Synthesis and spectroscopic studies on nickel(II), cobalt(II) and copper(II) complexes of tetrazolyl-1-acethydrazide. Crystal structure of $[Cu(TH\text{-}1)_2](ClO_4)_2$

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Abstract

Complexes of nickel(II), cobalt(II) and copper(II) with the potentially polydentate ligand tetrazolyl-1-acethydrazide (TH-1) were prepared and characterized by IR spectroscopy. The spectral data obtained suggested that TH-1 can act as both a bidentate and tridentate ligand, the hydrazide group forming a five-membered metal ring in both cases. The X-ray structural determination of the copper(II) compound $[Cu(TH\text{-}1)_2](ClO_4)_2$ was carried out. It has been shown that the compound has a chain structure and TH-1 performs the function of a tridentate-bridging ligand bonding the adjacent metal atoms through the chelate hydrazide fragment and the nitrogen atom in position 4 of tetrazole, respectively.

Introduction

Hydrazides of carboxylic acid, $RCONHNH_2$, as has been shown in numerous studies [1–3], act as N,O-chelating ligands upon metal coordination. Cases of monodentate linkage of the hydrazide group, scarcely referred to in the literature (for example, refs. [4–6] describe coordination through the oxygen atom, refs. 7 and 8 mention the nitrogen atom), are of either a hypothetical character or are based on an erroneous interpretation of the IR spectral data.

However, there is no unanimous approach to the evaluation of the coordination mode of the hydrazide fragment in the case of hydrazides with the substituents R which contain the donor nitrogen atoms. Thus, in the case of carbohydrazide (hydrazide which contain the hydrazine group in α-position), the formation of a six-membered metal ring due to N,N-bonding instead of the more stable typical five-membered ring was assumed in refs. 9 and 10. In the investigation of the coordination chemistry of the hydrazides of various pyridine- and pyrazolcarboxylic acids, the authors proposed for the hydrazide group either a monodentate coordination with the metal via the O atom [11, 12] or via the N atom [13–16] alongside the ordinary mode of coordination, or they in general denied any linkage of the hydrazide fragment with the metal which coordinated the ligand only via the N atom of the heterocycle [15, 17].

It should be noted that these conclusions were mainly based on IR data. At the same time, X-ray structural studies of some compounds among the above-mentioned characterize the hydrazide group only as the N,O-chelate [18–21].

In the course of our investigation of the potentially polydentate derivatives of carboxylic acids hydrazides, we synthesized tetrazolyl-1-acethydrazide (TH-1). It is known that 1-monosubstituted tetrazoles in complexes behave as monodentate ligands bonding to the metal atom via the ring N atom [22]. Accordingly, it was interesting to find out how the presence of the tetrazole ring would affect the coordination mode of the hydrazide fragment.

Since usually used anions, such as sulfate, chloride or nitrate, form strong hydrogen bonds with the ligand, which often substantially distort the spectral parameters of the complex compound and makes their interpretation difficult, we synthesized complex compounds of TH-1 with metal perchlorates whose anions are known to exhibit a weak tendency to form hydrogen bonds.

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Experimental

All chemicals used were of analytical grade. Perchlorate was analyzed as its Nitron salt [23].

Tetrazolyl-1-acetic ether (TAE) was prepared according to the method given in ref. 24 and was additionally purified by recrystallization from hexane (by cooling the saturated solution in hexane at room temperature to −10 °C), m.p. 46–47 °C (ref. 25 m.p. 32–34 °C). PMR data (δ,ppm): 9.47 (1H, s, *CH*), 5.6 (2H, s, CH_2), 4.22 (2H, q, J_{HH} 3.55 Hz, CH_2), 1.25 (3H, t, J_{HH} 3.5 Hz, CH_3).

Preparation of tetrazolyl-1-acethydrazide (TH-1)

A mixture of 6.25 g (0.04 mol) of TAE and 2.12 ml (0.044 mol) of hydrazine hydrate in 25 ml of isopropanol was heated to reflux and was left standing overnight at room temperature. The colourless crystals which formed were recrystallized from a mixture of 64 ml of isopropanol and 5 ml of water. Yield 4.6 g (81%), m.p. 118–118.5 °C. *Anal.*Calc. for $C_3H_6N_6O$: C, 25.35; H 4.23. Found: C, 25.57; H, 4.33%. PMR data (δ,ppm): 9.30 (1H, s, *CH*), 9.23 (1H, t, J_{HH} 10 Hz, N*H*), 5.13 (2H, s, CH_2), 4.40 (2H, d, J_{HH} 10 Hz, NH_2).

Preparation of bis(tetrazolyl-1-acethydrazide)copper(II) perchlorate (I)

0.29 ml (2.5 mmol) of a solution of 57% $HClO_4$ was added to a solution of 1.07 g (7.5 mmol) of TH-1 in 1.5 ml of water and then 0.95 g (2.5 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ was dissolved. Light-blue crystals were separated from the resultant solution upon standing overnight at 5–10 °C. Yield 0.94 g (69%), decomposition point (dec.p.) 250 °C. *Anal.*Calc. for $C_6H_{12}N_{12}Cl_2O_{10}Cu$: ClO_4, 36.41. Found: ClO_4, 36.0%.

Preparation of bis(tetrazolyl-1-acethydrazide)nickel(II) perchlorate (II)

A solution of 1.42 g (10 mmol) of TH-1 in 25 ml of glacial CH_3COOH was added to a stirred solution of 1.83 g (5 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ in the same solvent (10 ml). 15 ml of water were added and the mixture was slightly heated on a water bath until a clear solution was obtained. The volume was reduced by evaporation to about one half and the resultant blue precipitate was collected, washed with alcohol and dried in vacuum at 70 °C. Yield 1.57 g (58%), dec.p. 360 °C. *Anal.*Calc. for $C_6H_{12}N_{12}Cl_2O_{10}Ni$: ClO_4, 36.71. Found: ClO_4, 36.0%.

Preparation of tris(tetrazolyl-1-acethydrazide)nickel(II) perchlorate (III)

A solution of 0.6 g (1.6 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ in 3 ml of glacial CH_3COOH was added to a stirred solution of 0.7 g (4.9 mmol) of TH-1 in the same solvent (8 ml). The resultant blue precipitate was collected, washed with alcohol and dried in vacuum at 70 °C. Yield 1.07 g (98%), m.p. 260 °C. *Anal.*Calc. for $C_9H_{18}N_{18}Cl_2O_{11}Ni$: ClO_4, 29.08. Found: ClO^4, 29.9%.

Preparation of bis(tetrazolyl-1-acethydrazide)cobalt(II) perchlorate (IV)

0.73 g (2 mmol) of $Co(ClO_4)_2 \cdot 6H_2O$ was dissolved in a hot solution of 0.57 g (4 mmol) of TH-1 in 4 ml of water. The mixture was left standing to reach room temperature, the resultant crimson-colored precipitate was collected, washed with alcohol and dried. Yield 1.04 g (96%), dec.p. 305 °C. *Anal.*Calc. for $C_6H_{12}N_{12}Cl_2O_{10}Co$: ClO_4, 36.69. Found: ClO_4, 36.2%.

Caution: the complexes synthesized here explode upon hammer impact and on rapid heating on a hot plate.

Physical measurements

The IR spectra were recorded with a UKC-24 spectrophotometer as Nujol (1800–500, 1300–400 cm^{-1}) and hexachlorobutadiene (4000–1800, 1500–1300 cm^{-1}) mulls. Electron absorption spectra of water solution and Nujol mulls in the region of 350–800 nm were measured with a CΦ-20 spectrophotometer. ^1H NMR spectra were recorded at 60 MHz on a Tesla BS-467 spectrometer for solution in DMSO-d_6 at 25 °C with GMDS as internal standard.

X-ray structure determination

A monoclinic crystal I having approximate dimensions 0.4×0.3×0.2 mm was used for data collection at ambient temperature. Three-dimensional data were collected on a Syntex $P2_1$ automated four-circle diffractometer with the θ–2θ variable scan technique. Graphite-monochromatized Mo Kα radiation was used. The unit cell parameters were first calculated from 13 reflections and then were refined by a least-squares procedure, using the centered coordinates of 24 reflections with $7 \leqslant 2\theta \leqslant 35°$. The space group $P2_1/a$ was constituted with the systematic absences observed in the data. Data were collected in the range $4 \leqslant 2\theta \leqslant 55°$. Corrections for Lorentz and polarization effect were applied to the intensity data, but no absorption correction was carried out. Crystallographic data are tabulated in Table 1.

The structure was solved by locating the positions of the Cu atoms from inspection of the three-dimensional Patterson function; the remaining atoms were located from a subsequent Fourier synthesis. The structure was refined by a full-matrix least squares procedure. The function $\Sigma w(||F_0|-|F_c||)^2$ was

TABLE 1. Crystal data for $[Cu(TH\text{-}1)_2](ClO_4)_2$

Formula	$C_6H_{12}N_{12}O_{10}Cl_2Cu$
Molecular weight	546.45
Crystal class	monoclinic
Space group	$P2_1/a$
Extinction conditions	$h0l$: $h=2n$, $0k0$: $k=2n$
a (Å)	9.850(1)
b (Å)	15.437(2)
c (Å)	11.780(2)
β (°)	93.08(1)
V (Å^3)	1788.7(1.3)
Z	4
D_{calc} (g cm^{-3})	2.028
μ (cm^{-1}) (Mo Kα)	16.6
Radiation Mo Kα	$\lambda=0.71069$
Standard reflections	2 (measured every 100 reflections)
Octants collected	hkl, $hk\bar{l}$
Reflections collected	4365
Max. 2θ (°)	55
Min. 2θ (°)	4
No. unique reflections $I_{obs}>3\sigma(I)$	3560
No. parameters refined	328
R	0.056
R_w	0.060
GOF	1.434

minimized. Difference Fourier synthesis gave the positions of all hydrogen atoms. Anisotropic thermal parameters were used for all non-hydrogen atoms. Thermal parameters hydrogen atoms were isotropic and had normal values. Scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography and corrected for anomalous dispersion for Cu and Cl atoms. The final refinement resulted in $R=0.056$ and $R_w=0.060$ ($R=\Sigma(||F_0|-|F_c||)/\Sigma|F_0|$, $R_w=[\Sigma w(||F_0|-|F_c||)^2/\Sigma w|F_0|^2]^{1/2}$ and $w=1/\sigma(F_0^2)+cF_0^2$, $c=0.000625$).

All calculations were carried out using the SHELXTL system. Final atom positions are collected in Table 2 and distances are given in Table 3.

Results and discussion

The interaction of TH-1 with perchlorates of nickel(II), cobalt(II) and copper(II) in water immediately results in coloured complex compounds, though only cobalt compounds are isolated in the solid state. Acidification of the medium is required to obtain the copper complex; the nickel complex can be isolated in the form of an amorphous powder only upon the reaction in acetic acid medium. Nickel perchlorate gave bis- and tris-ligand complexes depending on the ratio of the components. In the case of cobalt and copper salts only a compound with two TH-1 molecules was obtained.

To identify the coordination mode the TH-1 ligand by IR spectroscopy it is necessary to know the position of the vibrational bands of the ligand. Therefore, the vibrational spectra of TH-1 and its deuterated analogs TH-1-d_3 and TH-1-d_4 were studied first [26]. The final band assignment of TH-1 in the IR spectrum is given in Table 4.

In the high frequency region, the IR spectrum of TH-1 has a broad absorption band at 3327 cm^{-1} and a medium intensity band at 3228 cm^{-1} due to the stretching vibration of the hydrazine group. In the spectra of the complexes, the stretching vibration bands of the N$-$H bond undergo both high and low frequency shifting versus the bands of free TH-1, which does not allow a unambiguous conclusion about the participation of the hydrazine group in the coordination. However, in a solution of non-polar $CHCl_3$ which suppresses the formation of intermolecular hydrogen bonds, in the high frequency region of the TH-1 spectrum the bands appear at 3404, 3334 and 3263 cm^{-1}. Comparison of these bands with those in the spectra of the complexes show that in the process of complex formation a shift of the N$-$H bond toward lower frequency takes place thus showing the participation of the amino group in the coordination.

Another criterion for determining the coordination of the amino group is the high frequency shifting of the bands of the amino group wagging (ωNH_2) and twisting (tNH_2) vibrations [27]. In the spectrum of free TH-1, the ωNH_2 band is positioned at 1002 cm^{-1}; in the spectra of the complexes this band disappears due to its shift towards the region overlapped by strong absorption of the perchlorate ion. The tNH_2 band in the spectrum of the free ligand is overlapped by the strong band R_5 of the deformation vibrations of the ring; the latter is usually shifted slightly upon coordination [22], while the tNH_2 band seems to appear in the region 1190 cm^{-1}.

The absorption band of the stretching vibration of the C=O bonds ('amide-I' band) in the TH-1 spectrum is observed at 1668 cm^{-1}. In the spectra of the complexes, the 'amide-I' band is positioned at 1667–1671 cm^{-1}, which is usually observed in the absence of the metal–oxygen bond. However, the absence of the 'amide-I' band shifting upon complex formation can be attributed to the participation of the carbonyl oxygen atom in intermolecular hydrogen bond in free TH-1. Substitution of a hydrogen bond for a coordination bond gives the same result in terms of spectroscopic parameters.

To clarify this question, the TH-1 spectrum was obtained in a solution of acetonitrile where the intermolecular hydrogen bonds are not so expressive. The 'amide-I' band in this case is observed at 1708

TABLE 2. Atomic coordinates ($\times 10^4$, for hydrogen $\times 10^3$) for I

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	1778(1)	−118(1)	2634(1)	N(10)	−1058(5)	1522(3)	3925(4)
Cl(1)	1452(2)	5984(1)	3867(1)	N(11)	2861(5)	−1704(3)	3508(4)
Cl(2)	1922(2)	3608(1)	790(2)	N(12)	2919(6)	−1237(4)	2466(4)
O(1)	2864(5)	6208(4)	3983(5)	C(1)	2819(6)	956(4)	949(5)
O(2)	1296(6)	5085(3)	4034(6)	C(2)	3035(7)	1318(5)	−217(5)
O(3)	908(6)	6196(5)	2759(4)	C(3)	4031(6)	−4382(4)	1199(4)
O(4)	730(6)	6440(4)	4685(5)	C(4)	2210(6)	−1335(4)	4316(5)
O(5)	1139(6)	2852(3)	934(5)	C(5)	2253(7)	−1770(4)	5473(5)
O(6)	1233(7)	4108(4)	−95(5)	C(6)	−637(6)	748(4)	3616(5)
O(7)	3219(6)	3427(5)	426(7)	H1(C2)	363(4)	098(5)	−054(3)
O(8)	1946(7)	4129(5)	1773(5)	H2(C2)	333(4)	195(4)	−020(4)
O(9)	1892(5)	435(3)	1095(3)	H(C3)	114(5)	004(4)	905(4)
O(10)	1611(5)	−640(3)	4178(3)	H1(C5)	231(4)	−243(5)	540(5)
N(1)	17(6)	−882(4)	1899(4)	H2(C5)	306(5)	−132(5)	596(5)
N(2)	4780(7)	−3258(4)	2074(5)	H(C6)	116(5)	972(4)	626(4)
N(3)	3694(7)	−3019(4)	1491(5)	H(N5)	435(5)	161(5)	164(4)
N(4)	3212(6)	−3724(4)	939(4)	H1(N6)	452(5)	48(4)	293(4)
N(5)	3725(6)	1195(4)	1752(4)	H2(N6)	351(5)	117(4)	329(4)
N(6)	3697(6)	785(4)	2826(4)	H(N11)	316(5)	−215(4)	370(5)
N(7)	533(5)	836(3)	3153(4)	H1(N12)	368(4)	−118(3)	235(5)
N(8)	803(6)	1688(4)	3179(5)	H2(N12)	263(5)	−160(5)	192(5)
N(9)	−126(7)	2111(4)	3640(5)				

cm^{-1}. Consequently, a low frequency shift by 41–37 cm^{-1} takes place upon complex formation, which unambiguously indicates the presence of a metal–oxygen bond.

In addition, the participation of the O and N atoms of the hydrazide fragment in coordination is indicated by the absence of the 'amide-II' band shifting. This band is basically due to the vibrations of the C−N bond positioned in the spectra of the compounds obtained in the region 1547–1542 cm^{-1}, typical for the hydrazide bound in a bidentate fashion in a five-membered chelate ring. If one of the atoms does not participate in coordination, this band shifts towards high [18] or low frequency [28].

The coordination chemistry of 1-substituted tetrazole has been the subject of many investigations, using IR spectroscopy [22, 29, 30]. Deuteration of the hydrazide group allowed eight bands (R_1–R_8) of the tetrazole ring vibrations in the TH-1 spectrum to be identified; the positions of these bands practically are not distinguished in the spectra of TH-1 and TH-1-d_3 since the vibrations of the tetrazole ring have relative specificity on frequency [31].

The bands of the stretching vibrations of the ring R_1 and R_2 (attributed mainly to the vibrations of the C=N and N=N bonds) and R_3 (C−N and N−N) in the spectra of compounds I, II and IV shift towards high frequency region as compared with free TH-1 by 27–16 cm^{-1}, which is typical for tetrazole ring coordinated to the metal atom [22]. Deformation vibrations of the ring R_4–R_8 are considerably less sensitive to coordination, though a shift of the bands towards a high frequency region takes place as well.

Complex III holds a specific place. The R_1–R_3 bands show low intensity and are poorly resolved, the R_3 band overlapping the amide-III band. The R_2 band in the spectrum of III practically does not shift, and the site of the R_1 band is difficult to establish due to poor resolution. However, taking into account the fact that three hydrazide groups in molecule III are bidentately bonded with the nickel atom it is possible to admit the absence of coordination of the metal atom with the tetrazole ring in this case.

According to the data given in ref. 22, the band of the stretching vibrations of the C–H bond in the tetrazole ring shifts towards high frequency upon coordination. In the case of the TH-1 complexes in the spectra of I–IV the band of C−H was split leading to both high and low frequency shifts. The authors of ref. 30 attribute the fact of the C–H band splitting upon the coordination of 2-alkyltetrazoles to the presence of isomerization due to the appearance of tetrazole in the coordination sphere of the metal by different donor nitrogen atoms, N_1 and N_4. However, the splitting of the band in the spectrum of the crystal sample can be assigned to the fact that the unit cell contains more than one molecule and, as a result, there appears a possibility of movement in the phase and out of the phase [32], or that the position of the ring in the coordination polyhedron of the metal may be different, either

TABLE 3. Bond distances (Å) and angles (°) for **I**

Coordination polyhedron			
Cu–O(9)	2.012(4)	Cu–O(10)	2.004(4)
Cu–N(1)	2.233(6)	Cu–N(6)	2.350(5)
Cu–N(12)	2.076(6)	Cu–N(7)	2.032(5)
Tetrazole fragment of the ligand			
N(1)–N(2)	1.366(9)	N(7)–N(8)	1.347(8)
N(2)–N(3)	1.293(9)	N(8)–N(9)	1.290(9)
N(3)–N(4)	1.341(9)	N(9)–N(10)	1.347(8)
N(1)–C(3)	1.305(8)	N(7)–C(6)	1.308(8)
N(4)–C(2)	1.457(9)	N(10)–C(5)	1.458(8)
N(4)–C(3)	1.323(9)	N(10)–C(6)	1.322(8)
Hydrazide fragment of the ligand			
C(1)–C(2)	1.509(9)	C(4)–C(5)	1.518(8)
C(1)–O(9)	1.236(8)	C(4)–O(10)	1.231(8)
C(1)–N(5)	1.318(8)	C(4)–N(11)	1.307(8)
N(5)–N(6)	1.416(7)	N(11)–N(12)	1.427(7)
Perchlorate groups			
Cl(1)–O(1)	1.433(5)	Cl(2)–O(5)	1.414(5)
Cl(1)–O(2)	1.411(5)	Cl(2)–O(6)	1.438(7)
Cl(1)–O(3)	1.422(5)	Cl(2)–O(7)	1.397(7)
Cl(1)–O(4)	1.415(6)	Cl(2)–O(8)	1.409(7)
Coordination polyhedron			
O(9)–Cu–O(10)	178.0(2)	O(9)–Cu–N(1)	87.4(2)
O(9)–Cu–N(7)	91.6(2)	O(10)–Cu–N(1)	92.3(2)
O(9)–Cu–N(6)	75.7(2)	O(10)–Cu–N(7)	86.6(2)
N(1)–Cu–N(6)	162.7(2)	N(1)–Cu–N(7)	91.8(2)
O(10)–Cu–N(6)	104.7(2)	N(7)–Cu–N(12)	166.0(2)
Tetrazole fragment of the ligand			
Cu–N(1)–N(2)	126.2(6)	Cu–N(7)–N(8)	125.5(4)
Cu–N(1)–C(3)	128.0(4)	Cu–N(7)–C(6)	127.6(4)
N(2)–N(1)–C(3)	105.8(5)	N(1)–N(2)–N(3)	109.9(6)
N(2)–N(3)–N(4)	106.7(6)	N(3)–N(4)–C(2)	120.8(6)
N(3)–N(4)–C(3)	108.4(5)	C(2)–N(4)–C(3)	130.8(6)
N(8)–N(7)–C(6)	106.7(5)	N(7)–N(8)–N(9)	110.0(6)
N(8)–N(9)–N(10)	106.6(6)	N(9)–N(10)–C(5)	121.5(5)
N(9)–N(10)–C(6)	108.3(5)	C(5)–N(10)–C(6)	130.1(5)
N(1)–C(3)–N(4)	109.3(5)	N(7)–C(6)–N(10)	108.5(5)
Hydrazide fragment of the ligand			
Cu–O(9)–C(1)	118.6(4)	Cu–O(10)–C(4)	114.1(4)
Cu–N(12)–N(11)	106.9(4)	Cu–N(6)–N(5)	103.8(4)
N(6)–N(5)–C(1)	118.1(5)	N(12)–N(11)–C(4)	116.8(5)
O(9)–C(1)–N(5)	124.0(6)	N(11)–C(4)–C(5)	118.0(5)
O(10)–C(4)–N(11)	122.3(6)	N(5)–C(1)–C(2)	115.3(6)
O(9)–C(1)–C(2)	120.6(6)	O(10)–C(4)–C(5)	119.6(5)
N(4)–C(2)–C(1)	111.1(5)	N(10)–C(5)–C(4)	109.7(5)

equatorial or axial. In this connection the interpretation given by the authors of ref. 30 does not seem convincing. Moreover, the X-ray structural analysis has shown that both 1-substituted and 2-substituted tetrazoles coordinate with the metal atom only via the N_4 atom in the case of the absence of steric hindrances [33, 34]. Besides, it should be noted that splitting is also observed for the C—H band in the spectrum of **III**, where the tetrazole ring is not coordinated at all. Consequently, it is most probable that the splitting of the C—H band is due to the crystallinity effect. As to the splitting of the band of non-planar deformational vibrations of the C—H (γ C—H) bond in the spectra of **I**, **II** and **IV** in the absence of those in the spectra of TH-1 and **III**, it can indicate, in our opinion, the differences in the positions of the tetrazole rings in the coordination polyhedron of the metal.

Since in the case of compounds **I**, **II** and **IV** the participation of both the hydrazide fragment and the tetrazole ring is established, TH-1 in these compounds behaves as a bridging tridentate ligand. This

TABLE 4. IR absorption spectra of solid TH-1 and its perchlorate complexes and vibrational assignments[a]

Assignment	L	$[CuL_2](X)_2$	$[NiL_2](X)_2$	$[NiL_3](X)_2$	$[CoL_2](X)_2$
νN–H	3327 s,br	3365s	3372s	3343sh	3369s
		3297s	3310vs	3287vs	3311vs
	3228m	3262s	3252s		3254s
		3241sh	3210sh	3197s,br	3213s
νC–H	3168s	3175sh	3175s	3197s	3169s
		3159s	3154s	3145s,sh	3154s
νCH_2	3066m	3099m	3085m	3087s	3087m
	3040m	3042m,3024m	3019m	3004s	3035, 3016m
	2873m	2971m	2966w	2965s	2961s
Amide-I	1668vs	1667vs	1671vs	1699vs	1662vs
δNH_2	1626s	1603s	1610s	1613s	1610s
Amide-II	1541s	1542m	1543m	1547w	1546s
R_1	1483s	1501s	1510s	1497w	1508s
$R_2 + \delta CH_2$	1437m	1453s	1457s	1435w	1455s
δCH_2	1414s	1407s	1411w	1420m	1413s
ωCH_2	1370s	1385s	1382sh	1380w	1384w
δNH	1311m	1303sh	1305sh	1310w	1305sh
Amide-III	1280m	1285sh	1271sh	1280w,sh	1271sh
R_3	1257m	1275s	1276m	1280m,sh	1277s
ρCH	1185sh	1194s	1193s	1187s	1189vs
R_4	1176s	1194m	1193s	1187s	1189m
tCH_2	1144m	1142s	1149s	1187s	1146s
R_5	1108vs	[b]	[b]	[b]	[b]
tNH_2	1102sh	1194vs	1193s	1187s	1189s
R_6	1032m	1037m	1029m		1025m
ωNH_2	1002s	[b]	[b]	[b]	[b]
R_7	972s	989m	1008m	997m	1003
νC–C, N–N	964m	961m	969m	960s	965m
	953m	950sh	952m	935m	951sh
	938m	930sh			930sh
γCH	873m	904w	903w	887w	932w
		885w	887w		885w
ρCH_2	790s	805s	806m	790m	803s
δN–CH_2	701s	735sh,720sh	737sh,721m	717sh	731s, 718sh
R_8	658m	655m	660m	651m	657s
		606sh	611sh		606sh
δNCC	562s	560m,540sh	544m	550br	546s
νM–O, M–N		496s	506m	500sh	500s
		465m	464w	483m	462m

[a] The Table shows the vibrations of the ligand only. [b] The absorption in these regions is masked by an anion band. Abbreviations:s, string; m, medium; w, weak; br, broad; sh; shoulder. ν = stretching vibration; δ, ω, t, ρ and γ = deformation scissors, wagging, twisting, rocking and out-of-planar vibrations, respectively.

coordination mode can result in steric strain in the ligand, which may affect the spectral characteristics. In fact, the band of rocking vibrations of the CH_2 group (ρ CH_2) situated in the free ligand and in compound **III** at 790 cm^{-1} was found to shift towards the region of 803–806 cm^{-1} in the spectra of **I**, **II** and **IV**.

The perchlorate group in the spectra of the complexes with TH-1 absorbs in the region of 1090 and 625 cm^{-1}, which is typical for ClO_4^- ions.

In the low frequency region of the spectra of the complexes new bands, as compared with the spectrum of free TH-1, appear at 506–497 and 483–462 cm^{-1} due to the vibrations of the M–O and M–N bands in the hydrazide metal ring (vibrations of the metal tetrazole bond, according to the data in ref. 30, are observed in the lower frequency region of 300–250 cm^{-1}).

Broad bands are observed in the electronic absorption spectrum of **I** in water solution and in Nujol mulls at 13 160 and 13 300 cm^{-1}, respectively, which is typical for copper complexes with tetragonally-distorted octahedral symmetry.

X-ray structural analysis of crystal **I** confirmed the conclusions made using the IR data and established the structure of the coordination compound of copper(II) with TH-1 (Fig. 1). The hydrazide groups of two TH-1 ligands form with the copper atom the ordinary five-membered rings. The remaining two positions of the coordination polyhedron are occupied by tetrazole N_4 atoms of two neighbouring ligands. Each chromophore of copper has the *cis*-octahedral structure, with the oxygen atoms of two TH-1 molecules occupying the *trans*-positions and the nitrogen atoms of the same molecules being in the *cis*-positions to each other. The nitrogen atoms of the tetrazole rings of two more TH-1 molecules are in the *trans*-positions towards them.

The Yahn–Teller distortion of the copper octahedron elongates the *trans*-bonds Cu–N(1) (tetrazole) to 2.233(6) Å and Cu–N(6) (hydrazide) to 2.350(5) Å. Average bond length with equatorial ligands Cu–N(7) and Cu–N(12) is 2.054(5) ± 0.023 Å; Cu–O(9) and Cu–O(10) is 2.008(4) ± 0.004 Å.

Each ligand constitutes a bridge between adjacent metal atoms by coordination through the chelate hydrazide fragment and the nitrogen atom in position 4 of tetrazole. Each pair of metal atoms is centrosymmetrically bonded by the two similar bridging ligands. Further on, the centrosymmetrical pair of the TH-1 ligands bonds the second metal atom with the third one and so on. As a result, a zigzag polymeric chain is formed.

Structure **I** contains two crystallographically independent ligands TH-1. First couple of ligands with N(7) and N(12) atoms occupy equatorial positions of both Cu octahedron (right part of Fig. 1), second one (atoms N(1) and N(6)) occupy axial positions in the copper octahedron (left part of Fig. 1). Consequently, the second couple TH-1 molecules is bonded with the copper atoms less strongly then the first one.

The tetrazole rings of the ligands are planar (maximum deviation of the atoms from the plane is 0.004 Å), while the chelate rings exhibit a slight crimping with a maximum deviation of the atoms from the mean plane of 0.02 Å. The angle between the planes of the two tetrazole rings situated in the *cis*-position of the octahedron is equal to 65°, the chelate rings are practically orthogonal (92°) and the angles between the pairs of the tetrazole and chelate rings are equal to 54 and 42°, respectively. The configuration of the ligand itself is substantially non-planar; the tetrazole and chelate rings in it expand with respect to each other by 120°.

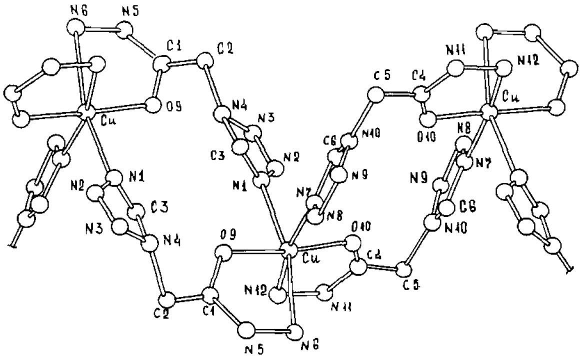

Fig. 1. The molecular structure of cation **I** with atom numbering scheme.

An identical picture of the distribution of the electronic density along the bonds is observed in both independent tetrazole rings: a multiple bond C=N is partly delocalized along the two C–N bonds (the average lengths are 1.306(8) and 1.322(9) Å); localization of the multiple bond N=N (1.290(9) and 1.293(9) Å) is more explicit, the other N–N bonds of the ring, however, are also shorter (their average length is to 1.356(9) Å). The length of the exocycle bond C–N is equal to 1.457(9) Å. In general, the lengths of the bond and valence angles in the tetrazole ring are close to the values obtained for the $ZnCl_2$ complex with 1-methyltetrazole [33] and the $Fe(BF_4)_2$ complex with 1-propyltetrazole [34].

The geometric parameters of the chelate rings are almost identical to each other as well; distortions in the copper octahedron manifesting themselves in the differences of the Cu–N bonds lengths are followed by a very slight redistribution of the electronic density along the metal ring: elongation of the Cu–N bond from 2.076(6) to 2.350(5) Å results in the shortening of the adjacent N–N bond from 1.427(7) to 1.416(7) Å and in a slight elongation of the next bond N–C from 1.307(8) to 1.318(8) Å. The length of the C=O bond does not change.

The perchlorate groups in structure **I** are positioned between the cation chains; these perchlorate groups bond them through the formation of hydrogen bonds of the O...H–N type where N represents the nitrogen atoms of the hydrazide groups. Contacts: 0(3)-H(1)N(12) 2.15, 0.(5)-HN(5) 2.05 and 0(6)-H(2)N(12) 2.19 Å.

Thus, in **I** the ligand exhibits its maximum dentativity and the presence of the additional donor atom in the hydrazide molecule does not result in a change of the bonding mode of the hydrazide group itself. A similar organization of the structure also seems to be realized in complexes of TH-1 with other metals except for complex **III** where, according to the ordinary stereochemistry of the Ni(II) complexes and spectral data, TH-1 is bidentate and the metal atom forms only five-membered metal chelates.

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