

# Preparation and some properties of copper(II) complexes with *N*-(3-aminopropyl)cyclohexylamine

L. MACÁŠKOVÁ and J. GAŽO

*Department of Inorganic Chemistry, Slovak Technical University,  
880 37 Bratislava*

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Preparations of new Cu(II) complexes with *N*-(3-aminopropyl)cyclohexylamine (ACHA) are reported. On the basis of their infrared and electronic absorption spectra as well as their magnetic properties it was decided that the red and blue modifications of the complex with a composition of  $\text{Cu(ACHA)}_2\text{Br}_2 \cdot \text{CH}_3\text{CN}$  serve as a further example for distortion isomers of copper(II) complexes.

В работе приводится описание приготовления новых комплексов Cu(II) с *N*-(3-аминопропил)циклогексиламином (АЧА). На основании инфракрасных и электронных спектров, а также магнитных свойств было заключено, что красная и синяя модификации комплекса  $\text{Cu(ACHA)}_2\text{Br}_2 \cdot \text{CH}_3\text{CN}$  являются дальнейшим примером дисторсионных изомеров комплексов меди.

## Experimental

### *Chemicals, analytical procedures, and equipments*

$\text{CuCl}_2$  was prepared by thermal dehydration of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in the stream of hydrogen chloride.  $\text{CuBr}_2$  was prepared by the reaction of hydrogen bromide acid with basic Cu(II) carbonate.  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Lachema, Brno) of anal. grade was used for preparation of a nitrate complex.  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  was obtained by the reaction of basic Cu(II) carbonate with dissolved (1:1) perchlorate acid. After filtration and evaporation of the solution on water bath a product was obtained which was washed with ether.

Ethanol was dried at first with sodium, afterwards with magnesium in the presence of iodine and finally it was distilled. Toluene of anal. grade was dried with sodium and distilled. *N*-(3-Aminopropyl)cyclohexylamine (Chemische Fabrik Buchs SG, Switzerland) was distilled before use at lower pressure and a temperature about 190°C. Acetonitrile was used after rectification (the fraction boiling at 81.5–82°C) and dried with calcium hydroxide.

Copper was determined complexometrically, murexid being used as indicator, chlorides and bromides potentiometrically with  $\text{AgNO}_3$ , perchlorate and nitrate group with nitron. Carbon, hydrogen, and nitrogen content was determined with an automatic Carlo Erba 11-02 analyzer.

Infrared absorption spectra were measured in Nujol mulls with Perkin—Elmer 225 and UR-10 spectrophotometers. Electronic absorption spectra of solid compounds were recorded on Perkin—Elmer 450 and Specord UV VIS spectrophotometers in the region of 10 000—40 000 and 12 000—30 000  $\text{cm}^{-1}$ , respectively. Thermoanalytical records were obtained with a derivatograph OD-102 (Hungary).

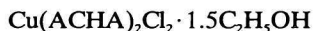
Magnetic susceptibilities were measured by the Gouy method. Copper(II) sulfate pentahydrate was used as standard [1]. The values of molar susceptibilities were corrected with the Pascal constants to diamagnetism. The effective magnetic moments (in B.M.) of all complexes were calculated according to the equation

$$\mu_{\text{eff}} = 798.1(\chi' MT)^{1/2}$$

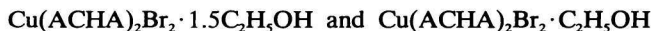
The density of crystals was determined by immersion method in mixtures of benzene and carbon tetrachloride.

### *Preparation of complexes*

In all cases under “solvent” it will be understood a mixture of ethanol and toluene in a volume ratio of 3 : 7.



Anhydrous copper(II) chloride was dissolved in solvent and 25  $\text{cm}^3$  of the 0.2 M solution were mixed with 5  $\text{cm}^3$  of ACHA. The solution was allowed to stand at room temperature for 1 h and then blue crystals were filtered off, washed with ether and dried by the air.



ACHA and anhydrous copper(II) bromide were each dissolved in the solvent ( $c = 0.2 \text{ M}$ ). The former solution (90  $\text{cm}^3$ ) was mixed with the latter (30  $\text{cm}^3$ ) and after some minutes blue crystals separated from the solution. They were filtered off, washed with ether and dried in an exsiccator. The composition of the complex just after the preparation was  $\text{Cu(ACHA)}_2\text{Br}_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$ . On exposure to the atmosphere a part of ethanol was released and a complex with the composition of  $\text{Cu(ACHA)}_2\text{Br}_2 \cdot \text{C}_2\text{H}_5\text{OH}$  was formed.



The blue crystals of  $\text{Cu(ACHA)}_2\text{Br}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ , prepared as given above, were mixed with excess of acetonitrile and kept in a closed flask for 72 h at room temperature. Scale-like crystals of  $\text{Cu(ACHA)}_2\text{Br}_2 \cdot \text{C}_2\text{H}_5\text{OH}$  were converted to dark-blue and red crystals which were isolated and separated under a microscope. Both forms of crystals were of the same composition corresponding to the complex  $\text{Cu(ACHA)}_2\text{Br}_2 \cdot \text{CH}_3\text{CN}$ , but of a different shape. The density of the blue crystals was  $1.475 \text{ g cm}^{-3}$ , whereas that of the red ones  $1.491 \text{ g cm}^{-3}$ .

The blue form was assigned as  $\alpha\text{-Cu(ACHA)}_2\text{Br}_2 \cdot \text{CH}_3\text{CN}$  and the red one as  $\beta\text{-Cu(ACHA)}_2\text{Br}_2 \cdot \text{CH}_3\text{CN}$ .

The  $\beta$  isomer can also be formed by a heterogeneous reaction of the above alcoholate with acetonitrile vapours (realized in an exsiccator during a three-days time).



Copper(II) nitrate trihydrate as well as ACHA were each dissolved in the solvent. 80 cm<sup>3</sup> of 0.2 M-ACHA solution were added to 40 cm<sup>3</sup> of 0.1 M copper(II) nitrate solution. The formed solution was evaporated at a low pressure and room temperature while blue crystals of the product were formed. The crystals were filtered off, washed with ether and dried in an exsiccator filled with KOH. The obtained compound had the composition  $\text{Cu(ACHA)}_2(\text{NO}_3)_2 \cdot \text{C}_2\text{H}_5\text{OH}$ .



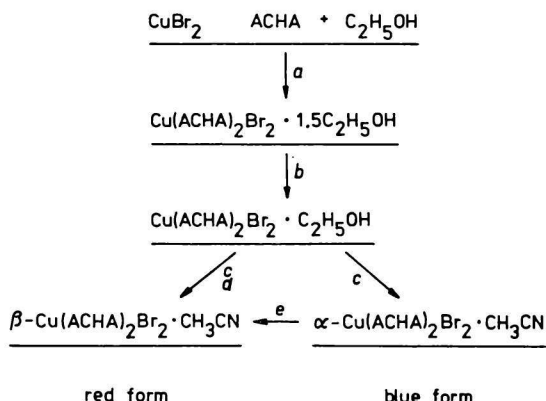
$\text{Cu(ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and ACHA were each dissolved in the solvent and 40 cm<sup>3</sup> of Cu(II) perchlorate solution (0.06 M) with 80 cm<sup>3</sup> of ACHA solution (0.2 M) were used in preparation. By evaporating the formed solution at a low pressure and room temperature violet crystals were obtained which were filtered, washed with ether and vacuum-dried.

All analysis results for the complexes under investigation are given in Table 1.

The complexes obtained by reactions of ethanol—toluene solutions of Cu(II) salts with *N*-(3-aminopropyl)cyclohexylamine are not of the same stoichiometric composition as those prepared by reactions with cyclohexylamine [2—5].

Many preparative experiments have shown that the character of the obtained complex depends on the concentration of starting Cu(II) compound in the solution, on the amount of ACHA used in preparation, and also on the solvent. Optimum conditions for preparations are those given in the above part.

The acetonitrile adduct of dibromo-bis[*N*-(3-aminopropyl)cyclohexylamine] copper(II) complex crystallizes as a mixture of two kinds of crystals: the blue form as needle-like crystals (prismatic shape), the red one as spherical crystals (pentagonal dodecahedra). The



Scheme 1

Mutual conversions of Cu(II) complexes with ACHA in dependence on conditions of their preparation

- a) Synthesis; b) desolvation on exposure to the atmosphere; c) resolution in acetonitrile; d) resolution in acetonitrile vapours; e) standing in acetonitrile solution.

Table 1

Analysis results for Cu(II) complexes with *N*-(3-aminopropyl)cyclohexylamine

Compound	Calculated %							Found %						
	Cl	Br	NO <sub>3</sub>	C	H	N	Cu	Cl	Br	NO <sub>3</sub>	C	H	N	Cu
Cu(ACHA) <sub>2</sub> Cl <sub>2</sub> · 1.5C <sub>2</sub> H <sub>5</sub> OH	13.76			48.82	9.57	10.85	12.31	13.58			48.70	9.58	10.82	12.21
Cu(ACHA) <sub>2</sub> Br <sub>2</sub> · 1.5C <sub>2</sub> H <sub>5</sub> OH		26.41		41.65	8.16	9.25	10.50		26.02		41.32	8.37	9.17	10.44
Cu(ACHA) <sub>2</sub> Br <sub>2</sub> · C <sub>2</sub> H <sub>5</sub> OH		27.46		41.27	7.96	9.62	10.91		27.42		41.02	7.99	9.66	10.89
β-Cu(ACHA) <sub>2</sub> Br <sub>2</sub> · CH <sub>3</sub> CN (red)		27.69		41.63	7.51	12.14	11.01		26.80		41.26	7.38	12.12	10.81
α-Cu(ACHA) <sub>2</sub> Br <sub>2</sub> · CH <sub>3</sub> CN (blue)		27.69		41.63	7.51	12.14	11.01		27.10		41.42	7.29	11.91	10.93
Cu(ACHA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · C <sub>2</sub> H <sub>5</sub> OH			22.82	43.98	8.49	15.39	11.63			22.63	44.12	8.47	15.19	11.59
			ClO <sub>4</sub>	C	H	N	Cu			ClO <sub>4</sub>	C	H	N	Cu
Cu(ACHA) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>			34.61	37.62	6.95	9.74	11.06			34.22	37.52	6.73	9.60	10.90

separation under a microscope is possible only in the case when crystals are filtered from the acetonitrile solution most a few days after the synthesis. The blue crystals, when allowed to stand in acetonitrile solution for a longer time, are converted to the red form. Unfortunately, conditions under which only one form would crystallize were not found (Scheme 1).

## Results and discussion

### *Thermal decomposition*

Thermal study of the complexes with a composition of  $\text{Cu(ACHA)}_2\text{Cl}_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$ ,  $\text{Cu(ACHA)}_2\text{Br}_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$  as well as  $\text{Cu(ACHA)}_2\text{Br}_2 \cdot \text{C}_2\text{H}_5\text{OH}$  and  $\text{Cu(ACHA)}_2(\text{NO}_3)_2 \cdot \text{C}_2\text{H}_5\text{OH}$  has shown that all complexes under investigation are thermally little stable. Release of ethanol starts for all complexes at a temperature of 25–35°C, showing an endothermic maximum at about 100°C for halide complexes and an exothermic maximum at about 125°C for the nitrate complex. The two modifications,  $\alpha$ - $\text{Cu(ACHA)}_2\text{Br}_2 \cdot \text{CH}_3\text{CN}$  and  $\beta$ - $\text{Cu(ACHA)}_2\text{Br}_2 \cdot \text{CH}_3\text{CN}$ , are at low temperatures sufficiently stable. The TG curves measured for them are almost the same and acetonitrile is released for both modifications at about 95°C. The DTA curves of the two modifications have two endothermic maxima in the temperature range 105–130°C.

Decomposition of  $\text{Cu(ACHA)}_2(\text{ClO}_4)_2$  in the range 150–250°C is accompanied with an explosive exothermic effect.

It is characteristic of all studied *N*-(3-aminopropyl)cyclohexylamine Cu(II) complexes that their TG curves are without any plateau corresponding to the formation of a desolvated complex. This can be most probably explained by a variety of hydrogen bonds which are broken successively by increasing the temperatures. Endothermic effect connected with desolvation distinctly for acetonitrile complexes only, is followed in all cases by an exothermic effect of decomposition which is apparently influenced also by oxidation properties of Cu(II) and by its catalytic effect on the decomposition.

### *Infrared absorption spectra*

Comparison of infrared absorption spectra of *N*-(3-aminopropyl)cyclohexylamine Cu(II) complexes with that of free ligand shows that all absorption bands assigned to the vibrations of ACHA molecule also occur in the spectra of the prepared Cu(II) complexes. Empiric assignment of frequencies has been made by comparing the spectrum of the free ligand with that of a coordinated one, taking into consideration also spectral data known for some metal complexes with cyclohexylamine and diaminopropane [5–10]. The values for frequencies found in infrared spectra and their assignments are listed in Tables 2 and 3.

Table 2

Maxima of absorption bands in infrared and electronic absorption spectra, and magnetic moments of Cu(II) complexes with *N*-(3-aminopropyl)cyclohexylamine

Compound	Infrared spectra, cm <sup>-1</sup>			Electronic spectra cm <sup>-1</sup>	$\mu_{\text{eff}}$ B.M. 293 K
	$\nu(\text{NH})$ , $\nu(\text{NH}_2)$	$\nu(\text{C}\equiv\text{N})$	$\delta(\text{NH})$ , $\delta(\text{NH}_2)$		
ACHA	3360 m 3280 m, b		1605 m, b		
Cu(ACHA) <sub>2</sub> Br <sub>2</sub> · C <sub>2</sub> H <sub>5</sub> OH	3350 sh 3280 m 3195 m 3120 m		1588 m	15 400	1.82
$\beta$ -Cu(ACHA) <sub>2</sub> Br <sub>2</sub> · CH <sub>3</sub> CN (red)	3480 m 3420 m 3200 sh 3100 s, b	2260 m	1640 w 1599 vs	21 000	1.77
$\alpha$ -Cu(ACHA) <sub>2</sub> Br <sub>2</sub> · CH <sub>3</sub> CN (blue)	3250 s 3190 m 3170 m 3110 s, b	2256 m	1600 vs 1610 sh	15 000	1.85

vs — very strong, s — strong, m — medium, w — weak, b — broad, sh — shoulder.

The frequencies for stretching vibrations  $\nu(\text{NH}_2)$  and  $\nu(\text{NH})$  in the free *N*-(3-aminopropyl)cyclohexylamine molecule are in the region of 3360—3280 cm<sup>-1</sup> while those for deformation modes  $\delta(\text{NH}_2)$  and  $\delta(\text{NH})$  are at 1605 cm<sup>-1</sup>. A shift of these bands to lower frequencies, observed in the spectra of Cu(II) complexes (with the exception of the red isomer  $\beta$ -Cu(ACHA)<sub>2</sub>Br<sub>2</sub> · CH<sub>3</sub>CN), when compared with that of the free ligand confirms that *N*-(3-aminopropyl)cyclohexylamine is in the investigated complexes a bidentate ligand. It is worth to mention the appearance of a band at about 3100 cm<sup>-1</sup> which signifies that one amine group forms a weak intermolecular hydrogen bond NH...H [9] in all complexes.

The narrow bands at 2260 and 2256 cm<sup>-1</sup> observed for the red  $\beta$ -Cu(ACHA)<sub>2</sub>Br<sub>2</sub> · CH<sub>3</sub>CN and the blue  $\alpha$  isomer, respectively, may be assigned to the stretching vibrations  $\nu(\text{C}\equiv\text{N})$  of free acetonitrile because the corresponding frequency for acetonitrile measured in CCl<sub>4</sub> occurs at 2255 cm<sup>-1</sup> [11]. It is possible to assume that acetonitrile molecules occupy the holes in the crystal lattice of solid complexes and their exact role in the structure may be resolved only by X-ray structure analysis.

Table 3

Maxima of absorption bands in infrared and electronic absorption spectra, and magnetic moments of Cu(II) complexes with *N*-(3-aminopropyl)cyclohexylamine

Compound	Infrared spectra, cm <sup>-1</sup>				Electronic spectra cm <sup>-1</sup>	$\mu_{\text{eff}}$ B.M. 293 K
	$\nu(\text{NH})$ , $\nu(\text{NH}_2)$	$\delta(\text{NH})$ , $\delta(\text{NH}_2)$	$\nu(\text{ONO}_2)$	$\nu(\text{ClO}_4)$		
Cu(ACHA) <sub>2</sub> Cl <sub>2</sub> · 1.5C <sub>2</sub> H <sub>5</sub> OH	3270 sh 3210 s 3130 s	1598 s			16 000	1.82
Cu(ACHA) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · C <sub>2</sub> H <sub>5</sub> OH	3270 m 3230 s 3210 sh 3165 m	1605 s	1765 m 1380 s 1320 s		16 500	1.81
Cu(ACHA) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	3310 m 3290 m 3250 s 3160 w	1590 s		1115 s 1050 s	17 800	1.88

An interesting feature regarding the infrared spectra of the red  $\beta$ -Cu(ACHA)<sub>2</sub>Br<sub>2</sub>·CH<sub>3</sub>CN should be mentioned: there occur further well distinguished medium bands in the region of stretching and bending vibrations of NH<sub>2</sub> and NH groups, namely the bands at 3480, 3420 as well as at 1640 cm<sup>-1</sup> which are shifted to higher frequencies when compared with those in the spectrum of the free ligand. With respect to the composition of the complex it is not possible to conclude that the intense bands in the region of 3480—3420 cm<sup>-1</sup> would be vibrations of OH groups. They represent vibrations of NH<sub>2</sub> group. The same was reported for polydentate amine ligands [12—14]. Infrared spectrum of a dipropylenetriamine (dptn) Cu(II) complex of a composition Cu(dptn)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> showed [12] beside the bands  $\nu_s(\text{NH}_2)$  at 3275 cm<sup>-1</sup> and  $\nu_{\text{as}}(\text{NH}_2)$  at 3335 cm<sup>-1</sup> also a band at 3375 cm<sup>-1</sup> which was assigned to the noncoordinated primary NH<sub>2</sub> group. The latter was not observed, however, for hydrate Cu(dptn)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O prepared from aqueous solution, but a new sharp band  $\nu(\text{OH})$  was registered at 3605 cm<sup>-1</sup>. This was explained by protonation of a free amine group, i.e. by forming a complex with the formula Cu(dptn)(dptnH)(OH)(ClO<sub>4</sub>)<sub>2</sub>. Quite similar conclusion was reported for diethylenetriamine (dien) Cu(II) complexes [13]. Additional bands (shoulders) in the range 3375—3310 and 3385—3265 cm<sup>-1</sup>, assigned to noncoordinated amine groups, were also found for Cu(dien)<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O and Cu(dien)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·0.5H<sub>2</sub>O.

Noncoordinated  $\text{NH}_2$  group has also been suggested [14] for  $\beta\text{-Cu}(3,22,3\text{-tet})\text{Cl}_2$  ( $\nu(\text{NH}_2)$  in the region of  $3500\text{--}3350\text{ cm}^{-1}$ ) where 3,22,3-tet is  $N,N'$ -di(3-aminopropyl)piperazine, being in the function of a linear tetraamine ligand. On the basis of own experimental data and those of other authors and their conclusions it is possible to assume that  $N$ -(3-aminopropyl)cyclohexylamine plays in the red  $\beta$  isomer the role of a monodentate ligand, being coordinated to the central atom of Cu(II) through its nitrogen atom of the secondary NH group.

The occurrence of an unsplit combination band  $\nu_1 + \nu_4$  at  $1765\text{ cm}^{-1}$  belonging to the nitrate group in  $\text{Cu}(\text{ACHA})_2(\text{NO}_3)_2 \cdot \text{C}_2\text{H}_5\text{OH}$  indicates ionic character of that group in these complexes due to the splitting of a band of the stretching vibration  $\nu(\text{NO}_3)$  in the spectrum of  $\text{Cu}(\text{ACHA})_2(\text{NO}_3)_2 \cdot \text{C}_2\text{H}_5\text{OH}$  at  $1320$  and  $1380\text{ cm}^{-1}$  ( $\Delta 60\text{ cm}^{-1}$ ).

Analogically, the splitting of a band corresponding to the stretching vibration  $\nu(\text{ClO}_4)$ , found for  $\text{Cu}(\text{ACHA})_2(\text{ClO}_4)_2$  in the range  $1115\text{--}1050\text{ cm}^{-1}$ , points to the covalent bond of perchlorate group in the complex [17].

### Electronic absorption spectra

Electronic absorption spectra of solid Cu(II) complexes with  $N$ -(3-aminopropyl)cyclohexylamine were measured in Nujol mulls in the region of  $13\,000\text{--}30\,000\text{ cm}^{-1}$ . The values for maxima of absorption bands are listed in Tables 2 and 3. Electronic absorption spectra of these complexes, with the exception of  $\beta\text{-Cu}(\text{ACHA})_2\text{Br}_2 \cdot \text{CH}_3\text{CN}$ , are to a great extent similar. All of them show a broad ligand band in the range  $15\,000\text{--}17\,800\text{ cm}^{-1}$  which is characteristic of Cu(II) complexes with pseudooctahedral structure [16].

The spectrum of the red  $\beta$  modification with a band at  $21\,00\text{ cm}^{-1}$  makes possible to suppose a tetragonal structure of the complex with a very strong axial distortion, practically close to planarity [1, 15, 16, 18].

Square planar coordination was also confirmed for unusual red copper(II) complex with  $N,N$ -diethyl- $\alpha$ -alaninate [19]. Other authors [20, 21] explained thermochromism of  $N,N$ -diethylenediamine (diethn) copper(II) complexes, i.e. a change of colour from red to violet at an elevated temperature, by weakening bonds in the plane of chromophore  $\text{CuN}_4$  and at the same time by strengthening axial interactions with anions of the complexes  $\text{Cu}(\text{diethn})_2\text{X}_2$ . As a result, the coordination of the complex is converted from square planar to octahedral which shows no change at higher pressure. By hydrating water molecules are also coordinated in axial positions forming so blue hydrates. The authors have found [21] that conversion from square planar to octahedral coordination is probably not accompanied with a change of a monodentate to a bidentate amine ligand. The assumption given by Lever [22] has been confirmed that thermochromism is



caused by a strengthening of interactions with ligands in axial positions at higher temperatures whereas a higher pressure causes a shortening of the bonds in equatorial plane and axial interactions are smaller. The red form has also been observed for hydrates of copper(II) complexes with *N*-isopropyl-2-methylpropane-1,2-diamine [23], having absorption maximum at  $21\,100\text{ cm}^{-1}$ , i.e. analogically as the  $\beta$ -Cu(ACHA)<sub>2</sub>Br<sub>2</sub>·CH<sub>3</sub>CN.

With regard to the infrared spectral data, the conversion  $\alpha \rightarrow \beta$  is assumed to be accompanied by distortion of the coordination polyhedron and simultaneously by release of a secondary amine group of *N*-(3-aminopropyl)cyclohexylamine. Steric configuration (conformation) of cyclohexyl ring may play an important role at fixation of square planar configuration because it may cause blocking of the axial positions in the coordination polyhedron, analogically as it has been observed for *N*-benzyl-D,L-valinate chelate [24, 25] and also supposed for complexes with bulky alkyl substituents of *N,N*-disubstituted ethylenediamine as ligand [21].

### Magnetic properties

All complexes under investigation belong to magnetic diluted Cu(II) complexes [18] as it is apparent from the values of their magnetic moments (Tables 2 and 3). On the basis of their infrared and electronic absorption spectra as well as the values of their magnetic moments it is possible to assume that all of the complexes except the red  $\beta$  isomer have similar stereochemical arrangement around the central atom forming most probably a chromophore CuN<sub>4</sub>X<sub>2</sub>. The magnetic moment measured for the red  $\beta$  isomer ( $\mu_{\text{eff}} = 1.77\text{ B.M.}$ ) approximates to the spin only value ( $\mu_{\text{eff}} = 1.73\text{ B.M.}$ ) which can be a sign of both a good separation of Cu(II) atoms in crystal structure and a little influence of spin-orbital interaction.

On the basis of the above-mentioned results we deduce that the red and blue modifications of the complex Cu(ACHA)<sub>2</sub>Br<sub>2</sub>·CH<sub>3</sub>CN are the example of distortion isomers of Cu(II) complexes [26, 27].

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