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Coordination Compounds of Copper(II) with Bis(5-amino-1,2,4-triazol-3-yl)alkanes

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Abstract—Procedures for synthesis of coordination compounds of copper(II) with bis(5-amino-1,2,4-triazol-3-yl)alkanes as ligands. A conclusion was drawn that the coordination polyhedron of copper(II) has different configurations depending on the structure of the ligand and on the coordination mode.

The aim of the present work was to synthesize coordination compounds of copper with bis(5-amino-1,2,4-triazol-3-yl)alkanes and to examine how the configuration of the polyhedron varies with the structure of the ligand [1].

Bond localization in coordination compounds is still under discussion [1]. Monoaminotriazoles most commonly coordinate with central atoms via endocyclic nitrogen atoms [2–5]. Biazole compounds have poorly been studied as ligands [6]. Thus, a coordination compound of Fe(III) with 4,4'-bipyridine as ligand has been reported [6]. The closest analog of the title compounds is $Co(NCS)_2(BTA)_2H_2O$ {BTA is 4,4'-bi(1,2,4-triazole) [7]}. According to [7], the IR spectra of 1,2,4-triazole derivatives have the following common features: the bands of bending ring vibrations are below 900 cm^{-1}, the bands of out-of-plane C–H vibrations are of medium intensity and locate near 880 cm^{-1}; the bands of out-of-plane (torsion) ring vibrations always locate at 600–700 cm^{-1} and are sensitive to symmetry (C_s and C_{2v}); and the bands of in-plane ring vibrations are at 950–1550 cm^{-1}. Characteric of these compounds is a strong δ(CH) band at ~1080 cm^{-1}.

Since in our case the ligand contains a 5-amino-1,2,4-triazole moiety, we consider it expedient to dwell on its IR spectrum (see table).

The IR spectra of 5-amino-1,2,4-triazole (**I**) (ATA) and its complexes, specifically $Cu(ATA)_{1.5}(NO_3)_2$, have been studied by Haasnot and Groenveld [9]. The referees found that the differences in the spectral patterns are largely determined by the number of ligands **I** in the complexes rather than the nature of the anion or metal.

The spectrum of heterocycle **I** displays C–H absorption bands and medium-intensity bands of bending vibrations of the ring, including broad (700, 775, 800 cm^{-1}). The ring vibration bands are at 1000–1620 cm^{-1}, i.e. they are shifted to higher frequencies compared with those of unsubstituted 1,2,4-triazole, which is characteristic of aminotriazole derivatives [1, 9]. The band considered characteristic [7] is shifted to 1000 cm^{-1} and is very strong.

The weak bands at 2730–3400 cm^{-1} are broadened, which suggests intermolecular hydrogen bonding [1].

Complex formation decreases stretching–bending and stretching ring absorption frequencies (1000–1620 cm^{-1}) [9]. Moreover, the 915 and 1000 cm^{-1} absorption frequencies increase by 10–15 cm^{-1}. These fact, as well as increased intensities of the 1620 and 1420 cm^{-1} bands [10] imply coordination by a "pyridine" nitrogen atom [1], which is consistent with the electron density distribution in aminotriazole **I** [1].

Complex formation is much affected by the nature of the salt anion. The nitrate anion increases the coordination number of copper to 6 and favors formation of octahedral structures [1].

Leonova *et. al.* [11] have considered the structure of transition metal complexes with 1,5-diamino-1,2,3,4-tetrazole and nitrate anions. It was shown that the presence of NO_3^- absorption is explained, according to [11], by coordination with Cu(II). Evidence for this explanation comes from the observation in the spectra of complexes **IIa**–**IVa** of a strong narrow band at 1058 cm^{-1}, a broad strong band at 1435 cm^{-1}, and a band at 1280 cm^{-1}. The absorption bands of the amino group at 3300 and 3200 cm^{-1} are unaffected by coordination [10], which may imply lack of interaction through exocyclic nitrogen atoms and is consistent with conclusions in [1].

Let us further compare the experimental IR spectra of 5-amino-1,2,4-triazole and bis(5-amino-1,2,4-tri-

Assinment of principal bands in the IR spectra of 5-amino-1,2,4-triazole (**I**), 5-amino-1,2,4-triazole complexes **IIa**–**VIIIa**, and ligands **IIb**–**VIIIb**[a]

Comp. no.	$\nu(NH_2)$	$\nu_r(NH_2)$	$\nu(NH)$	$\delta(NH_2)$	δ_r, $\delta(NH_2)$	$\delta(NH_2)$	ν_r	ν_r	ν_r, $\nu(NO_3^-)$	ν_r, $\delta(NH_2)$	$\rho(NH_2)$	δ_r, $\delta(NO_3^-)$	$\delta(CH)$, $\beta(NH_2)$	$\gamma(CH)$, $\beta(NO_3^-)$	$\gamma(CH)$	λ_r
I	3400, 3300	3160, 3030	2980, 2890, 2730		1620	1570	1470		1385, 1325	1240, 1225	1200, 1100 (br)		1000, 925, 910 (br)	800	775, 775	700, 650 (br)
IIa	3345		2918	1670	1620	1563	1470	1415	1387	1254	1143	1050	991	898	756	670
IIb	3350	3190	2775, 2925, 2850	1640, 1664, 1640	1590, 1610	1540, 1500	1489	1425	1300, 1390, 1310	1253, 1260	1110, 1120, 1102	1057, 1078	982, 986	824, 830	736, 742, 725	653, 670, 638
IIIa	3332	3158	2930	1634	1594	1532	1485	1403	1390	1290	1175	1128	1068	875	726	670
IIIb	3425, 3456	3158, 3180	2852, 2926, 2856	1655, 1675, 1635	1567, 1600	1510, 1558	1515, 1473	1418	1339, 1380	1260	1160	1107, 1130	1076	830, 800, 838	730	632, 630, 675
IVa	3352	3178	2925	1675	1592	1535	1475	1400	1330	1218		1108	1053			670
IVb	3355	3162	2850, 2930, 2858	1632, 1675, 1635	1565, 1603	1515, 1547	1495	1415	1385, 1342	1274	1173	1125, 1100	930, 1039	831	720	656, 645
Va	3350	3185	2930	1670	1610	1555	1480	1415	1395	1270	1165	1130	1040	837	728	670
Vb	3355	3175	2862, 2930	1630, 1675	1560, 1610	1510, 1565	1496	1425	1355, 1393	1285	1170	1055, 1133	1055, 1070	892	725	628, 670
VIa			2870	1635					1310	1265		1090	1035	825	745	638
VIb	3453, 3352, 3450	3270, 3170, 3250	2949, 2841, 2960	1614, 1640, 1652	1600, 1590, 1630	1550, 1515, 1592, 1560	1480, 1437, 1495	1400, 1416, 1435	1400, 1337, 1380, 1344	1278, 1260, 1300, 1218	1162, 1168, 1103	1068, 1100, 1130, 1009	1065, 1045, 918	828, 850	780, 725	680, 635, 653, 570
VIIa	3456	3300	2045	1675	1595	1555	1475	1415	1360	1280	1107	1058	900	875	785	670
VIIb	3458	3200, 3225	2840, 2957	1630, 1660	1622	1515, 1579	1498	1440	1385, 1295	1290, 1265	1178	1075, 1059	985	840, 845	773	625, 675, 630
VIIIa	3445	3290	2949	1650	1590	1550	1460	1410	1390	1285	1155	1055	962	880	780	675
VIIIb	3450	3220, 3250	2860, 2969	1638, 1665	1620	1525, 1570	1482	1492	1335, 1400	1290, 1280	1186	1045, 1060	980	845, 850	770	625, 685, 655

[a] For abbreviations and notations, see [8].

azol-3-yl)alkanes to find characteristic absorption frequencies, as it has been done in [12, 13] for 1,2,4-triazole and its derivatives. The calculations in [13] established the following characteristic frequencies of 1,2,4-triazole: 1558–1610, 1516–1550, 1400–1480, 1330–1390, and 1240–1300 cm^{-1}. Comparing the spectra of 5-amino-1,2,4-triazole and ligands **IIb**–**VIIIb**, we can note that the latter spectra lack $\delta(NH_2)$ and ν_r (1400–1440 cm^{-1}) and $\delta(CH)$ and $\beta(NH_2)$ (1050–1095 cm^{-1}) absorption frequencies. Such a sharp difference may suggest changes in the electron density on the amino group and in the steric arrangement of the rings. Actually, the absorption band of the amino group that experiences the electron-acceptor effect of the two triazole rings is split into two components (1620 cm^{-1} in the complex and 1620 and 1664 cm^{-1} in the ligands) due to strengthening of the coordination bond. As the length of the methylene chain in the ligand increases (more than three methylene units), the absorption frequencies decrease because of the weakening effect of the triazole rings. It is appropriate at this point to note that complex formation first shifts $\delta(NH_2)$ to higher frequencies (compounds **IIb** and **IIIb**), then to lower frequencies (compounds **IVb** and **Vb**), and then again to higher frequencies (compounds **VIb**–**VIIIb**) (see table). This trend may be explained by changes in the steric arrangement of the rings or in the molecular configuration.

In our first molecular mechanics calculations of the structures of ligands **IIb** and **IIIb** we found that the angles between the triazole ring planes in the ligands are 0.2° and 30°, respectively [14]. Further on, as the number of methylene units increases, interaction between the rings enhances due to formation a sandwich structure like ferrocene [15]. In this structure, whose formation is confirmed by calculations, the rings are attracted to each other by van der Waals forces (the distance between the rings and metal is 1.65–1.66 Å) [15].

Complex formation decreases the 1400–1440 cm^{-1} frequencies by 10–25 cm^{-1}. According to [2–4], such shift is evidence in favor of coordination via a “pyridine” nitrogen atom.

Our previous calculations [14] showed that ligands **IIb** and **IIIb** prefer to coordinate via N^4 and $N^{4'}$. In solution, however, electron density redistribution takes place, and, as found by IR spectroscopy [10], the coordination involves the N^1 and N^2 atoms of each of the triazole rings.

Vibration bands of bis(5-amino-1,2,4-triazol-3-yl)-alkanes are also observed in the 1050–1095 cm^{-1} range, which is not unexpected, since bending vibrations are characteristic of complex bis-systems, especially of those containing bulky ligands.

In the 600–700 cm^{-1} range (torsion ring vibrations), there are two resolved bands (670–675 cm^{-1}) of medium and low (625–645 cm^{-1}) intensity. The first band almost does not change its position, while the second shifts to lower frequencies. This fact provides one more evidence for nonequivalence of the rings, and, on the other hand, points to different M^{2+} environments.

The presence of two out-of-plane vibration bands (bending and torsion vibrations) is associated with the C_s symmetry of 1,2,4-triazole. In our case, like with cobalt(II) complexes (coordination entity CoN_6) with 4,4'-bis(1,2,4-triazolyl), 1,1'-bicoordination and C_s symmetry are preferred [7].

The ESR spectra confirm the pseudooctahedral coordination of Cu(II) with 4-ethyl-1,2,4-triazole ($g_{\$|_|}$ 2.24, $g_\perp$ 2.05) [16]. The copper(II) ions are bound by a double bridge of 1,2-bidentately coordinated heterocyclic ligands; the isothiocyanate ions act as monodentate ligands [16].

Park and Almlof [17] have shown that bis(μ-perchlorato)[bis(μ-imidazolato)bis(perchlorato)octakis-(imidazole)tricopper(II)] is a trinuclear octahedral copper(II) complex with two imidazolate bridges.

The *g* factors of the Cu(II) aminotriazole **I** complexes (1 : 3, pH 4.3) are as follows: $g_{||}$ 2.27, $g_\perp$ 2.05. At higher ligand : metal ratios, the ESR spectra acquire a nitrogen hyperfine structure (seven lines), which suggests coordination of more than two nitrogen atoms [4]. As the number of ligands in the coordination sphere increases, the octahedron undergoes axial distortion due to spin–orbit coupling, and the magnetic moment decreases [4].

The ESR spectra of $CuT_3](NO_3)_2)\cdot 0.5H_2O$ and $CuT_2(NO_3)_2\cdot 0.5\ H_2O$ point to the presence of four nitrogen atoms in the nearest environment of Cu(II). The average *g* factors of these complexes are coincident (g_{av} 2.118) [18]. Increased, compared with purely spin, μ_{eff} values imply exchange interaction but not always relate to bridged complexes. For example, in [19], a net structure was deduced from X-ray diffraction data.

The ESR spectrum of the complex of Cu(II) with 3,5-diamino-1,2,4-triazole shows a weak signal. Apparenty, the compound is actually polynuclear. The fact that μ_{eff} decreases with decreasing temperature suggests antiferromagnetic interaction between the Cu(II) ions. The $1/\chi$–T dependence in nonlinear in the temperature range studied [20]. According to speculations in [20], the complex compound comprises clusters with an uneven number of Cu(II) ions whose exchange interaction occurs via bridging nitrogen atoms. Varied μ_{eff} values poorly fit the triangle cluster model, and, therefore, a structure with a linear chain of three Cu(II) ions bridged by ligands and with a distorted octahedral coordination of the Cu(II) ions is proposed [20].

The μ–T dependence for the complex $CuL_2(NO_3)_2$ (L is 1,5-diamino-1,2,3,4-tetrazole) adheres to the Curie law (μ_{eff} 1.83 Mx). The effective magnetic moment only slightly depends on temperature [11]. This fact might be considered to provide evidence in favor of bidentate cyclic coordination, but the ESR and IR spectra point to bidentate bridging coordination. The ESR spectrum contains broad diffuse bands, which suggests a polynuclear structure [11].

Azole complexes like $MX_2\cdot 2L$ have various configurations [21]. Thus, the transfer from tetrahedral and planar configurations to octahedral has been discussed in detail by Benelli *et al.* [19] on an example of benzoxazole complexes of transition metal nitrates.

The structures of complexes **IIa**–**IVa** were studied by ESR spectroscopy. The spectra of complexes **Ia** and **IIa** display symmetrical bands (g_{av} ~2.16 and 2.12, respectively). The g factors determined from the nomogram [22] are as follows: $g_{||}$ ~2.24, $g_{\perp}$ ~2.06; 2.18 and 2.05, respectively. The lack of resolution anisotropy of the hyperfine component may result from exchange interaction. Moreover, ESR bands may also be narrowed by fast motion of paramagnetic species relative to each other, delocalization of unpaired electrons, and their exchange interaction, which indeed occurs on coordination of Cu(II) which possesses an unpaired electron (d^9). Complex **IIa** has a lower g factor ($g_{||}$ ~2.09, $g_{\perp}$ ~2.02), implying a weaker exchange interaction, and a changed anisotropy of ESR bands, which results in resolution of the hyperfine component.

Thus, the exchange interaction weakens in the series **IIa** > **IIIa** > **IVa**, in parallel with the increasing size of the ligand. The symmetry of the ESR band of complex **IIa** points to an almost octahedral environment of the metal ion.

The closest analog of compound **IIa** is a binuclear complex of copper(II) with 4-ethyl-1,2,4-triazole (ETA), $Cu(ETA)_2(NCS)_2$, as a distorted octahedron [16]. According to the experimental evidence in [16], the complex comprises a polynuclear chain bound with a double bridge of 1,2-bidentate 4-ethyl-1,2,4-triazole ligands, as well as monodentate isocyanate ions. The coordination entity is CuN_6 (μ_{eff} 1.86 Mx).

Analysis of the interplanar spacings corresponding to the most intense reflexes of ligand **IIa** suggests an orthorhombic cell (a 5.0, b 3.3, and c 7.1 Å) comprising one molecule. The X-ray diffraction pattern of complex **IIa** is quite similar to that of complex **I**. Obviously, one copper(II) ion falls on two cells. Neighboring molecules may be shifted by half-period (3.5 Å) along the C–C axis for steric reasons. The complexes with nickel and cobalt nitrates exhibit a lower crystallinity. Therewith, complexes are definitely present, since the X-ray patterns lack crystal reflexes of the nitrates and bis(5-amino-1,2,4-triazol-3-yl)alkanes. The complex of $Cu(NO_3)_2$ with an octamethylene ligand is amorphous. Apparently, the long flexible chain prevents crystallization. The complex of $Cu(NO_3)_2$ with a three-methylene ligand is crystalline and structurally similar to compound **IIa**.

The X-ray diffraction pattern of crystalline complex **IIIa** shows two groups of reflexes much differing in intensity. The group of strong reflexes is likely to be associated with the heavy copper atom. Therewith, one cell comprises one metal atom. Consequently, we can propose a structure having copper(II) ions locating along the C–C bond chain between the rings. Such fragments form layers shifted relative to each other by $C/2$ = 3.5 Å by steric reasons.

Additional information on the structure of the complexes could be obtained by thermal analysis. Copper(II) nitrate decomposes in three stages. The first (20–55°C) involves loss of moisture (2.5%), accompanied by a slight endothermic effect. The second stage (98–170°C) is very fast, and the weight loss corresponds to the loss of both crystallization and inner-sphere water. However, the weight loss in this stage is ~35 wt%, whereas the three water molecules contribute ~22 wt%. In this stage, the nitrate ions begin to decompose, with liberation of molecular nitrogen. Moreover, part of the oxygen is consumed for oxidation of copper(II), as evidenced by the prevailing endothermic effect. Recalculation from the dry residue gives 24%, whereas the theoretical copper content is 26%.

Thermolysis of ligand **IIb** begins with a loss of 0.5 wt% of moisture (up to 80°C). The characteristic narrow endothermic peak (130°C) may relate to loss of crystallization water (0.5 wt%). The more intense endothermic peak corresponding to a loss of 16 wt% (149°C) was assigned to decomposition of amino groups. It will be emphasized that the thermal analysis, too, establishes that the triazole rings are chemically nonequivalent. Thermolysis occurs in two stages (second endothermic peak is at 160°C). The third stage involves an exothermic effect that corresponds a loss of 9 wt% and was assigned on decomposition of the methylene bridge. The very intense exothermic peak (300°C) at the highest decomposition rate (285–325°C) corresponds to thermolysis of the rings and active oxidation of thermolysis products.

The thermogram of ligand **III** in the range 110–125°C displays a characteristic endothermic peak (principal) corresponding to moisture loss. The three stage of pyrolysis of ligand **IIIb** are the same as with ligand **IIb** but shifted to higher temperatures (260, 440, and 463°C). The changed decomposition pattern points to a weaker mutual π effect of the quasiaromatic triazole systems.

The thermograms of complexes **IIa** and **IIIa** are simpler than those of the corresponding ligands, and show that the coordination with the metal has slightly increased the thermal stability of the molecules.

The themolysis pattern of complex **IIa** differs from that of the corresponding ligand in that the first peak

(120–160°C) is exothermic and may correspond to decomposition of outer-sphere ligands (explosophoric nitrate group decomposes faster). The weight loss in the second stage (307–342°C) is 49 wt%, which on recalculation per molecular weight gives the formula $CuL(NO_3)_2 \cdot mH_2O$. Thus, according to the thermograms, complex **IIa** contains, per copper oxide (from DTG), 18.0% of copper; from the formula, 17.4%. Thermolysis of complex **IIIa** occurs as described above. It should be noted that the latter complex is more stable. The first thermolysis stage occurs at 175–185°C and the second, at 310–345°C. The exothermic peak in the second stage is 1.5 times stronger. The copper content calculated from the formula is 16% (from DTG, 13.6%).

Thus, differential thermal analysis showed that the thermal stability of the complexes increases in going from **IIa** to **VIIIa**, the complexes have the general formula $CuL(NO_3)_2$, and the coordination entity of compound **IVa** is CuN_4.

Since the structural assessment could not be checked by X-ray diffraction analysis (appropriate single crystal could not be obtained), complexes **Ia**–**IVa** were examined by solid-state high-resolution ^{13}C NMR spectroscopy. The observed broadening of ligand CH_2 signals near 27 ppm compared with the signal near 154 ppm (carbon ring signals) suggests a polynuclear structure of complexes **IIa**–**IVa**. The signal broadening may point to coordination and enhanced interaction between molecular fragments. Comparison of band areas gave evidence for the composition $CuL(NO_3)_2$. Moreover, the signal at 154 ppm shifted downfield with increasing size of the ligand, in parallel with increasing force constants.

The evidence in hand allowed us to propose the following speculations as to the structures of complexes **Ia**–**VIIIa**: a triple-bridge system: a linear trinuclear complex like $Ni_3(TA)(NO_3)_6(H_2O)_8$ [9], but such structure is possible on 1,2-bicoordination, and we ruled out it; a double-bridge structure is possible on both 1,2 and 1,1' coordination of bistriazole, but the latter coordination is preferable; in our case, at the coordination by N^4 and $N^{4'}$, the double-bridge structure, too, should be ruled out on the basis of stoichiometry and IR data; the structure with one bridge, the bistriazole molecule, is a two-dimensional polynuclear layered structure with metal ions coordinating one ligand molecule; by steric reasons, this structure is impossible in the case of 1,2-coordination of bistriazole. This structure is similar to that of the complex $M(TA)_2(NCS)_2$ (TA is 1,2,4-triazole) described in [23].

Complexes **IIa**–**IVa** are most likely polynuclear with a tetrahedral coordination entity CuN_4 and the ligands coordinated with different Cu^{2+} ions. As the size of the ligand increases (beginning with that having three methylene units), the *g* factor decreases, and the hyperfine component grows, implying changes in the first coordination sphere [22]; probably, complex **IVa** is octahedral with a CuN_6 coordination entity.

EXPERIMENTAL

The IR spectra were obtained on an IKS-29 spectrophotometer at 400–4000 cm^{-1} for suspensions in fluorinated or Vaseline oil, or for thin films.

X-ray analysis was performed on a DRON-3 diffractometer (CuK_α radiation, pressure 1.3 Pa).

The mass spectra were measured on an MKh-1310 instrument, resolution 100000. Ionizing energy 70 eV, collector current 40–80 μA, source temperature 80°C. Samples were admitted via a direct inlet probe at 80–230°C. The exact masses were determined automatically from the total spectrum of a sample and perfluorokerosen (reference) using an SM-4 computer. The background mass spectrum contained no peaks of appreciable intensity, except for those of air (*m*/*z* 18, 28, 32, 40, 44), whose intensities were two orders of magnitude lower than peak intensities in the mass spectra of samples.

The solid-state high-resolution ^{13}C NMR spectra were measured on a Bruker CXP-100 spectrometer (100 MHz). Magic-angle spinning (3.5 kHz) and cross polarization techniques were applied.

The ESR spectra were recorded at 298 K on an IES-3B *X*-spectrometer, modulation 100 kHz, microwave power 200 μW, modulation amplitude 1 A/m.

Thermal analysis (DTA and TGA) was performed on a Paulik–Paulik–Erdey derivatograph at 20–1000°C, heating rate 10 deg/min, sample weight 100 mg, reference aluminum oxide.

The complexes of copper(II) with bis(5-amino-1,2,4-triazol-3-yl)alkanes were obtained for the first time [24].

Analysis for metal was performed by complexometry after digestion with concentrated perchloric acid [25]. Elemental analysis was performed on a CHN-1 analyzer.

Dinitratobis[(5-amino-1,2,4-triazol-3-yl)]copper (IIa). Compound **IIb**, 4.95 g, was dissolved with stirring in 300 ml of boiling water, and 3.62 g $Cu(NO_3)_2 \cdot H_2O$ was added to this solution. After 30-min stirring, a precipitate formed and was filtered off, washed with water and ethanol, and dried to constant weight. Yield

5.83 g (63%), mp 212–214°C. Found, %: C 23.65; H 2.99; Cu 15.76; N 33.95; O 23.56. $C_8H_{12}CuN_{10}O_6$. Calculated, %: C 23.53; H 2.94; Cu 15.69; N 34.31; O 23.53.

Dinitratobis[(5-amino-1,2,4-triazol-3-yl)metane]-copper (IIIa). A solution of 3.62 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 ml of distilled water was added to 100 ml of a solution of 5.39 g of bis(5-amino-1,2,4-triazol-3-yl)methane (**IIIb**) at 95°C. The reaction was allowed to stand with cooling for 1 day to precipitate complex **IIIa**. Yield 5.66 g (69%), mp 259–264°C. Found, %: C 25.54; H 2.99; Cu 15.27; N 33.48; O 22.72. $C_9H_{14}CuN_{10}O_6$. Calculated, %: C 25.59; H 3.32; Cu 15.17; N 33.18; O 22.74.

Dinitratobis[(5-amino-1,2,4-triazol-3-yl)ethane]-copper (IVa) (mp 265–266°C) and dinitratobis-[(5-amino-1,2,4-triazol-3-yl)propane]copper (**Va**) were prepared in a similar way.

Dinitratobis[(5-amino-1,2,4-triazol-3-yl)butane-aqua]copper (VIa). Bis(5-amino-1,2,4-triazol-3-yl)-butane (**VIb**), 6.65 g, was dissolved with stirring in 100 ml of hot distilled water, after which 50 ml of a 5.6% soluion of copper(II) nitrate was added dropwise. The reaction mixture was stirred for 1 h. Yield of complex **IVa** 3.76 g (65%), mp 185°C (decomp.). Found, %: C 31.25; H 4.39; Cu 14.02; N 29.86; O 20.48. $C_{12}H_{20}CuN_{10}O_6$. Calculated, %: C 31.04; H 4.31; Cu 13.79; N 30.17; O 20.69.

Dinitratobis[(5-amino-1,2,4-triazol-3-yl)pentane-aqua]copper (VIIa) was synthesized in a similar way, mp 180°C (decomp.).

Dinitratobis[(5-amino-1,2,4-triazol-3-yl)octane-aqua]copper (VIIIa). Bis(5-amino-1,2,4-triazol-3-yl)-octane (**VIIIb**), 1.66 g, was dissolved with stirring in 50 ml of 5% NaOH, after which a solution of 2.89 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 ml of distilled water was added. The reaction mixture was stirred for 30 min and then treated with 100 ml of ethanol to precipitate complex **VIII**. Yield 1.82 g (63%), mp 172°C (decomp.). Found, %: C 35.76; H 4.99; Cu 12.53; N 27.48; O 19.24. $C_{15}H_{26}CuN_{10}O_6$. Calculated, %: C 35.57; H 5.14; Cu 12.65; N 27.67; O 18.97.

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