Electrosynthesis and studies of adducts of 2-amino-1-methylbenzimidazole with metal chelates based on 2-tosylamino-*N*-salicylideneaniline

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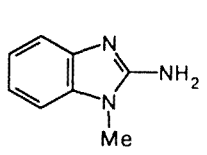
For the first time the adducts of 2-amino-1-methylbenzimidazole (L) with cobalt, copper, and zinc chelates based on 2-tosylamino-*N*-salicylideneaniline were electrochemically synthesized, and the properties and structures of these adducts were studied. According to the IR and ^{1}H NMR spectral data on the adducts obtained and X-ray structural analysis of the copper complex, the adducts of composition $mL \cdot ML' \cdot nH_2O$ (m = 1 or 2; n = 0, 1, or 2) contain the L moiety bonded to the metal atom through the pyridine-type N atom of the imidazole ring.

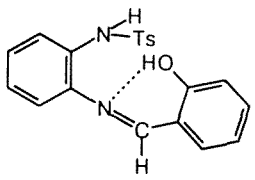
Key words: aminobenzimidazole, metal chelate, electrochemical synthesis, IR and ^{1}H NMR spectra, X-ray structural analysis.

In spite of continuing interest in metallocomplexes of amino derivatives of azoles and azines,[1–5] which arose because of their use for modeling the processes of binding of metals by biologically important objects,[6–8] the adducts of potentially bidentate *N,N'*-donor bases with tridentate metal chelates are not documented yet.

In this connection, we synthesized for the first time and studied the adducts of 2-amino-1-methylbenzimidazole (**1**, L) containing the coordinatively active imidazole fragment of purine nucleotides (adenosine, guanosine, and inosine)[6,7] with chelates of "the metals of life" (cobalt, copper, and zinc)[8] obtained on the basis of the tridentate N,N,O-donor ligand, namely, 2-tosylamino-*N*-salicylideneaniline (**2**, $L'H_2$).



1 (L)



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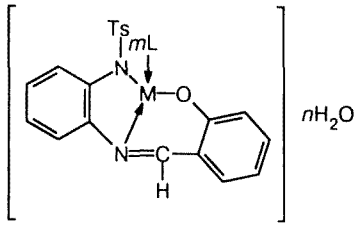

3a–c

M = Cu (**a**), Co (**b**), Zn (**c**);
m = 1 (**a**), 2 (**b**, **c**); n = 1 (**a**), 2 (**b**), 0 (**c**)

Experimental

The IR spectra were recorded on a Perkin—Elmer 180 instrument. The ^{1}H NMR spectra were measured on a Bruker WM-250 instrument in $CDCl_3$ and DMSO-d_6 solutions relative to $SiMe_4$. Magnetochemical measurements were carried out on an instrument designed at the Rostov State University using the Faraday method.[9] Elemental analysis of the ligand and the complexes was performed on an automated Carlo Erba EA 1108 microanalyzer.

X-ray structural analysis of the single crystal (obtained from methanol) of dimensions of 0.12×0.15×0.25 mm was carried out on an automated Syntex $P2_1$ diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique,

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Table 1. Fractional atomic coordinates and temperature parameters (U_{eq}/U_{iso}) in the structure of **3a**

Atom	x	y	z	U_{eq}/U_{iso}
Cu	0.2808 (2)	−0.0068 (1)	0.2864 (1)	0.0456 (6)
S	0.1745 (4)	−0.2968 (3)	0.1801 (2)	0.058 (2)
O(1)	0.240 (1)	−0.3915 (8)	0.1668 (5)	0.078 (5)
O(2)	0.153 (1)	−0.2316 (7)	0.1037 (4)	0.074 (4)
O(3)	0.196 (1)	0.1209 (7)	0.2913 (5)	0.065 (4)
N(1)	0.284 (1)	−0.1822 (7)	0.2719 (5)	0.055 (4)
N(2)	0.258 (1)	−0.0320 (8)	0.4133 (5)	0.046 (4)
N(3)	0.406 (1)	0.0599 (7)	0.1926 (5)	0.047 (4)
N(4)	0.248 (1)	0.1611 (9)	0.1172 (6)	0.059 (5)
N(5)	0.493 (1)	0.1631 (7)	0.0811 (5)	0.053 (4)
C(1)	0.314 (1)	−0.216 (1)	0.3608 (7)	0.057 (5)
C(2)	0.300 (1)	−0.1353 (9)	0.4367 (6)	0.046 (5)
C(3)	0.330 (1)	−0.160 (1)	0.5263 (7)	0.060 (6)
C(4)	0.375 (2)	−0.257 (1)	0.5420 (8)	0.066 (6)
C(5)	0.389 (2)	−0.335 (1)	0.468 (1)	0.076 (7)
C(6)	0.357 (2)	−0.316 (1)	0.3784 (8)	0.072 (7)
C(7)	0.219 (1)	0.038 (1)	0.4698 (6)	0.055 (5)
C(8)	0.175 (1)	0.1415 (9)	0.4522 (7)	0.053 (5)
C(9)	0.163 (1)	0.180 (1)	0.3637 (7)	0.053 (5)
C(10)	0.115 (1)	0.281 (1)	0.3539 (8)	0.064 (6)
C(11)	0.078 (2)	0.342 (1)	0.427 (1)	0.076 (7)
C(12)	0.091 (2)	0.306 (1)	0.5128 (8)	0.076 (7)
C(13)	0.140 (2)	0.208 (1)	0.5255 (7)	0.065 (6)
C(14)	−0.020 (1)	−0.374 (1)	0.2029 (6)	0.054 (6)
C(15)	−0.122 (2)	−0.316 (1)	0.1984 (7)	0.060 (6)
C(16)	−0.269 (2)	−0.369 (1)	0.2191 (8)	0.063 (6)
C(17)	−0.322 (1)	−0.493 (1)	0.2467 (7)	0.054 (6)
C(18)	−0.218 (2)	−0.552 (1)	0.2490 (7)	0.060 (6)
C(19)	−0.071 (2)	−0.5009 (9)	0.2263 (7)	0.055 (6)
C(20)	−0.474 (2)	−0.546 (1)	0.2764 (9)	0.080 (7)
C(21)	0.545 (1)	0.0469 (9)	0.1831 (6)	0.041 (5)
C(22)	0.632 (1)	−0.011 (1)	0.2264 (7)	0.053 (5)
C(23)	0.768 (2)	−0.008 (1)	0.2018 (8)	0.061 (6)
C(24)	0.823 (2)	0.055 (1)	0.1308 (9)	0.078 (7)
C(25)	0.735 (2)	0.115 (1)	0.0860 (8)	0.067 (6)
C(26)	0.602 (1)	0.1147 (9)	0.1128 (6)	0.045 (5)
C(27)	0.502 (2)	0.247 (1)	0.0113 (8)	0.078 (7)
C(28)	0.374 (2)	0.1332 (9)	0.1303 (7)	0.079 (6)
O(w)	0.165 (1)	0.3589 (9)	0.0445 (6)	0.109 (6)
H[1N(4)]	0.182	0.144	0.150	0.05
H[2N(4)]	0.210	0.198	0.081	0.05
H(3)	0.321	−0.106	0.578	0.05
H(4)	0.396	−0.272	0.605	0.05
H(5)	0.415	−0.406	0.481	0.05
H(6)	0.368	−0.369	0.325	0.05
H(7)	0.205	0.002	0.527	0.05
H(10)	0.107	0.306	0.293	0.05
H(11)	0.047	0.414	0.420	0.05
H(12)	0.064	0.352	0.564	0.05
H(13)	0.147	0.186	0.587	0.05
H(15)	−0.088	−0.230	0.179	0.05
H(16)	−0.340	−0.323	0.215	0.05
H(18)	−0.247	−0.637	0.268	0.05
H(19)	−0.001	−0.546	0.227	0.05
H(22)	0.614	−0.045	0.259	0.05
H(23)	0.831	−0.053	0.234	0.05
H(24)	0.920	0.057	0.111	0.05
H(25)	0.775	0.160	0.034	0.05
H(31)	0.512	0.331	0.029	0.05
H(32)	0.595	0.254	0.009	0.05
H(33)	0.423	0.229	−0.042	0.05
H(34)	−0.484	−0.641	0.278	0.05
H(35)	−0.481	−0.506	0.337	0.05
H(36)	−0.556	−0.536	0.249	0.05

$2\theta_{max} = 56°$). Of 7838 reflections measured, 2079 reflections with $I \geq 2\sigma(I)$ were used in structure solution. Crystals of **3a** ($C_{28}H_{27}N_5O_4SCu$) are triclinic: $a = 9.185(5)$, $b = 11.274$, $c = 14.772(8)$ Å, $\alpha = 97.28(5)$, $\beta = 100.64(4)$, $\gamma = 113.20(4)°$, $V = 1347.7$ (1.5) Å^3, $\rho_{calc} = 1.47$ g cm^{-3}, $\mu = 5.1$ cm^{-1}, mol. weight 595.2, $F(000) = 616$, $Z = 2$, space group $P\bar{1}$. The structure was solved by the heavy-atom method. The positions of hydrogen atoms of the phenyl cycles were calculated from geometric considerations. The remaining atoms, except for atoms of water molecules, were located from the difference electron density syntheses. Calculations were carried out on an IBM AT-386 computer using the SHELX-90 program. Positional and thermal parameters of nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method. Hydrogen atoms were refined with a common isotropic temperature factor. The final values of the R factor were as follows: $R = 0.063$, $R_w = 0.055$, $W = 1/\sigma^2(|F_0|)$, and GOOF = 1.42.

Atomic coordinates and temperature parameters U_{eq} (U_{iso} for H atoms) are given in Table 1; interatomic distances and bond angles are listed in Tables 2 and 3, respectively.

2-Amino-1-methylbenzimidazole (1) was synthesized by direct amination of 1-methylbenzimidazole with sodium amide in xylene, m.p. 200—202 °C.[10]

2-Tosylamino-*N*-salicylideneaniline (2) was prepared by boiling (15 min) a methanolic solution containing equimolar amounts of *o*-(*N*-tosylamino)aniline and salicylaldehyde. Cool-

Table 2. Bond lengths (d) in the structure of **3a**

Bond	d/Å	Bond	d/Å
Cu—O(3)	1.889 (9)	Cu—N(1)	1.947 (8)
Cu—N(2)	1.967 (7)	Cu—N(2)	1.996 (9)
S—O(1)	1.43 (1)	S—O(2)	1.447 (7)
S—N(1)	1.596 (8)	S—C(14)	1.77 (1)
O(3)—C(9)	1.33 (1)	N(1)—C(1)	1.42 (1)
N(2)—C(2)	1.42 (1)	N(2)—C(7)	1.27 (1)
N(3)—C(21)	1.37 (2)	N(3)—C(28)	1.38 (1)
N(4)—C(28)	1.30 (2)	N(4)—H[1N(4)]	0.83 (1)
N(4)—H[2N(4)]	0.82 (1)	N(5)—C(26)	1.36 (2)
N(5)—C(27)	1.48 (1)	N(5)—C(28)	1.38 (2)
C(1)—C(2)	1.41 (2)	C(1)—C(6)	1.38 (2)
C(2)—C(3)	1.39 (1)	C(3)—C(4)	1.34 (2)
C(4)—C(5)	1.37 (2)	C(5)—C(6)	1.37 (2)
C(7)—C(8)	1.42 (2)	C(8)—C(9)	1.43 (1)
C(8)—C(13)	1.40 (2)	C(9)—C(10)	1.39 (2)
C(10)—C(11)	1.37 (2)	C(11)—C(12)	1.38 (2)
C(12)—C(13)	1.37 (2)	C(14)—C(15)	1.34 (2)
C(14)—C(19)	1.43 (2)	C(15)—C(16)	1.35 (2)
C(16)—C(17)	1.43 (2)	C(17)—C(18)	1.36 (2)
C(17)—C(20)	1.45 (2)	C(18)—C(19)	1.37 (2)
C(21)—C(22)	1.34 (2)	C(21)—C(26)	1.42 (1)
C(22)—C(23)	1.36 (2)	C(23)—C(24)	1.40 (2)
C(24)—C(25)	1.37 (2)	C(25)—C(26)	1.35 (2)

Table 3. Bond angles (ω) in the structure of **3a**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(3)CuN(1)	159.0 (4)	C(9)C(10)C(11)	121 (1)	C(26)N(5)C(28)	109.9 (9)
O(3)CuN(3)	94.8 (4)	C(11)C(12)C(13)	120 (1)	C(27)N(5)C(28)	123 (1)
N(1)CuN(3)	97.9 (4)	SC(14)C(15)	120.9 (9)	C(28)N(4)H[2N(4)]	136 (1)
O(1)SO(2)	117.5 (5)	C(15)C(14)C(19)	119 (1)	N(1)C(1)C(2)	115.2 (9)
O(1)SC(14)	109.3 (5)	C(15)C(16)C(17)	121 (1)	C(2)C(1)C(6)	119 (1)
O(2)SC(14)	106.8 (5)	C(16)C(17)C(20)	121 (1)	N(2)C(2)C(3)	126 (1)
CuO(3)C(9)	129.5 (7)	C(17)C(18)C(19)	125 (1)	C(2)C(3)C(4)	121 (1)
CuN(1)C(1)	111.3 (7)	N(3)C(21)C(22)	134 (1)	C(4)C(5)C(6)	121 (1)
CuN(2)C(2)	111.3 (6)	C(22)C(21)C(26)	119 (1)	N(2)C(7)C(8)	127 (1)
C(2)N(2)C(7)	123.4 (9)	C(22)C(23)C(24)	121 (1)	C(7)C(8)C(13)	118 (1)
CuN(3)C(21)	125.5 (7)	C(24)C(25)C(26)	120 (1)	O(3)C(9)C(8)	122 (1)
N(3)C(28)N(4)	125 (1)	N(5)C(26)C(25)	132 (1)	C(8)C(9)C(10)	118 (1)
N(5)C(28)N(4)	127 (1)	O(3)CuN(2)	92.2 (4)	C(10)C(11)C(12)	121 (1)
C(26)N(5)C(27)	127 (1)	N(1)CuN(2)	83.5 (4)	C(8)C(13)C(12)	121 (1)
C(28)N(4)H[1N(4)]	123 (1)	N(2)CuN(3)	154.3 (4)	SC(14)C(19)	120.3 (9)
H[1N(4)]N(4)H[2N(4)]	101 (1)	O(1)SN(1)	111.2 (5)	C(14)C(15)C(16)	123 (1)
N(1)C(1)C(6)	126 (1)	O(2)SN(1)	106.4 (5)	C(16)C(17)C(18)	115 (1)
N(2)C(2)C(1)	115.4 (9)	N(1)SC(14)	105.0 (5)	C(18)C(17)C(20)	123 (1)
C(1)C(2)C(3)	119 (1)	CuN(1)S	121.4 (5)	C(14)C(19)C(18)	118 (1)
C(3)C(4)C(5)	120 (1)	SN(1)C(1)	119.5 (7)	N(3)C(21)C(26)	107.8 (9)
C(1)C(6)C(5)	120 (1)	CuN(2)C(7)	125.2 (8)	C(21)C(22)C(23)	121 (1)
C(7)C(8)C(9)	123 (1)	CuN(3)C(28)	126.1 (7)	C(23)C(24)C(25)	119 (1)
C(9)C(8)C(13)	119 (1)	C(21)N(3)C(28)	108.2 (9)	N(5)C(26)C(21)	106.4 (9)
O(3)C(9)C(10)	120 (1)	N(3)C(28)N(5)	108 (1)	C(21)C(26)C(25)	121 (1)

ing of the solution afforded yellow crystals, yield 65 %, m.p. 139—140 °C (from MeOH). Found (%): C, 65.42; H, 4.80; N, 7.71; S, 8.79. $C_{20}H_{18}N_2O_3S$. Calculated (%): C, 65.57; H, 4.95; N, 7.65; S, 8.74. IR, ν/cm^{-1}: 1612 (νC=N). ^{1}H NMR (DMSO-d_6), δ: 11.8 (OH); 9.8 (NHTs); 8.2 (CH=N).

Complex compounds 3a—c (M = Co, Cu, or Zn) were synthesized electrochemically by the reactions of ligands **1** and **2** and the corresponding metals (the ratio of reagents was 1 : 1 : 1) in MeCN according to the procedure reported in Refs. 11 and 12 (for reviews, see also Refs. 13 and 14).

Complex 3a, brown crystals, yield 64 %, m.p. 237—238 °C (from MeCN). Found (%): C, 56.00; H, 4.46; N, 12.45; S, 5.53. $C_{28}H_{25}CuN_5O_3S \cdot H_2O$. Calculated (%): C, 56.67; H, 4.55; N, 11.80; S, 5.40. IR, ν/cm^{-1}: 1608 (νC=N); 3508 ($\nu_{as}NH_2$); 3329 (ν_sNH_2); 1649 (δNH_2).

Complex 3b, green crystals, yield 58 %, m.p. 208—210 °C (decomp., from MeCN). Found (%): C, 57.76; H, 5.20; N, 14.38; S, 3.78. $C_{36}H_{34}CoN_8O_3S \cdot 2H_2O$. Calculated (%): C, 57.37; H, 5.04; N, 14.87; S, 4.25. IR, ν/cm^{-1}: 1610 (νC=N); 3435 ($\nu_{as}NH_2$); 3348 (ν_sNH_2); 1641 (δNH_2).

Complex 3c, yellow crystals, yield 72 %, m.p. 262—263 °C (from MeCN). Found (%): C, 59.59; H, 4.85; N, 15.71; S, 4.58. $C_{36}H_{34}N_8O_3SZn$. Calculated (%): C, 59.75; H, 4.42; N, 15.49; S, 4.42. IR, ν/cm^{-1}: 1608 (νC=N); 3425 ($\nu_{as}NH_2$); 3348 (ν_sNH_2); 1650 (δNH_2). ^{1}H NMR (DMSO-d_6), δ: 8.79 (1 H, HC=N); 3.5 (6 H, NMe).

Results and Discussion

Complexes **3a—c**, which are reported for the first time, were synthesized electrochemically taking into account the efficiency of this method in the preparation of related compounds.[14—17] According to the data of elemental analysis, the adducts of the general formula $mL \cdot ML' \cdot nH_2O$, where $m = 1$ (M = Cu, $n = 1$) or $m = 2$ (M = Co, $n = 2$; or M = Zn, $n = 0$) formed. Actually, the ^{1}H NMR spectrum of the Zn complex confirms that two molecules of the 2-amino-1-methylbenzimidazole ligand in the Co and Zn complexes are coordinated; this spectrum shows the double intensity signal of two N—Me groups at δ 3.50. Based on the data of IR and ^{1}H NMR spectroscopy, magnetochemical measurements, and X-ray structural analysis of the Cu complex, we assigned structure **3a** (Figs. 1 and 2) to this adduct and structures **3b** and **3c** to the Co and Zn complexes, respectively.

The IR spectra of adducts **3a—c** show intense absorption bands of coordinated azomethine group in the 1608—1610 cm^{-1} region, which indicates that chelate structures form. This suggestion is supported by the fact that in the ^{1}H NMR spectrum of adduct **3c**, the signals of protons of the OH (δ 11.90) and HNTs (δ 9.80) groups of ligand **2** are absent and the signal of the proton of the CH=N group shifts downfield by 0.60 ppm; previously, this shift was also observed upon chelation.[18] Complex **3a** exhibits a magnetic moment of 1.80 μ_B, which is consistent with the monomeric structure of the chelate under consideration. In this connection note that dimers **4**, which are very typical of Cu complexes obtained with the use of tridentate ligands of type **2**, are characterized by reduced values of magnetic moments, which are attributable to the antiferromagnetic interaction through the Y-bridging fragment (Y = O or S).[17,19,20]

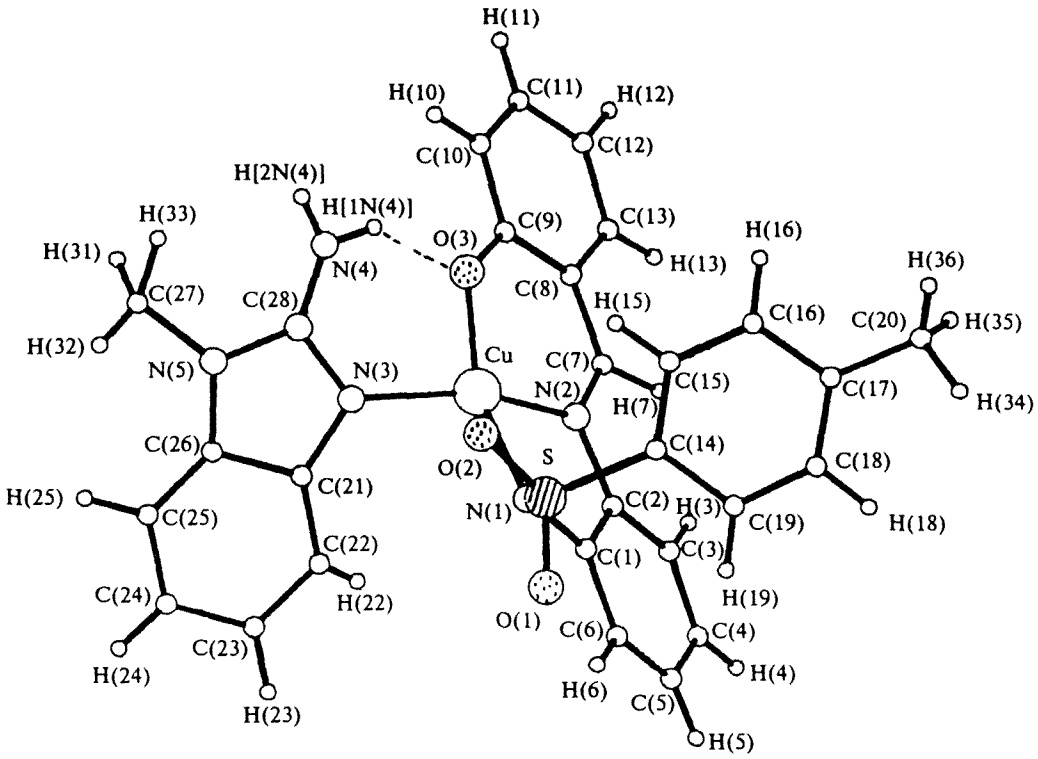
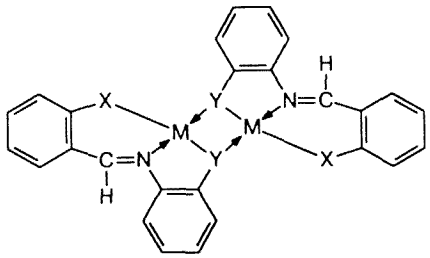


Fig. 1. Structure of complex **3a**.



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As mentioned above, the structure of complex **3a** was unambiguously established by X-ray structural analysis (see Fig. 1). The coordination number of the Cu atom in this complex is 4; the Cu atom has a slightly tetrahedrally distorted planar-square configuration (the deviation from the mean N(1)N(2)N(3)O(3) plane is ±0.4 Å). The Cu atom deviates from this plane by 0.06 Å. When the ligands are coordinated, three metallacycles are closed: the five-membered CuN(1)C(1)C(2)N(2) cycle, the six-

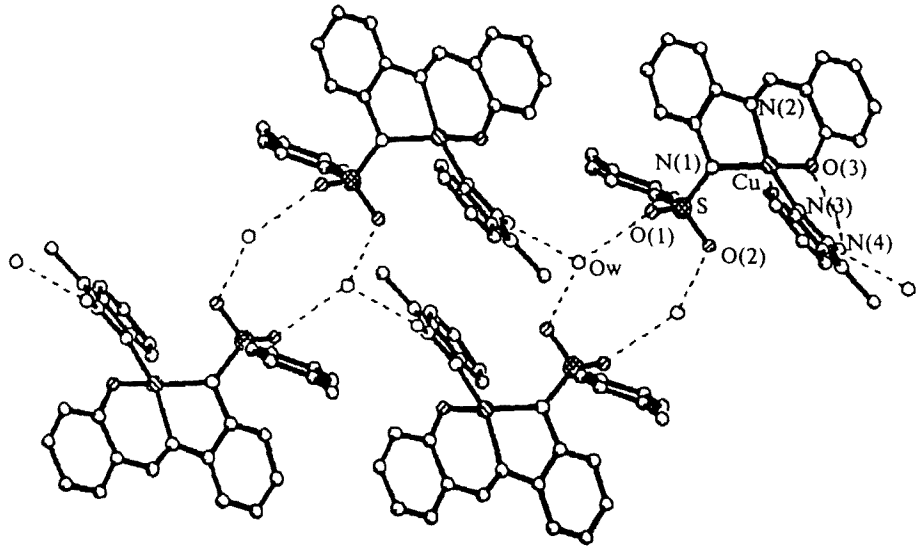

Fig. 2. Fragment of the infinite ribbon formed by H-bonds in the structure of **3a** (the projection along the *x* axis).

membered CuN(2)C(7)C(8)C(9)O(3) cycle, and the six-membered cyclic fragment containing an intramolecular NH···O bond, namely, CuO(3)···HN(4)C(28)N(3). The N(4)—H[1N(4)]···O(3) hydrogen bond is characterized by the following parameters: N(4)—O(3) 2.76, N(4)—H[1N(4)] 0.83, H[1N(4)]···O(3) 2.11 Å, the N(4)H[1N(4)]O(3) angle is 135°. The distances in the coordination polyhedron about Cu have normal values: Cu—N 1.974(8), 1.967(7), 1.996(9) Å, and Cu—O 1.889(9) Å. The endochelate angles are 83.5(4), 92.2(4), and 94.8(4)° in the five-membered, six-membered, and H,M-cycles, respectively. The five-membered metallacycle is slightly folded along the N(1)···N(2) line by ~9°; the six-membered cycle is slightly folded along the N(2)···O(3) line by ~7°. The phenyl groups fused with the corresponding fragment of the metallacycles are coplanar with them. It is unlikely that the smallest distance between the Cu atom and the O atom of the SO_2 group (Cu···O(2) is 3.12 Å) corresponds to the bond (*cf.* Refs 21—23) because this direction deviates substantially from the normal to the plane of the coordination square: the O(2)CuO(3), O(2)CuN(1), O(2)CuN(2), and O(2)CuN(3) angles are 119°, 51°, 126°, and 71°, respectively.

The water molecule is not involved in coordination with metal and acts as a trifunctional bridging fragment. The oxygen atom of this group accepts one proton from the NH_2 group. In addition, the water molecule is the donor in two bonds with oxygen atoms of SO_2 groups of adjacent metallocomplexes: $O(w)\cdots O(1)_{(x,1+y,z)}$ 2.89 and $O(w)\cdots O(2)_{(-x,-y,-z)}$ 2.99 Å. As a result, centrosymmetric dimers form (see Fig. 2); these dimers are linked in infinite ribbons along the x axis of the crystal through the acceptor N(4)—H[2N(4)]···O(w) bonds (N(4)···O(w) 2.89, N(4)—H[2N(4)] 0.83; H[2N(4)]···O(w) 2.12 Å, the N(4)H[2N(4)]O(w) angle is 148°).

Therefore, in complexes **3a—c**, 2-amino-1-methylbenzimidazole is bonded to the tridentate chelating fragment through the endocyclic pyridine-type N atom. Note that this mode of location of the coordination bond is also the most typical of metallocomplexes of aminoazoles and aminoazines with ordinary Lewis acids (metal salts).[3,4]

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