Neutron and synchrotron X-ray powder study of copper(II) chloride complex with deuterated 1-ethyltetrazole

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Abstract. The structure of the copper(II) chloride complex with deuterated 1-ethyltetrazole has been investigated in the temperature range of 2–290 K using neutron and synchrotron X-ray powder diffraction. The compound was found to exhibit structural transformation at *ca* 180 K, without change of space group and main structural motif. At higher temperatures, the complex reveals positional disorder of the ethyl group, whereas no disorder is observed at lower temperatures. Temperature dependence of the lattice parameters, obtained from synchrotron X-ray data, showed main lattice changes at the transformation, explained by structural features of the complex. From the magnetic measurements, the effect of the disorder on paramagnetic behaviour of the compound was found. Detailed structural data of the compound at 2 and 290 K, obtained from neutron powder diffraction data, are reported.

1. Introduction

Complexes of copper(II) chloride with substituted tetrazoles attract attention because of their magnetic properties at low temperatures. Among these compounds, there are layered coordination polymers of composition CuCl_2L_2 , where L is 1-substituted tetrazole, with square grids of only Cu and Cl atoms. No similar halide complexes of 2-substituted tetrazoles are known (Gaponik, Voitekhovich, Ivashkevich, 2006).

Crystal structures of several examples of the above square grid complexes CuCl_2L_2 have been described, including those for 1-ethyltetrazole (Virovets, Podberezskaya, Lavrenova, 1995), 1-allyltetrazole (Virovets, Baidina, Alekseev, Podberezskaya, Lavrenova, 1996), 1-(2-

azidoethyl)terazole (Ivashkevich, Lyakhov, Gaponik, Bogatkov, Govorova, 2001), 1-(2-chloroethyl)tetrazole (Stassen, Kooijman, Spek, Jos de Jongh, Haasnoot, Reedijk, 2002), 1-benzyltetrazole (Ivashkevich, Voitekhovich, Lyakhov, 2005), 1-methyltetrazole (Ivashkevich, Lyakhov, Ivashkevich, Degtyarik, Gaponik, 2005), and 1-(2-hydroxyethyl)tetrazole (Ivashkevich, Lyakhov, Serebryanskaya, Gaponik, 2008). All these compounds crystallize in the space group $P2_1/c$ and are isotypic.

Magnetic studies of square grid complexes CuCl_2L_2 of 1-substituted tetrazoles were mainly concerned with experimental measurements of magnetic susceptibility and magnetization of the compounds (Lavrenova, Bogatkov, Sheludyakova, Ikorskii, Larionov, Gaponik, 1991; Lavrenova, Ikorskii, Larionov, Bogatkov, Gaponik, 1993; Lavrenova, Bogatkov, Ikorskii, Sheludyakova, Boguslavskii, Gaponik, Larionov, 1996; Lavrenova, Bikzhanova, Bogatkov, Ikorskii, Sheludyakova, Virovets, Podberezskaya, Gaponik, Larionov, 1996; Stassen *et al.*, 2002; Shvedenkov, Ikorskii, Romanenko, Lavrenova, Bogatkov, Voitekhovich, Gaponik, 2003). All investigated compounds were found to be ferromagnets at low temperatures.

The present paper continues structural investigations of the above square grid complexes, and is devoted to complex $\text{CuCl}_2(d\text{-EtTz})_2$, where *d*-EtTz is fully deuterated 1-ethyltetrazole. For non-deuterated analogue, $\text{CuCl}_2(\text{EtTz})_2$, single crystal X-ray structural data, obtained at room temperature, were reported earlier by Virovets *et al.* (1995); magnetic studies (Lavrenova, Bikzhanova *et al.*, 1996; Shvedenkov *et al.*, 2003) showed that a Curie temperature (T_C) of the compound was *ca* 5 K.

Our primary intention was to carry out a low temperature (2 K) neutron diffraction investigation of the complex $\text{CuCl}_2(d\text{-EtTz})_2$ for obtaining its magnetic structure using available X-ray structural data at room temperature. However, a preliminary synchrotron X-ray powder diffraction investigation revealed a structural transformation over the temperature range 174–190 K. This circumstance was a reason of the present structural investigation of $\text{CuCl}_2(d\text{-EtTz})_2$, car-

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ried out by neutron and synchrotron powder diffraction. Structural aspects of magnetic behaviour of the complex are also discussed here.

2. Experimental

2.1 Sample preparation

For synthesis of $\text{CuCl}_2(d\text{-EtTz})_2$, fully deuterated ligand, 1-deuteroethyl-5*D*-tetrazole, was synthesized by the following specially developed technique.

Synthesis of 1-deuteroethyl-5*D*-tetrazole. Ethyl iodide $\text{C}_2\text{D}_5\text{I}$ (20 g, 0.124 mol) was added with stirring to a suspension of 1*H*-tetrazole (9.0 g, 0.124 mol) and K_2CO_3 (18.0 g, 0.124 mol) in boiling acetone (70 ml) for 0.5 h. Reaction mixture was stirred under reflux for 10 h. After cooling to room temperature, inorganic components were filtered off and the filtrate was evaporated under vacuum giving a mixture of 1- and 2-deuteroethyl-5*H*-tetrazole (12.0 g, yield 94%). After removing 2-isomer by vacuum distillation, 4.0 g of 1-deuteroethyl-5*H*-tetrazole (yellowish liquid, $n_{\text{D}}^{20} = 1.4600$) was obtained.

For deuteration of 5*H*-tetrazole atom, 1-deuteroethyl-5*H*-tetrazole (4.0 g) was added to a solution of annealed Na_2CO_3 (4.5 g) in 15 ml of D_2O . The mixture was stirred for 20 h. Product was extracted with dichloromethane and dried over anhydrous magnesium sulphate. Solvent was evacuated under vacuum giving 1-deuteroethyl-5*D*-tetrazole (3.1 g, $n_{\text{D}}^{20} = 1.4594$, deuteration *ca* 97%).

Synthesis of $\text{CuCl}_2(d\text{-EtTz})_2$. A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.96 g, 0.0115 mol) in 5 ml of methanol was added dropwise with stirring to a solution, containing 1-deuteroethyl-5*D*-tetrazole (2.4 g, 0.023 mol) in methanol (5 ml) and two drops of a solution of DCl in D_2O . The reaction mixture was stirred for 0.5 h. Light-green polycrystalline complex $\text{CuCl}_2(d\text{-EtTz})_2$ was filtered off and washed with 15 ml of a mixture of ethanol and diethyl ether (*v/v* = 1:2), and then with 10 ml of diethyl ether. Cooled D_2O (20 ml) was added to the obtained complex, placed into a glass, and the mixture was intensively stirred for 5 min. $\text{CuCl}_2(d\text{-EtTz})_2$ was filtered off and dried on air (yield 72%).

Purity of the sample was verified by laboratory X-ray powder diffraction data obtained on a HZG 4A diffractometer (Carl Zeiss, Jena).

2.2 Synchrotron X-ray powder diffraction

In situ structural studies of $\text{CuCl}_2(d\text{-EtTz})_2$ were carried out at the synchrotron facility HASYLAB/DESY (Hamburg, Germany) with the powder diffractometer at beamline B2 (Knapp, Baetz, Ehrenberg, Fuess, 2004). Low-temperature diffraction experiments were performed in Debye–Scherrer capillary geometry (0.7 mm quartz capillaries) using a closed-cycle cryostat with a capillary spinner (Ihringer, Küster, 1993). Temperature-dependent dataset series were collected in the temperature range of 12–290 K at a cooling cycle using an image-plate detector (Knapp, Joco, Baetz, Brecht, Berghaeuser, Ehrenberg, von Seggern, Fuess, 2004), in the 2 range of 4–55°. A

wavelength of 0.50192 Å was selected using a Si(111) double flat-crystal monochromator and determined from eight reflection positions of LaB_6 reference material (NIST SRM 660a).

Registered powder patterns were used to estimate unit cell dimensions of the compound at different temperatures, by means of the Rietveld refinement (Rietveld, 1969) as implemented in the program FULLPROF (Rodriguez-Carvajal, 1993). Only the unit cell dimensions, overall displacement parameter, scale, background, zero-shift, and peak shape parameters were refined. The atomic coordinates and displacement parameters were taken from either the single-crystal investigation (Virovets *et al.*, 1995) or the present 2 K neutron powder diffraction data.

2.3 Neutron powder data

Neutron powder diffraction measurements were carried out on the fine resolution neutron powder diffractometer E9 at the Berlin Neutron Scattering Center (Helmholtz Center Berlin, Germany).

Neutron powder patterns of $\text{CuCl}_2(d\text{-EtTz})_2$ were collected at room temperature (290 K) and 2 K for a sample placed in a vanadium can of 8 mm diameter. The incident neutron wavelength was of 1.79764 Å. Diffraction data were obtained in the 2θ angular range of 6–150°.

The unit cell dimensions of $\text{CuCl}_2(d\text{-EtTz})_2$ at 2 K were determined from neutron diffraction data using the program TREOR (Werner, Eriksson, Westdahl, 1985). For this purpose, only the angular range $2\theta = 6\text{--}35^\circ$ was used, because rather broad reflections did not provide adequate peaks positions for high-angle range due to peaks overlapping. As a result of indexing, two monoclinic unit cells were found, with the dimensions $a = 13.143$, $b = 6.760$, $c = 7.107$ Å, $\beta = 112.23^\circ$ (cell-I), $a = 12.351$, $b = 6.760$, $c = 7.107$ Å, $\beta = 99.95^\circ$ (cell-II). For both cells, related by the vector transformations $\mathbf{a}^{\text{II}} = \mathbf{a}^{\text{I}} + \mathbf{c}^{\text{I}}$, $\mathbf{b}^{\text{II}} = -\mathbf{b}^{\text{I}}$, $\mathbf{c}^{\text{II}} = -\mathbf{c}^{\text{I}}$, the space group $P2_1/c$ did not contradict to the observed neutron reflections. These crystal data are close to those in the paper (Virovets *et al.*, 1995), indicating structural resemblance at 2 K and room temperature. However essential difference in the unit cell volume at these temperatures pointed to absence of total structural similarity. The structural distinction was found from the Rietveld refinement, performed by using neutron patterns at 2 and 290 K with the program FULLPROF.

In the Rietveld refinement against the experimental data obtained at 2 and 290 K, the following used refinement details were the same. Pseudo-Voigt profile function convoluted with axial divergence asymmetry function was applied (Finger, Cox, Jephcoat, 1994). Correction for profile asymmetry was performed for reflections below $2\theta = 25^\circ$. Background intensity was found by Fourier filtering technique as implemented in the FULLPROF program, under visual inspection of the resulting background curve. Initial atomic coordinates were taken from the paper (Virovets *et al.*, 1995) and refined independently including the deuterium atoms. All atoms were refined isotropically. $B_{\text{iso}}(\text{D})$ of the methyl and the methylene groups were refined as one parameter for all D atoms of each group.

Table 1. Details of neutron data collection and Rietveld refinement of $\text{CuCl}_2(d\text{-EtTz})_2$.

Temperature (K)	2	290
Crystal data		
Chemical formula	$\text{CuCl}_2(\text{N}_8\text{C}_6\text{D}_{12})$	$\text{CuCl}_2(\text{N}_8\text{C}_6\text{D}_{12})$
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.3610(2)	13.2065(5)
b (Å)	6.75534(12)	6.7573(2)
c (Å)	7.11108(12)	7.2748(3)
β (deg)	100.0239(18)	107.283(3)
V (Å ³)	584.731(19)	619.89(4)
Z	2	2
d_{calc} (g/cm ³)	1.946	1.836
Data collection		
Wavelength (Å)	1.79764	1.79764
$2\theta_{\text{min}}$ (deg)	6.0	6.0
$2\theta_{\text{ma}}$ (deg)	150.0	150.0
No. of points	2881	2881
Refinement		
No. of reflections	804	847
No. of fitted parameters	66	86
R_p	0.035	0.034
R_{wp}	0.044	0.045
R_{exp}	0.027	0.030
R_B	0.063	0.085
R_F	0.032	0.069
$GOOF$	1.6	1.5

As starting lattice parameters, the data of paper (Virovets *et al.*, 1995) (290 K) and the values found from the present neutron diffraction (2 K) were used.

In the structure refinement for 290 K, it was found from the essentially large displacement parameters of the ethyl group atoms (mainly of the terminal methyl group atoms), that the group was disordered over two positions. By introducing a disorder model, initial occupancies of the positions were taken equal to 0.5 and further refined. Isotropic displacement parameters of atoms of disordered ethyl group were taken the same in both positions. At the initial stage of the refinement, soft restraints on inter-atomic distances and bond angles of the disordered group were used, but final refinement was carried out without any restraints.

For visualization of the obtained crystal data, the program PLATON was used [Spek, 2003].

Main crystal data and refinement details are given in Table 1¹. Figure 1 shows final Rietveld plots.

¹ Supplementary Material: Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 706288 and 706289. Copies of available material can be obtained, free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting. The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

The list of F_o/F_c -data is available from the author up to one year after the publication has appeared.

Fig. 1. The Rietveld plots showing the observed (circles), calculated (lines) and difference neutron patterns for $\text{CuCl}_2(d\text{-EtTz})_2$ at 2 and 290 K. The reflection positions are shown above the difference patterns.

2.4 Magnetic measurements

Magnetic susceptibility of polycrystalline sample of $\text{CuCl}_2(d\text{-EtTz})_2$ was measured with a commercial Quantum Design MPMS-5 SQUID magnetometer within the temperature range of 5–300 K in the magnetic field of 100 Oe.

3. Results and discussion

Figure 2 presents X-ray synchrotron powder patterns of $\text{CuCl}_2(d\text{-EtTz})_2$ registered at several temperatures. The two distinct temperature ranges, $T \leq 174$ K and $T \geq 190$ K, are clearly revealed, indicating the structural transformation within 174–190 K. This fact is in agreement with neutron diffraction data showing a difference of patterns obtained at 2 and 290 K (Fig. 3).

Detailed structural analysis of $\text{CuCl}_2(d\text{-EtTz})_2$, performed by using neutron diffraction data, allowed to clarify a nature of the transformation.

Fig. 2. Fragments of X-ray powder diffraction patterns of $\text{CuCl}_2(d\text{-EtTz})_2$ at several temperatures (only selected temperatures are plotted).

Fig. 3. Neutron diffraction patterns of $\text{CuCl}_2(d\text{-EtTz})_2$ registered at temperatures 2 and 290 K (only 2θ range 6–70° is shown).

3.1 The structure of $\text{CuCl}_2(d\text{-EtTz})_2$ at 290 K

As was mentioned in Section 2.3, the Rietveld refinement with 290 K neutron data resulted in too large isotropic displacement parameters of the methyl group atoms of ligand molecule. This was a reason of introducing positional disorder model for the ethyl group atoms.

In the disorder model, two positions (A and B) were specified for all atoms of the methyl group, and for two D atoms of the methylene group (Fig. 4).

Fig. 4. Disorder of the ethyl group in the crystal structure of $\text{CuCl}_2(d\text{-EtTz})_2$ at 290 K as a result of the Rietveld refinement. All atoms are presented as spheres of arbitrary radii. Dashed lines show bonds of atoms in position A.

Fig. 5. A polymeric layer in the crystal structure of $\text{CuCl}_2(d\text{-EtTz})_2$ viewed along the a axis (290 K). For clarity, the ethyl group is omitted.

As a result of the refinement, positions A and B have close occupancies, 0.45(1) and 0.55(1), respectively. In both positions, the ethyl group shows staggered conformation.

It should be noted that no disorder model was applied in the paper (Virovets *et al.*, 1995) by investigating the complex $\text{CuCl}_2(\text{EtTz})_2$ at room temperature. However, inspection of the results obtained in the above paper reveals necessity of introducing disorder model in a final stage of the structural analysis. Moreover, it was found in our earlier paper (Ivashkevich *et al.*, 2008) that in the crystal structure of isotypic complex with 1-(2-hydroxyethyl)tetrazole, 2-hy-

Fig. 6. The crystal structure of $\text{CuCl}_2(d\text{-EtTz})_2$ at 2 K (top) and 290 K (bottom) viewed along the b axis. For 290 K, dashed lines show bonds of atoms in a disorder position A.

droxyethyl substituent of the tetrazole ring was also disordered. These facts show that disordering of non-rigid substituents of the tetrazole ring is a non-rare phenomenon in the square grid complexes CuCl_2L_2 of 1-substituted tetrazoles.

Figures 5 and 6 show two projections of the crystal structure of $\text{CuCl}_2(d\text{-EtTz})_2$. Polymeric layers, parallel to the bc plane, are built of square grids of the copper and chlorine atoms and 1-ethyltetrazole molecules, coordinated via the tetrazole ring atom N4. In the layer, the ligand molecules are located on both sides of the grid.

3.2 The structure of $\text{CuCl}_2(d\text{-EtTz})_2$ at 2 K

The Rietveld refinement of $\text{CuCl}_2(d\text{-EtTz})_2$ with 2 K neutron data was performed for both alternative unit cells (Sect. 2.3). It was found that cell-II corresponded to that in the paper (Virovets *et al.*, 1995). This unit cell was used in further analysis.

The obtained data show that the structure of $\text{CuCl}_2(d\text{-EtTz})_2$ at 2 and 290 K is practically the same (Fig. 5), however the ethyl group reveals positional disorder at 290 K in contrast to the structure at 2 K.

The following question, concerned with the Rietveld refinement with 2 K neutron data, should be noted. As seen, reasonable structural data and a good agreement of the observed and calculated patterns was obtained without consideration of neutron scattering on the magnetic structure. This shows that nuclear scattering dominates magnetic scattering, and, moreover, it is difficult to separate nuclear and magnetic scattering in order to find the magnetic structure. Probably, a special approach should be applied to solve this problem.

There is a remarkable difference in the lattice parameters a , the monoclinic angle β and the cell volume of $\text{CuCl}_2(d\text{-EtTz})_2$ at 2 and 290 K (Table 1), which may be caused not only by disorder effect but also by thermal expansion of the lattice. In view of this, we investigated temperature dependence of the unit cell dimensions of the compound using X-ray synchrotron powder data.

3.3 Temperature dependence of unit cell parameters of $\text{CuCl}_2(d\text{-EtTz})_2$

Figure 7 illustrates the variation in lattice parameters with temperature, obtained in the Rietveld refinement using

Fig. 7. Temperature dependence of cell parameters of $\text{CuCl}_2(d\text{-EtTz})_2$ found from synchrotron X-ray powder data.

synchrotron X-ray data in the temperature range 12–290 K.

As seen, the unit cell dimension b is practically the same in the range 12–290 K. The length of the c axis exhibits a monotone increase with temperature, which corresponds to thermal expansion of the lattice. The a axis, the β angle and cell volume, rising with temperature, undergo a “jump” over the range 174–190 K, which is due to order-disorder transformation for the ethyl group. There is no detailed experimental data to specify the disorder freezing temperature more exactly, however, it may be estimated as *ca* 180 K.

These data show that the observed significant difference in the lattice parameter a and the monoclinic angle β of the compound at 2 and 290 K is caused mainly by the ethyl group disorder at 290 K. At the two temperatures, the difference in volume of *ca* 6% is due to thermal expansion as well as disorder effect for 290 K.

Low disorder response of the cell dimensions b and c may be explained by structural features of the compound. As a rule, positional disorder requires an additional volume in the crystal. In the case of $\text{CuCl}_2(d\text{-EtTz})_2$, this requirement can not be satisfied by variation in the b and c cell dimensions, because (Cu, Cl) square grids, parallel to the bc plane, are rather hard networks, preventing remarkable variations in these parameters. However, an increase of interlayer space due to a rise in the parameter a along with variation in the monoclinic angle β provide a good condition for the ethyl group disordering.

3.4 Magnetic behaviour

Our main intent of the magnetic study of $\text{CuCl}_2(d\text{-EtTz})_2$ was to find out whether there is an effect of the ethyl group disorder on magnetic properties of the complex. Also, it was interesting to compare magnetic behaviour of the deuterated complex with that of the non-deuterated one described earlier (Lavrenova *et al.*, 1996; Shvedenkov *et al.*, 2003). Figure 8 presents temperature dependence of reverse magnetic susceptibility of $\text{CuCl}_2(d\text{-EtTz})_2$.

In the temperature range of 50–200 K, magnetic susceptibility follows the Curie-Weiss law [$\chi = C/(T - \theta)$], with a Curie constant C of $0.44 \text{ cm}^3 \text{ K mol}^{-1}$ and a Curie-

Fig. 8. Reverse magnetic susceptibility vs. temperature of $\text{CuCl}_2(d\text{-EtTz})_2$ (circles present measured data, dash and dot lines show linear fitting in the regions 50–200 K and 200–300 K, respectively).

Weiss temperature $\theta = 19 \text{ K}$. A Curie temperature was found to be *ca* 5 K. Because of ferromagnetic interactions, deviation from the paramagnetic Curie-Weiss law is observed at low temperatures. These parameter values agree with those obtained in the paper (Lavrenova *et al.*, 1996) for non-deuterated complex.

However, detailed inspection of the dependence $\chi^{-1}(T)$ reveals another linear part in the curve, ranging from *ca* 200 to 300 K (Fig. 8). This part is characterized by a Curie constant $C' = 0.35 \text{ cm}^3 \text{ K mol}^{-1}$ and a Curie-Weiss temperature $\theta' = 62 \text{ K}$. As we know that structural transformation due to order-disorder transition of the ethyl group takes place at *ca* 180 K, this linear part in the $\chi^{-1}(T)$ dependence may be attributed to the paramagnetic behaviour of the disordered complex.

No similar peculiarity of the $\chi^{-1}(T)$ curve was reported earlier for the complex $\text{CuCl}_2(\text{EtTz})_2$ (Lavrenova *et al.*, 1996; Shvedenkov *et al.*, 2003). Because the ethyl group is disordered also in the non-deuterated complex (see Section 3.1), it should reveal similar magnetic behaviour. Probably, its observation was out of view of the above authors.

4. Conclusion

From short-scan synchrotron X-ray powder data analysis in the temperature range of 12–290 K, it was found that complex $\text{CuCl}_2(d\text{-EtTz})_2$ exhibits a structural transformation at *ca* 180 K. Neutron powder diffraction patterns, collected at 2 and 290 K, were studied in order to find a difference in the crystal structure of the compound at these temperatures. It was established from the neutron powder data, that there was the positional disorder of the ethyl group present at the temperatures above *ca* 180 K, which disappears at lower temperatures. Transformation from the ordered to disordered structure is followed by significant increase in the lattice parameter a , the monoclinic angle β , and the cell volume, whereas the b and c parameters show low response to the order-disorder transition. This fact may be explained by presence in the structure of rather hard (Cu, Cl) square grids parallel to the bc plane.

Order-disorder transition, taking place at *ca* 180 K, is revealed also in the paramagnetic behaviour of the complex so that there are two distinct temperature ranges, below and above 180 K, where $\chi^{-1}(T)$ curve is described by two different sets of the Curie-Weiss law parameters.

Using neutron powder data, a detailed structural analysis of the compound at 2 and 290 K was carried out. It showed, that a good agreement of experimental and calculated neutron patterns at 2 K was reached without consideration of neutron scattering on the magnetic structure. This means that there is difficulty to separate nuclear and magnetic scattering in order to find the magnetic structure of the complex.

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