added to a methanol solution (50 mL) of the oximes L^1H_2 or L^2H (0.01 mol). The reaction mixture is boiled for 30 min, then cooled; the formed solid is filtered, washed with hot ethanol (3 × 5 mL) and dried in a vacuum oven at 100°C.

The copper complex of L^1H_2 is also obtained in the molar ratio "copper acetate : ligand" 1 : 2 in basic medium (a pH ~ 9 is reached by addition of a methanol solution of KOH (1 mL) to the reaction mixture). The same complex is formed starting from $CuCl_2$ in the molar ratio of the initial components 1 : 1 and pH ~ 9.

Electrochemical Synthesis of the Complexes

Direct electrochemical synthesis is carried out according to the methods described in Refs. 13–17. Sheets of copper, nickel or zinc are used as sacrificial anodes, and platinum is used as the cathode. Methanol is used as a solvent and $LiClO_4$ – as a supporting electrolyte. The ligand (0.5 g) is dissolved in methanol (30 mL) by heating and then the obtained solution is cooled to room temperature. The electrolysis is carried out during 1 h (current: 20 mA; applied voltage: 20–30 V). The formed solid is filtered, washed by hot methanol (3 × 5 mL) and dried in air. The analytical and related data of the synthesized complexes are presented in Table I.

Physico-chemical Study

Elemental analysis (C,H,N,S,M) is carried out in a microanalyzer CARBO-ERBA 1108. The IR spectra were obtained in a spectrophotometer PERKIN-ELMER 180 (Table II). The magnetic study in the solid phase at 77–298 K is carried out by Faraday's method (Table III). The EPR spectra are obtained under the same conditions in the Zeiss ER-9 (Table IV).

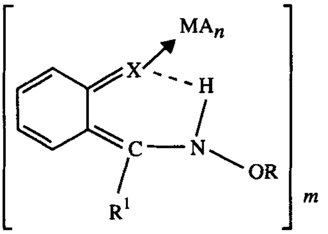
TABLE I Elemental analysis and related data of synthesized metal chelates

No.	Ligand	Composition	Formula	*Elem. anal. data (found/calc., %)*					Color	M.p. (°C)	μ_{eff}
		M : L (medium)		*C*	*H*	*N*	*S*	*M*			B.M. (*T*, K)
1	H_2L^1	CuL^1	$C_{14}H_{13}N_2O_3SCu$	48.47	3.50	7.43	9.65	17.60	Brown	> 250 dec.	1.36 (288)
		1 : 1 (neutr.)		47.65	3.68	7.93	9.09	18.05			0.82 (83)
2	H_2L^1	CuL^1	$C_{14}H_{13}N_2O_3SCu$	46.95	3.05	8.45	8.70	18.95	Brown	> 250 dec.	
		1 : 1 (acid.)		47.65	3.68	7.93	9.09	18.05			
3	H_2L^1	CuL^1	$C_{14}H_{13}N_2O_3SCu$	48.20	3.67	7.53	8.46	18.81	Brown	> 250 dec.	
		1 : 2 (basic)		47.65	3.68	7.93	9.09	18.05			
4	H_2L^1	CuL^1	$C_{14}H_{13}N_2O_3SCu$	48.15	3.92	7.53	9.87	18.90	Brown	> 250 dec.	1.48 (288)
		1 : 1 (fr. $CuCl_2$)		47.65	3.68	7.93	9.09	18.05			0.87 (82)
5	H_2L^1	CuL^1	$C_{14}H_{13}N_2O_3SCu$	48.47	3.71	7.53	8.40	18.95	Brown	> 250 dec.	1.33 (286)
		(recr. with Py)		47.65	3.68	7.93	9.09	18.05			1.13 (80)
6	H_2L^1	CuL^1_2*	$C_{28}H_{26}N_4O_6S_2Cu$	53.01	4.81	9.07	10.50	10.25	Red-brown	207	2.20 (293)
				52.37	4.08	8.72	9.99	9.89			
7	H_2L^1	NiL^1_2*	$C_{28}H_{26}N_4O_6S_2Ni$	52.42	4.91	8.44	9.57	8.90	Green	> 250	3.04 (289)
				52.76	4.11	8.79	10.06	9.20			
8	H_2L^1	ZnL^1_2*	$C_{28}H_{26}N_4O_6S_2Zn$	52.98	4.07	9.20	9.48	11.00	White	> 250	
				52.22	4.03	8.70	9.95	10.15			
9	HL^2	CuL^2_2	$C_{30}H_{30}N_4O_6S_2Cu$	54.05	4.29	8.10	9.27	9.71	Red-brown	> 250	2.20 (296)
				53.76	4.51	8.36	9.56	9.49			1.91 (78)
10	HL^2	NiL^2_2	$C_{30}H_{30}N_4O_6S_2Ni$	54.36	4.64	8.30	9.32	8.41	Green	278	3.39 (297)
				54.15	4.54	8.42	9.63	8.83			
11	HL^2	CoL^2_2	$C_{30}H_{30}N_4O_6S_2Co$	54.61	4.90	8.20	9.33	8.45	Red-brown	> 250	4.57 (297)
				54.13	4.54	8.42	9.62	8.86			4.33 (78)
12	HL^2	CuL^2_2*	$C_{30}H_{30}N_4O_6S_2Cu$	53.96	4.60	8.64	9.31	9.75	Red-brown	> 250	2.04 (289)
				53.76	4.51	8.36	9.56	9.49			
13	HL^2	NiL^2_2*	$C_{30}H_{30}N_4O_6S_2Ni$	54.40	4.62	8.50	9.34	8.49	Green	> 250	3.37 (289)
				54.15	4.51	8.42	9.63	8.83			

* Complexes electrochemically obtained from elemental metals.

RESULTS AND DISCUSSION

The oximes[1–8] could be considered as ambidentate ligands,[18] which connect metal ions in several ways. In addition to formation of the standard chelate types **2** and **3** (universally adopted) for the ligand systems **1**, it is necessary to consider the possibility of formation of the molecular adduct **4**. Such complexes are formed mostly from metal halides ($MHal_n$) in non-aqueous media.[18–21]



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X, R, R^1 (see 1); A = Hal, NO_2, NCY (Y = O, S, Se); $m, n = 1–5$

In order to carry out a selective (controlled) synthesis of chelates of the type **2** (X = NTs) and molecular complexes of the type **4** (X = NTs), we have used metal acetates and chlorides in the conventional synthetic methods as well as zero-valent bulk metals in the direct electrosynthesis.

The elemental analysis data (Table I) show that the complexes ML^1 (M = Cu) are formed from the ligand L^1H_2 and copper acetate or chloride, while the electrosynthesis leads to the complex compounds of the types $M(L^1H)_2$. Using the ligand L^2H, the complexes ML^2_2 (where M = Cu, Ni, Co, Zn) have been obtained from chemical or electrochemical synthesis (Table I). The structures of the synthesized compounds are discussed from the IR and EPR spectra, as well as the magnetic properties.

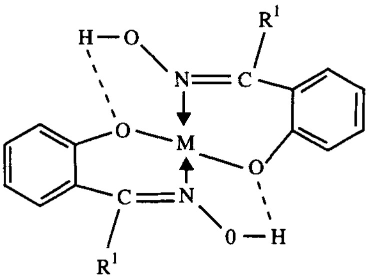
The frequencies of the valence oscillations of the C=N bond are observed in the spectra of the ligands and complexes, $1620\,cm^{-1}$ (in the spectrum of L^1H_2), $1600\,cm^{-1}$ (in the spectrum of L^2H) and $1583–1606\,cm^{-1}$ (in the spectra of the complexes), (Table II). A decrease of these frequencies is caused, as for other azomethinic complexes,[22,23] by bonding between the nitrogen atom of the chelating C=N group with the metal atom. The chelate formation could be confirmed by disappearance of the frequencies of the valence oscillations of the NH ($3060\,cm^{-1}$) and OH groups ($3393\,cm^{-1}$) in the complexes ML^1 (ligand **1**, X = NTs, R = R^1 = H).

TABLE II IR spectral data of the ligands and their metal complexes

No.	*Compound*	*Composition* (*medium*)	ν(OH) (cm^{-1})	ν(NH) (cm^{-1})	ν(C=N) (cm^{-1})	$\nu_{as}(SO_2)$ (cm^{-1})	$\nu_s(SO_2)$ (cm^{-1})	ν(N–O) (cm^{-1})
	H_2L^1		3393	3060	1620 w, 1593 w	1313vs	1140vs	986vs
1	CuL^1	1 : 1 (neutr.)		1606m, 1587m	1276s	1126vs	1007s	
2	CuL^1	1 : 1 (acid.)		1600m, 1587m	1276s	1126vs	1007s	
3	CuL^1	1 : 2 (basic)		1600m, 1587m	1276s	1126vs	1006s	
4	CuL^1	1 : 1 (fr. $CuCl_2$)		1600m, 1587m	1276s	1126vs	1007s	
5	CuL^1	(recr. from Py)		1600m, 1587m	1276s	1126vs	1007s, 1013s	
6	CuL_2^1*	1 : 2		1583vs	1287vs, 1274vs	1120vs	1007m	
7	NiL_2^1*	1 : 2		1583vs	1287vs, 1274vs	1117vs	1002m, 1020m	
8	ZnL_2^1*	1 : 2		1600m, 1537m	1287vs, 1273vs	1120vs	1002s, 1020vs	
	HL^2		3313br		1600m	1280vs	1146vs	906s, 967m
9	CuL_2^2	1 : 2		1593s	1280vs	1126vs	1020m	
10	NiL_2^2	1 : 2		1595s	1273vs	1121vs	953s, 1026s	
11	CoL_2^2	1 : 2		1596s	1273vs	1126vs	947s, 1030m	
12	CuL_2^2*	1 : 2		1590vs	1276vs	1121vs	940s, 1020m	
13	NiL_2^2*	1 : 2		1590vs	1270vs	1121vs	950s, 1020vs	

* Complexes electrochemically obtained.

Similar IR spectra are observed in the complexes ML^1_2, obtained from the ligand **1** (X = NTs, R = Me, R^1 = H) by chemical and electrochemical methods. The frequencies of the OH group are also absent in the examined region (LiF) of the IR spectra of the electrochemically synthesized chelates $M(L^1H)_2$ (ligand **1**, X = NTs, R = R^1 = H). This effect was observed earlier for crystal samples of the complexes of salicylidenoximes[2] and could be explained by the presence of a strong intra-molecular hydrogen bond.[2]



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However, in the case **2** (X = NTs), this structural type cannot exist; the lack of definition of the frequencies of the OH group could be explained by the presence of an inter-molecular OH···O bond with the oxygen atom of the oxime fragment.

The IR spectra of the complexes obtained from copper acetates and chlorides are very similar (Table II), excluding existence of the molecular complex 4, which could be formed as a result of interaction between the ligands and $CuCl_2$.[19-21] The frequencies of the NO group of the oxime fragment (Table II) are observed at 986 cm^{-1} (ligand L^1H_2), 906 and 967 cm^{-1} (ligand L^2H), and 940–1030 cm^{-1} (complexes); this result coincides with the reported data on salicylidenaldoximes.[24] The symmetric and asymmetric oscillations of the SO_2 group decrease (Table II), which also agrees with the reported data,[23,25] related to participation of the oxygen atom of the tosyl fragment in bonding with the metal.[23,25]

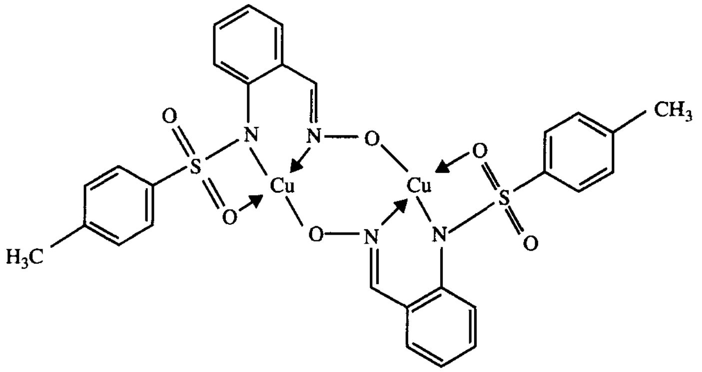
The magnetic properties of the complexes CuL^1 in the temperature region 80–300 K are presented in Table III. Independent of the synthetic method, at room temperature the effective magnetic moments of all the metal chelates have values lower than expected for spin. Decreasing magnitudes with decreasing temperature confirms the presence of an exchange antiferromagnetic interaction between copper ions. Taking into account the peculiarities of the structure of the ligand system of type **1** (X = NTs,

TABLE III Magnetic properties of copper complexes $(\mathrm{CuL}^1)_2$

a. Obtained from copper acetate in neutral medium (compound 1)											
T, K	297.0	272.6	250.7	206.0	185.9	151.7	128.0	112.0	99.5	78.0	
$\chi_\mu^{\prime\mathrm{exp}}\cdot 10^6$ (cm^3/mol)	2302	2412	2530	2838	2973	3220	3394	3375	3295	2940	
$\mu_{\mathrm{eff}}^{\prime\mathrm{exp.}}$, B.M.	1.65	1.62	1.59	1.53	1.49	1.40	1.32	1.23	1.14	0.96	
$\chi_\mu^{\prime\mathrm{teor.}}\cdot 10^6$ (cm^3/mol)	2249	2386	2524	2844	3001	3262	3387	3396	3320	2884	
$\mu_{\mathrm{eff}}^{\prime\mathrm{teor.}}$, B.M.	1.63	1.61	1.59	1.53	1.49	1.41	1.32	1.23	1.15	0.95	
$2J = -132\,\mathrm{cm}^{-1}$, $g = 2.03$, $r = 1.2\%$											
b. Obtained from copper acetate in acidic medium (compound 2)											
T, K	290.0	261.0	232.0	201.0	177.0	141.0	99.0	91.0	82.0		
$\chi_\mu^{\prime\mathrm{exp}}\cdot 10^6$ (cm3/mol)	1556	1657	1657	1757	1757	1757	2058	2159	2460		
$\mu_{\mathrm{eff}}^{\prime\mathrm{exp.}}$, B.M.	1.35	1.32	1.25	1.19	1.11	1.00	0.90	0.90	0.90		
c. Obtained from copper acetate in basic medium (compound 3)											
T, K	292.0	268.0	248.0	227.0	209.0	187.0	167.0	142.0	102.0	90.0	83.0
$\chi_\mu^{\prime\mathrm{exp}}\cdot 10^6$ (cm^3/mol)	1836.3	1836.3	1836.3	1933.9	1933.9	2031.4	2031.4	2031.4	2031.4	2031.4	2031.4
$\mu_{\mathrm{eff}}^{\prime\mathrm{exp.}}$, B.M.	1.46	1.40	1.35	1.33	1.27	1.23	1.16	1.07	0.91	0.86	0.82
$\chi_\mu^{\prime\mathrm{teor.}}\cdot 10^6$ (cm^3/mol)	1309.1	1864.4	1911.5	1954.8	1934.0	2005.3	2006.5	1932.3	1955.6	2004.1	2063.1
$\mu_{\mathrm{eff}}^{\prime\mathrm{teor.}}$, B.M.	1.45	1.41	1.38	1.33	1.29	1.22	1.16	1.06	0.89	0.85	0.83
$2J = -200\,\mathrm{cm}^{-1}$, $g = 2.00$, $r = 2.28\%$, $f = 19\%$											
d. Obtained from copper chloride (compound 4)											
T, K	288.0	272.0	250.0	218.5	203.0	182.0	121.0	99.0	88.0	82.0	
$\chi_\mu^{\prime\mathrm{exp}}\cdot 10^6$(cm^3/mol)	1895	1895	1997	2007	2110	2190	2140	2130	2145	2180	
$\mu_{\mathrm{eff}}^{\prime\mathrm{exp.}}$, B.M.	1.48	1.44	1.41	1.35	1.31	1.14	1.02	0.92	0.87	0.85	
$\chi_\mu^{\prime\mathrm{teor}}\cdot 10^6$ (cm^3/mol)	1890	1939	2004	2090	2124	2158	2164	2124	2104	2133	
$\mu_{\mathrm{eff}}^{\prime\mathrm{teor.}}$, B.M.	1.48	1.45	1.42	1.35	1.31	1.13	1.01	0.91	0.87	0.84	
$2J = -258\,\mathrm{cm}^{-1}$, $g = 2.0$, $r = 1.0\%$, $f = 19\%$											
e. Obtained by recrystallization from a pyridine–methanol mixture (compound 5)											
T, K	286.0	261.0	236.0	216.0	188.0	166.5	141.0	86.0	80.0		
$\chi_\mu^{\prime\mathrm{exp}}\cdot 10^6$ (cm^3/mol)	770.5	770.5	805.6	805.6	945.7	1033.3	1156.0	1821.7	1997.0		
$\mu_{\mathrm{eff}}^{\prime\mathrm{exp.}}$, B.M.	1.33	1.27	1.23	1.18	1.19	1.17	1.14	1.12	1.13		

$\mu_{\mathrm{eff}}^{\prime\mathrm{exp.}}$ is an effective magnetic moment, calculated to one copper atom in the dimer.
$\mu_{\mathrm{eff}}^{\prime\mathrm{exp.}}$ is an effective magnetic moment, calculated to one copper atom in the dimer.

R = H), these magnetic properties could be explained by the existence of either dimer **6**, or polymeric structures.



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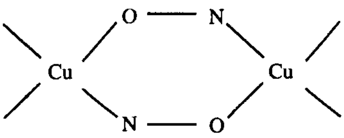
A satisfactory interpretation of the magnetochemical behavior of the complexes in the limits of the dimer isotropic model NDVV[26,27] has been reached only in the case of the copper chelate obtained from copper acetate in neutral medium ($2J = -132\,\mathrm{cm}^{-1}$, $g = 2.03$, $r = 1.2\%$). Evidently, only this compound corresponds to a structure of type **6**; antiferromagnetic character of the interaction could take place for exchange fragment[28] **7** (according to X-ray diffraction data, a similar fragment exists in the dimethylindium dimer):[29]



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According to the data in Table III for complexes prepared from copper chloride and from acetate in basic medium, it is necessary to use a large amount of the paramagnetic impurity ($f \sim 19\%$) in order to interpretate the magnetic properties in the limits of the isolated dimer model. It is not in agreement with the elemental analysis data of the synthesized complexes, or with the consistency of the results for recrystallized complexes (Table III, recrystallized from a mixture pyridine : methanol). It is possible that a polymer structure where the exchange interaction has not the isolated character of the pair exchange could exist for these metal chelates.

TABLE IV EPR spectral data of the obtained complexes

Compound	*Spectral parameters*		
	g_x	g_y	g_z
1. $(CuL^1)_2$	—	—	—
6. CuL^1_2*	2.020	2.150	2.172
9. CuL^2_2	2.040	2.200	2.250

Remarks: EPR signals are not observed at r.t. or 77 K an anisotropic spectrum is observed both at r.t. and at 77 K, which has narrow peaks (belonging to the mononuclear compound). The anisotropic character confirms a low-symmetry structure, which, probably, is caused by additional coordination of SO_2 groups with the copper atom.
*Complex electrochemically obtained.

The formation of a binuclear structure with a strong antiferromagnetic interaction is confirmed by EPR spectra: solid samples of the complexes do not produce signals at room temperature, or at 77 K.

Copper complexes of the ligands **1** ($X = NTs$, $R = R^1 = H$; $X = NTs$, $R = Me$, $R^1 = H$), obtained by chemical and electrochemical syntheses have the compositions $Cu(L^1H)_2$ and CuL^2_2, and exhibit different magnetic properties and EPR data. These compounds are monomeric, have normal magnetic moments at 298 and at 77 K (Table IV) and produce clear signals in EPR spectra with normal parameters,[30,31] consistent with a structure of type **2** ($X = NR$, $R = H$, Me; $R^1 = H$).

Taking into account literature data,[20,25,32] it is highly probable that the described copper complexes $Cu(L^1H)_2$ and CuL^2_2 ($X = NTs$) have a tetrahedral structure. This could be reinforced by the fact that the analogous nickel complexes are paramagnetic and have effective magnetic moments of 3.04 and 3.39 B.M. (compounds 7 and 10, Table I). The cobalt complex (complex 11, Table I) is also tetrahedral, according to its magnetic moment.

CONCLUSIONS

Using different ligand systems L^1H_2 and L^2H and different synthetic methods (chemical and electrochemical), it is possible to carry out controlled synthesis of chelates of the oximes of 2-(N-tosylamino)benzaldehydes having different physico-chemical properties.

Although electrochemical synthesis was used by Chugaev many years ago to obtain metal oximates,[33,34] data on the electrosynthesis of chelates of type **2** ($X = O$, S) have not been reported.[16,35] The main advantages of electrochemical synthesis of transition metal chelates are the high yields of final products (85–97%) and the absence of anions which are frequently present in chelates prepared by traditional methods.[36–38]

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