Polish J. Chem., **76**, 1371–1380 (2002) **INORGANIC CHEMISTRY**

Regioselective Synthesis of New Chelating Bistetrazole Ligands and Study of Their Copper(II) Complexes

by S.V. Voitekhovich, P.N. Gaponik, D.S. Pytleva, A.S. Lyakhov and O.A. Ivashkevich

Research Institute for Physical Chemical Problems of the Belarusian State University, 14 Leningradskaya str., 220050 Minsk, Republic of Belarus
E-mail: azole@bsu.by

(Received April 8th, 2002)

Synthesis of some new N-substituted bistetrazoles is described. 1,5-Bis(2-*tert*-butyl-5-tetrazolyl)-3-oxopentane (btop) is obtained by regioselective alkylation of 1,5-bis(5-tetrazolyl)-3-oxopentane with *tert*-butyl alcohol in 96% sulphuric acid media. 1,5-Bis(1-methyl-5-tetrazolyl)-3-oxopentane (mtop) is synthesized by exhaustive methylation of 1,5-bis(2-*tert*-butyl-5-tetrazolyl)-3-oxopentane followed by the removal of *tert*-butyl group from the formed tetrazolium methyl sulphate in acidic conditions. Isomeric tetrazolium perchlorate is converted in analogous conditions to perchlorate of 1,5-bis(1-methyl-5-tetrazolyl)-3-oxopentane. Synthesized bistetrazoles are found to react with copper(II) chloride in ethyl alcohol or acetone solutions giving solid $[Cu(mtop)Cl_2]$ and $[Cu(btop)Cl_2]$ complexes. Perchlorate of 1,5-bis(1-methyl-5-tetrazolyl)-3-oxopentane reacts with copper(II) chloride in ethyl alcohol leading to formation of complex $[Cu(mtop)Cl_2]$, whereas in aqueous solution complex $[Cu(mtop)_2](ClO_4)_2$ is formed. According to X-ray study of chloride complexes, Cu(II) is surrounded by a tridentate chelating ligand and two halide anions resulting in distorted square pyramidal geometry.

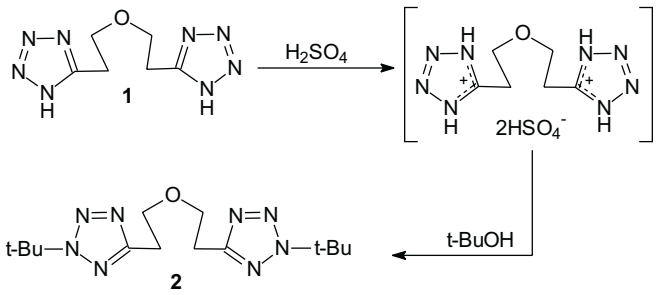
Key words: tetrazoles, tetrazolium salts, selective alkylation, chelating ligands, complexes with copper(II) chloride, X-ray structures

N-Substituted tetrazoles are of considerable interest as ligands due to unusual properties of their complexes with salts of transition metals. Specifically, complexes of mononuclear 1-alkyl- and 1-alkenyltetrazoles with copper(II) chloride were found to be a low-temperature ferromagnetics [1], while coordination compounds of iron(II) tetrafluoroborate with 1-alkyltetrazoles are characterized by thermal- and light-induced spin transitions [2]. At the same time, the data on synthesis and properties of N-substituted binuclear tetrazoles are rather restricted, in spite of their attractiveness as chelating agents [3] and initial compounds for synthesis of 1-, 2- and 3D metal containing systems [4]. Only in recent years several papers concerning investigations of some complexes of N-substituted binuclear tetrazoles were published [3–10]. More intensive development of investigations in this area is retarded by the absence of convenient methods for synthesis of N-substituted bistetrazoles [11]. Recently we have revealed a new approach to regioselective synthesis of binuclear 1,5- and 2,5-substituted tetrazoles based on alkylation of 5-substituted ones [11]. In this paper we report on synthesis of new chelating bistetrazoles using this approach and on investigation of their complexes with copper(II) chloride.

RESULTS AND DISCUSSION

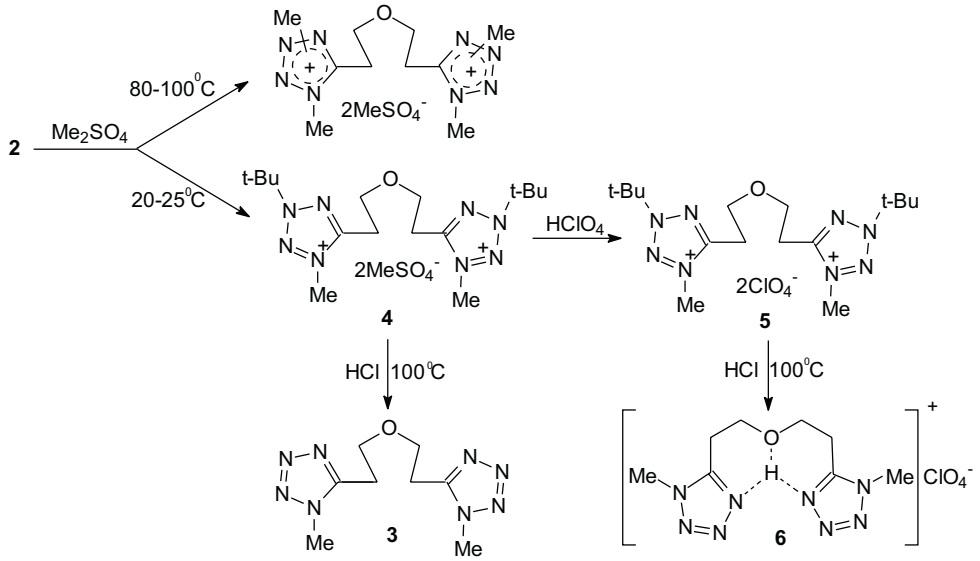
Synthesis of bistetrazoles. 1,5-Bis(5-tetrazolyl)-3-oxopentane **1**, which contains two tetrazole rings bonded by a flexible ether chain, was chosen as the starting material. Bistetrazole **1** was found to react readily with *tert*-butyl alcohol in 96% sulphuric acid media. Alkylation proceeds regioselectively on N2 atoms of both tetrazole rings leading to formation of 1,5-bis(2-*tert*-butyl-5-tetrazolyl)-3-oxopentane **2** with 78% yield.

Scheme 1



The regioselectivity of *tert*-butylation is determined by full protonation of tetrazole **1** on the most nucleophilic N4 atoms resulting in formation of bis-1H-4H-5R-tetrazolium cation, in which N2(N3) atoms only are accessible for electrophilic attack [11]. The obtained bistetrazole **2** was used for synthesis of 1,5-bis(1-methyl-5-tetrazolyl)-3-oxopentane **3** by exhaustive methylation of tetrazole **2** followed by the removal of *tert*-butyl group from the tetrazole ring.

Scheme 2

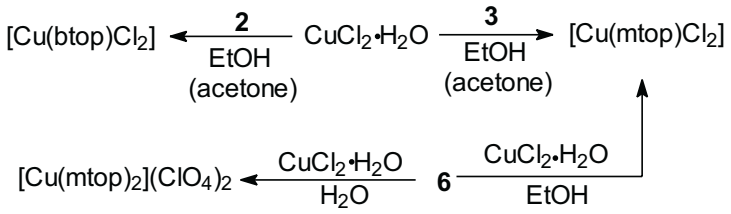


The selective quaternization of bistetrazole **2** is observed when the reaction proceeds without heating. An increasing of the temperature leads to formation of a mixture of the methylation products. This is probably conditioned by the possibility of proceeding of thermally induced de*tert*-butylation of bistetrazole **2** or tetrazolium salt **4** followed by the exhaustive non-selective methylation. De*tert*-butylation of the salt **4** is achieved under refluxing of the latter with hydrochloric acid. Suprisingly, expected tetrazole **3** was obtained by dealkylation of tetrazolium methyl sulphate **4** only, while dealkylation of isomeric perchlorate **5** in analogous conditions results in formation of salt **6**. N-Substituted tetrazoles are known to be weak bases ($-pK_{BH^+}$ = 2.2–3.7) [12] and, probably, for this reason their salts are not stable in aqueous solutions [13]. Unexpectedly, bistetrazolium salt **6** is stable under refluxing with water. Such unusual stability of this salt is likely to be determined by its symmetrical structure stabilized by formation of two six-membered rings at the expence of hydrogen atom bonding with three main donor centers, namely, N4 atoms of the tetrazole cycles and oxygen atom as exemplified by the data of NMR spectra (see Experimental). The proposed structure of salt **6** and its unusual stability allow one to assume that tetrazole **3** reacts with proton with formation of a stable cation similarly to "proton sponges" [14].

The obtained compounds **2** and **3** were attributed to 2,5- and 1,5-disubstituted tetrazoles correspondingly according to data of ^{13}C NMR chemical shifts (CS) of C5 atom of the heterocycle. The latter for bistetrazoles **2** and **3** correspond to well-known literature data on dialkyltetrazoles whereby CS of C5 atom for 2,5-disubstituted tetrazoles are displaced to a low weak field by ~10 ppm in comparison with those of isomeric 1,5-disubstituted tetrazoles [15].

Synthesis of complexes. It was found that bistetrazoles **2** and **3** react easily without heating with copper(II) chloride in ethyl alcohol or acetone giving coordination compounds $[Cu(btop)Cl_2]$ and $[Cu(mtop)Cl_2]$ (btop = 1,5-bis(2-*tert*-butyl-5-tetrazolyl)-3-oxopentane; mtop = 1,5-bis(1-methyl-5-tetrazolyl)-3-oxopentane) irrespective of the reagents ratio. Perchlorate **6** reacts with copper(II) chloride in ethyl alcohol also leading to formation of complex $[Cu(mtop)Cl_2]$, whereas in water complex of another composition $[Cu(mtop)_2](ClO_4)_2$ is formed.

Scheme 3



IR spectra. Table 1 contains the data on frequencies and relative intensities for the main absorption bands of the ligands and complexes. The assignment of these bands was made in accordance with [16]. The complexation is found to result in significant change in absorption bands of endocyclic bonds of bistetrazole **2**. In particular, ν(C=N) and ν(N=N) bands are subjected to high-frequency displacement

about 20 cm^{-1}. This is probably caused by the coordination of ligand *via* the ring nitrogen atom. The complexation is accompanied by the increase of intensity of ν(N=N) band due to polarization of N=N bond under formation of Cu–N bond (Table 1). It should be noted that similar changes were observed under complexation of 2-methyl-5-vinyltetrazole with palladium(II) chloride, where formation of Pd–N4 bond was found [17]. The similar changes in IR spectra are observed under complexation of ligand **3**. In the free ligand, ν(C=N) band appears at 1531 cm^{-1}, whereas in complexes $[Cu(mtop)Cl_2]$ and $[Cu(mtop)_2](ClO_4)_2$ and salt **6** it is shifted to 1540, 1544 and 1584 cm^{-1} correspondingly.

Table 1. Characteristic IR bands of the ligands and the complexes (in cm^{-1})[a].

Bands	**2**	**3**	**6**	$[Cu(btop)Cl_2]$	$[Cu(mtop)Cl_2]$	$[Cu(mtop)_2](ClO_4)_2$
ν(C=N)	1489 s	1531 s	1595 m	1510 s	1540 s	1544 m
ν(N=N)	1398 w	1422 m	1509 m	1418 m	1482 s	1484 s
Asym (C–O–C)	1123 s	1119 s	1098 s	1085 s	1104 m 1080 s 1064 m	1100 vs

[a]vs – very strong; s – strong; m – medium; w - weak.

Some changes are observed for bands of asymmetric stretching vibrations of C–O–C bonds, which are located at 1085–1120 cm^{-1} in IR spectra of dialkylethers [18]. Bands of these vibrations for ligands **2** and **3** are shifted to lower frequencies by 38 and 19 cm^{-1} under formation of $[Cu(btop)Cl_2]$ and $[Cu(mtop)_2](ClO_4)_2$ complexes respectively. The spectra of $[Cu(mtop)Cl_2]$ show three strong bands at the above mentioned region. This fact indicates that coordination can occur *via* oxygen too. It is known [18] that alkyl ethers are weak n-donors and capable to form coordination compounds with some metal salts.

Structure of complexes. The crystal structures of $[Cu(btop)Cl_2]$ and $[Cu(mtop)Cl_2]$ complexes have been determined by X-ray analysis. It should be noted that these complexes are the first ever reported representatives of molecular chelate complexes of the binuclear N-substituted tetrazoles. The crystal data and details of the structure refinement for $[Cu(btop)Cl_2]$ are collected in Table 2. The full set of crystallographic data for $[Cu(mtop)Cl_2]$ was reported previously in separate communication [19]. The selected geometric parameters of the determined structures are summarized in Table 3. Both $[Cu(btop)Cl_2]$ and $[Cu(mtop)Cl_2]$ are molecular complexes, in which a coordination polyhedron of copper(II) is square pyramid (4+1) (see Figs. 1 and 2). The basal positions are occupied by the two chlorine atoms and two N4 atoms of the ligand molecule. The oxygen atom lies in an apical position of the pyramid. The Cu–O distance in $[Cu(mtop)Cl_2]$ (2.499 Å) is significantly longer than that in $[Cu(btop)Cl_2]$ (2.395 Å). These distances are somewhat longer than usual Cu–O bonding distances [20]. The Cu–N distances (Table 3) are usual for copper(II) complexes with N-substituted tetrazoles [21,22]. The ligand molecules are tridentate. It should be noted that the oxygen atom of the ligand molecule in $[Cu(btop)Cl_2]$ lies on a twofold axis resulting in

the twofold internal symmetry of the ligand. In both investigated complexes the tetrazole cycles are practically planar and somewhat differ in geometry. This is caused by the presence of substituents at different positions of the tetrazole ring. The ligand molecule of $[Cu(mtop)Cl_2]$ is characterized by the geometry typical of 1,5-substituted tetrazoles [23] and their copper(II) complexes [21–23], in which the shortest bond is N2–N3, while N1–C5 bond is somewhat longer than N4–C5 one (Table 4). In 2,5-substituted tetrazole rings of $[Cu(btop)Cl_2]$ the shortest bond is N2–N3, whereas N4–C5 bond is longer than N1–C5 one. Similar geometry of the tetrazole ring is observed for 2,5-substituted tetrazoles [11,23].

Table 2. Crystal data and structure refinement for $[Cu(btop)Cl_2]$.

Empirical formula	$C_{14}H_{26}N_8OCuCl_2$
Formula weight	456.87
Temperature	293(2) K
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	*a* = 18.312(4) (Å)
	b = 6.8250(9) (Å)
	c = 18.587(3) (Å)
	α = 90 (°)
	β = 115.750(14) (°)
	γ = 90 (°)
Volume	2092.3(6) ($Å^3$)
Z	4
Density (calculated)	1.450 (Mg/m^3)
Absorption coefficient	1.320 (mm^{-1})
F(000)	948
Crystal size	0.40 × 0.35 × 0.15 (mm)
θ range for data collection	2.43 to 30.07 (°)
Index ranges	$-25 \le h \le 0$, $-9 \le k \le 0$, $-23 \le l \le 26$
Reflections collected	3284
Independent reflections	3079 [Rint = 0.0263]
Completeness to θ = 30.07°	100.0 %
Absorption correction	Psi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3079 / 0 / 122
Goodness-of-fit on F^2	1.051
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0459, wR2 = 0.1318
R indices (all data)	R1 = 0.0513, wR2 = 0.1368
Largest diff. peak and hole	0.572 and –0.811 (e $Å^{-3}$)

Table 3. Selected bond distances [Å] and bond angles [°] in determined structures.

	[Cu(mtop)Cl_2]		[Cu(btop)Cl_2]
Cu–N4	2.002(2)	2.003(2)	1.9829(19)
Cu–Cl	2.2464(7)	2.2557(7)	2.2514(7)
Cu–O	2.499(2)		2.395(2)
N1–N2	1.354(3)	1.354(2)	1.334(3)
N2–N3	1.280(2)	1.291(2)	1.308(3)
N3–N4	1.361(2)	1.361(2)	1.320(2)
N4–C5	1.321(2)	1.321(2)	1.343(3)
N1–C5	1.334(2)	1.334(2)	1.322(3)
N4–Cu–N4′	166.75(11)		166.77(7)
N4–Cu–Cl1	91.64(6)		92.97(5)
N4′–Cu–Cl1	91.14(7)		92.02(5)
N4–Cu–Cl2	91.14(7)		91.29(5)
N4′–Cu–Cl2	91.64(6)		90.79(5)
Cl1–Cu–Cl2	155.77(4)		148.75(3)
N4–Cu1–O	83.37(6)		81.73(6)
N4′–Cu1–O	83.37(6)		85.31(6)
Cl1–Cu–O	102.11(2)		100.50(4)
Cl2–Cu–O	102.11(2)		110.75(5)

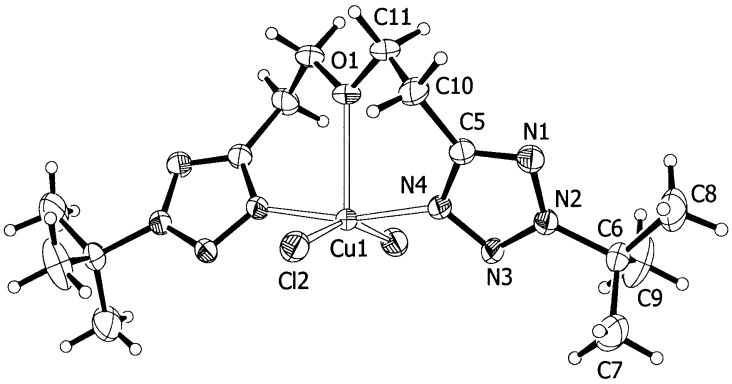


Figure 1. Atom numbering in the structure of [Cu(btop)Cl_2] (displacement ellipsoids are shown at the 30% probability level).

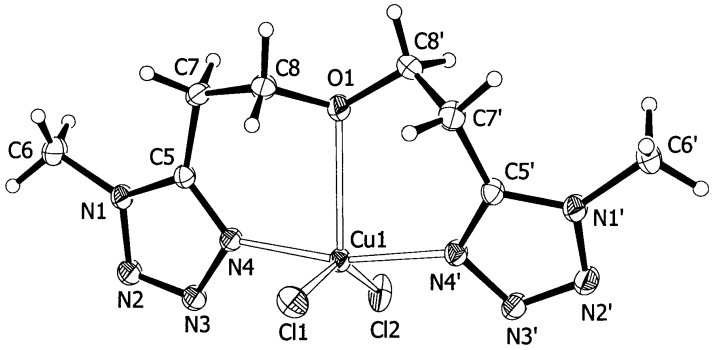


Figure 2. Atom numbering in the structure of [Cu(mtop)Cl_2] (displacement ellipsoids are shown at the 30% probability level).

Inspecting the packing of the two discussed structures, the following peculiarities may be found. There are no classic hydrogen bonds in these structures, however, some intermolecular contacts may be indicated (Table 4). These weak interactions are responsible for the forming of infinite one-dimensional chains of [010] direction in the structure of $[Cu(btop)Cl_2]$ (Fig. 3). In the $[Cu(mtop)Cl_2]$ these interactions lead to the sheets parallel to (010) plane (Fig. 4).

Table 4. Hydrogen bonding geometry (Å, °).

Complex	D–H···A	D–H	H···A	D···A	D–H···A
$[Cu(btop)Cl_2]$	C11–H11A···Cl2[a]	0.97	2.79	3.729(3)	164
$[Cu(mtop)Cl_2]$	C7–H7A···Cl2[b]	0.97	2.79	3.697(2)	156
	C7′–H7′···N3[c]	0.97	2.59	3.484(3)	154

Symmetry codes: (*a*) *x*, 1+*y*, *z*; (*b*) *x*–1, *y*, *z*; (*c*): *x*–1/2, 1/2–*y*, *z*–1/2.

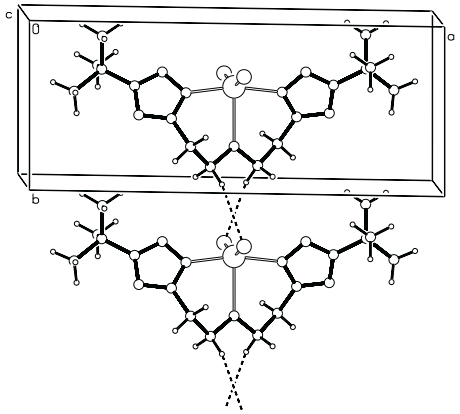


Figure 3. Weak interactions in the structure of $[Cu(btop)Cl_2]$ marked by thin dashed lines.

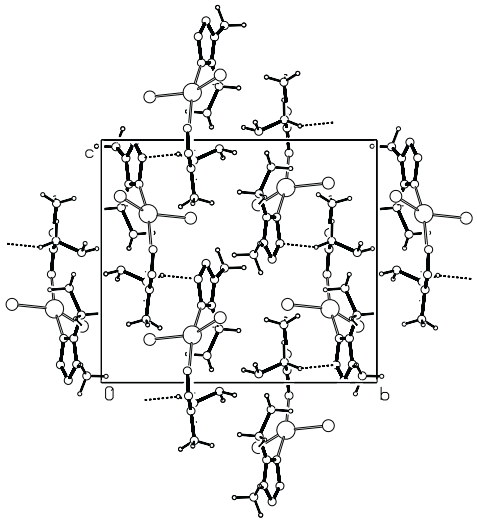


Figure 4. Packing diagram of $[Cu(mtop)Cl_2]$ (view along the *a* axis).

EXPERIMENTAL

General. M.p.s' were determined in capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Tesla BS 567A spectrometer operating at frequencies of 100.028 and 25.142 MHz correspondingly with hexamethyldisiloxane as internal standard and hexadeuteriuodimethylsulfoxide or trideuteriuoacetonitrile as a solvent. IR spectra were measured with FT-IR "Spectrum 1000" Perkin-Elmer spectrophotometer. Metal contents of the complexes were determined using "Specol 21" spectrophotometer in a solution prepared by decomposing the complexes by heating with concentrated perchloric acid and dissolving the residue in aqueous ammonia. 1,5-Bis(5-tetrazolyl)-3-oxopentane **1** was obtained according to [24].

1,5-Bis(2-*tert*-butyl-5-tetrazolyl)-3-oxopentane 2. *Tert*-butanol (2.2 ml, 23 mmol) was added dropwise with stirring to a solution of 1,5-bis(5-tetrazolyl)-3-oxopentane **1** (2.3 g, 11 mmol) in sulphuric acid (96%, 15 ml). The mixture was further stirred at room temperature for 2 h. Then the reaction mixture was poured into ice (50–70 g). The precipitate was filtered, washed with cold water and dried *in vacuo*. Crystallization from diethyl ether – hexane (1:1) miture gave compound **2** (2.8 g, 78%). M.p. 49–51°C. ^{1}H NMR (CD_3SOCD_3), δ: 3.84 (t, 4H, $2CH_2O$), 3.04 (t, 4H, $2CH_2$), 1.67 (s, 18H, 6Me). ^{13}C NMR (CD_3SOCD_3), δ: 166.9 ($2C_{(5)}$), 71.7 ($2CH_2O$), 67.1 ($2\underline{C}Me_3$), 32.6 (6Me), 29.7 ($2CH_2$). Anal. (%). Calcd. for $C_{14}H_{26}N_8O$ (322.41): C 52.15; H 8.13; N 34.76. Found: C 52.25; H 8.20; N 34.67.

1,5-Bis(1-methyl-5-tetrazolyl)-3-oxopentane 3. Solution of tetrazole **2** (3.2 g, 10 mmol) and dimethyl sulphate (2.7 ml, 30 mmol) in acetonitrile or trichloromethane (5 ml) was stirred at room temperature for 4 days. Then hydrochloric acid (36%, 50 ml) was added and the mixture was stirred for 1 h. The upper layer of the mixture containing salt **4** was separated and heated in water bath for 5 h. Removal of the solvent *in vacuo* yielded white solid, recrystallization of which from water gave colourless crystals of compound **3** (1.2 g, 49%). M.p. 77–79°C. ^{1}H NMR (CD_3CN), δ: 3.95 (s, 6H, 2Me), 3.87 (t, 4H, $2CH_2O$), 3.11 (t, 4H, $2CH_2$). ^{13}C NMR (CD_3SOCD_3), δ: 157.6 ($2C_{(5)}$), 71.5 ($2CH_2O$), 37.8 (6Me), 27.7 ($2CH_2$). ^{13}C NMR (CD_3CN), δ: 149.4 ($2C_{(5)}$), 65.7 ($2CH_2O$), 32.3 (6Me), 23.0 ($2CH_2$). Anal. (%). Calcd. for $C_8H_{14}N_8O$ (238.25): C 40.33; H 5.92; N 47.03. Found: C 39.78; H 5.45; N 47.99.

Salt 5. Solution of tetrazole **2** (3.2 g, 10 mmol) and dimethyl sulphate (2.7 ml, 30 mmol) in acetonitrile or trichloromethane (5 ml) was stirred at room temperature for 4 days. Then water (30 ml) and perchloric acid (62%, 10 ml) were added and the reaction mixture was stirred for 1 h. Colourless crystals of salt **5** (4.2 g, 76%) were precipitated on cooling of the formed solution to 0–5°C. M.p. 174–176°C. ^{1}H NMR (CD_3SOCD_3), δ: 4.29 (s, 6H, 2Me), 3.88 (t, 4H, $2CH_2O$), 3.39 (t, 4H, $2CH_2$), 1.78 (s, 18H, 6Me). Anal. (%). Calcd. for $C_{16}H_{32}Cl_2N_8O_9$ (551.38): C 34.85; H 5.85; N 20.32; Cl 12.86. Found: C 35.26; H 5.20; N 20.69; Cl 12.06.

Salt 6. Suspension of tetrazolium salt **5** (3.3 g, 6 mmol) in hydrochloric acid (36%, 50 ml) was heated under water bath for 5 h. Colourless crystals of salt **6** (1.6 g, 79%) were precipitated on cooling of the formed solution to 0–5°C. M.p. 145–147°C. ^{1}H NMR (CD_3CN), δ: 4.20 (s, 6H, 2Me), 4.05 (t, 4H, $2CH_2O$), 3.43 (t, 4H, $2CH_2$). ^{13}C NMR (CD_3CN), δ: 148.9 ($2C_{(5)}$), 62.9 ($2CH_2O$), 34.6 (6Me), 22.6 ($2CH_2$). Anal. (%). Calcd. for $C_8H_{15}ClN_8O_5$ (338.71): C 28.37; H 4.46; N 33.08; Cl 10.47. Found: C 27.86; H 5.11; N 33.78; Cl 11.01.

General procedure for synthesis of complexes. The corresponding ligand (1 mmol) was dissolved in acetone or ethyl alcohol (10 ml). A solution of copper(II) chloride dihydrate (1 mmol) in the above mentioned solvents (15 ml) was added to ligand solution and mixture was left for 2 h. The precipitate of the complex was then filtered, washed with acetone and dried *in vacuo* at room temperature. **[Cu(btop)Cl_2]**. Blue crystals decomposed at 190°C. Yield 65% (acetone), 53% (ethyl alcohol). Anal. (%). Calcd. for $C_{14}H_{26}Cl_2N_8O$ (456.87): Cu 13.91; Cl 15.52. Found: Cu 13.50; Cl 14.10. **[Cu(mtop)Cl_2]**. Green crystals decomposed at 215°C. Yield 56% (acetone), 45% (ethyl alcohol), 40% (synthesis from salt **6** in aqueous solution). Anal. (%). Calcd. for $C_8H_{14}Cl_2N_8O$ (372.71): Cu 17.05; Cl 19.02. Found: Cu 17.28; Cl 18.01.

$[Cu(mtop)_2](ClO_4)_2$. A solution of salt **6** (2 mmol) and copper(II) chloride dihydrate (1 mmol) in 10 ml of water was left for 2 h. The precipitate of the complex $[Cu(mtop)_2](ClO_4)_2$ was then filtered, washed with water and dried *in vacuo* at room temperature. Blue crystals decomposed >290°C. Yield 66%. Anal. (%). Calcd. for $C_8H_{15}ClN_8O_5$ (738.95): Cu 8.60; Found: Cu 8.35.

X-ray analysis of complexes. X-ray data were collected on a Nicolet R3m diffractometer (graphite-monochromated MoKα radiation, ω-2θ scans). The intensity data were corrected for Lorentz and polarization effects and for absorption (psi-scan absorption correction [25]). The structure was solved by direct methods (SIR 97 [26]). Refinement on F^2 was carried out by full matrix least-squares techniques (SHELXL-97 [27]). Anisotropic displacement parameters were used for all non-hydrogen atoms. All the hydrogen atoms were introduced at calculated positions and included in the refinement riding on their carrier atoms (with $U_{iso}(H)$ equal to $1.2U_{eq}$ of the corresponding carrier atom and $1.5U_{eq}$ for the methyl groups). Crystal data and numerical details of the structure determination are given in Tables 2–4.*

REFERENCES

1. Lavrenova L.G., Ikorskii V.N., Larionov S.V., Bogatikov A.N. and Gaponik P.N., *Zh. Neorg. Khim.,* **38**, 1517 (1993).
2. Lavrenova L.G. and Larionov S.V., *Koord. Khim.,* **24**, 403 (1998).
3. Downard A.J., Steel P.J. and Steenwijk J., *Austral. J. Chem.,* **48**, 1643 (1995).
4. Saalfrank R.W., Schobert K., Trummer S. and Wolski A., *Z. Naturforsch*., **50b**, 642 (1995).
5. Gaponik P.N., Karavai V.P., Davshko I.E., Degtyarik M.M. and Bogatikov A.N., *Khim. Geterotsikl. Soedin.,* 1528 (1990).
6. Lavrenova L.G., Bogatikov A.N., Sheludyakova L.A., Ikorskii V.N., Larionov S.V. and Gaponik P.N., *Zh. Neorg. Khim.,* **36**, 1220 (1991).
7. Pandey R.N., Kumari R. and Kumar N., *Asian J. Chem.,* **7**, 285 (1995).
8. Van Koningsbruggen P.J., Garcia Y., Kooijman H., Spek A.L., Haasnoot J.G., Moscovici J., Provost K., Michalowicz A., Renz F. and Gutlich P., *Inorg. Chem.,* **39**, 1891 (2000).
9. Van Koningsbruggen P.J., Garcia Y., Kooijman H., Spek A.L., Haasnoot J.G., Kahn O., Linares J., Codjovi E. and Varret F., *J. Chem. Soc. Dalton Trans.,* **4**, 466 (2001).
10. Gaponik P.N., Voitekhovich S.V., Maruda I.I., Kulak A.A. and Ivashkevich O.A., *Vesti NAN Belarusi, Ser. Khim.,* 62 (2001).
11. Gaponik P.N., Voitekhovich S.V. and Lyakhov A.S., *Khim. Geterotsikl. Soedin.,* 387 (2000).
12. Naumenko V.N., Gaponik P.N., Koren A.O. and Degtyarik M.M., *Vesti NAN Belarusi, Ser. Khim.,* 64 (1993).
13. Gaponik P.N., Voitekhovich S.V., Maruda I.I., Kulak A.A. and Ivashkevich O.A., *Polish J. Chem.,* **72**, 2247 (1998).
14. Pozharskii A.F., *Usp. Khim.,* **67**, 1 (1998).
15. Begrtup M., Elguero J., Faure R., Camps P., Estopa C., Ilavsky D., Fruchier A., Marzin C. and Mendoza J., *Magn. Res. Chem.,* **26**, 134 (1988).
16. Degtyarik M.M., Gaponik P.N., Naumenko V.N., Lesnikovich A.I. and Nikanovich M.V. *Spectrochim. Acta,* **43A**, 349 (1987).
17. Aliev Z.G., Goncharov T.K., Grachev V.P., Kurmaz S.V. and Roschupkin V.P., *Koord. Khim.,* **17**, 1101 (1991).
18. Wieser H. and Krueger P.J., *Spectrochim. Acta,* **26A**, 1349 (1970).
19. Lyakhov A.S., Gaponik P.N., Voitekhovich S.V., Ivashkevich D.O., Pytleva D.S. and Ivashkevich L.S., *Acta Cryst.,* **C57**, 1374 (2001).

*CCDC No. 1870651 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk)

20. Orpen A.J., Brammer L., Allen F.H., Kennard O., Watson D.G. and Taylor R., *J. Chem. Soc. Dalton Trans.,* S1-S83 (1989).
21. Ivashkevich D.O., Gaponik P.N., Bogatikov A.N. and Govorova A.A., *Acta Cryst.,* **E57**, m335 (2001).
22. Palkina K.K., Kuz'mina N.E., Lyakhov A. S., Gaponik P.N., Bogatikov A.N., Govorova A.A. and Ivashkevich L.S., *Zh. Neorg. Khim.,* **46**, 1495 (2001).
23. Allen F.H. and Kennard O., *Chem. Des. Autom. News*, **8**, 31 (1993).
24. Ermakova M.I., Shikhova I.A., Ignatenko I.K. and Latosh N.I., *Zh. Obsch. Khim.,* **53**, 1364 (1983).
25. North A.C.T., Phillips D.C. and Mathews F.S., *Acta Cryst.*, **A24**, 351 (1968).
26. Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C., Guagliardi A., Moliterni A.G.G., Polidori G. and Spagna R., *J. Appl. Cryst.*, **32**, 115 (1999).
27. Sheldrick G.M., Program for crystal structure refinement, University of Goettingen, 1997.