

Extended Hückel Calculations in Spectral and Magnetic Studies of Two Distortion Isomers of Bis(1,3-diaminobutane)copper(II) Perchlorate

Rolf Ugglå,^a Milan Melník,^b Jaana Valo,^a Aarne Pajunen^a and Markku R. Sundberg^{a,†}

^aDepartment of Chemistry, Inorganic Chemistry Laboratory, Box 55, FIN-00014 University of Helsinki, Finland and ^bDepartment of Inorganic Chemistry, Slovak Technical University, Radlinského 9, 81237 Bratislava, Slovakia

Ugglå, R., Melník, M., Valo, J., Pajunen, A. and Sundberg, M.R., 1995. Extended Hückel Calculations in Spectral and Magnetic Studies of Two Distortion Isomers of Bis(1,3-diaminobutane)copper(II) Perchlorate. – Acta Chem. Scand. 49: 585–588 © Acta Chemica Scandinavica 1995.

Two isomeric forms of bis(1,3-diaminobutane)copper(II) perchlorate were separated by recrystallisation. The spectral and electronic properties of the blue–violet and red–violet isomers were investigated. The perchlorate anion is coordinated more strongly in the blue–violet isomer, which is seen in the IR and electronic spectra and the oxygen atom contribution to the axial MO. Extended Hückel calculations show that tetragonality has an effect on the effective charge on the central copper(II) ion, but not on the amount of *d*–*s* mixing. The isomers obey the Curie–Weiss law in the temperature range 70–310 K with $C = 0.388(6)$ and $\Theta = 6(1)$ for the blue–violet isomer and $C = 0.365(5)$ and $\Theta = 7(1)$ for the red–violet isomer. The Curie constants accord with the differences in the ligand field.

The structure and bonding of copper(II) compounds are of continuous interest in inorganic chemistry.¹ A much studied topic is isomerism.² Copper(II) compounds of 1,3-diaminobutane (bdn hereafter) have not been studied as extensively as the complexes of other diaminoalkanes. In an early report the bdn complexes of Cu(II) and Ni(II) were compared with other nitrogen-containing ligands.³ Lever and Mantovani have prepared and studied compounds of the composition Cu(1,4-diaminobutane)X₂ (X = Cl, Br).⁴ In some of these compounds two different isomers have been observed. The preparation of two isomeric forms of Cu(bdn)₂(ClO₄)₂ was described in our previous paper.⁵ The subsequent X-ray structure determination showed that both isomers crystallise in the space group *P*2₁/*c* with two formula units in the unit cell. Both isomers contain the copper(II) ion in an essentially tetragonal environment with the bdn ligands coordinated to form an approximately square coplanar structure. The axial positions are occupied by the monodentately coordinated perchlorate ions. The essential differences are the conformations of the six-membered rings and perchlorate groups (Fig. 1). The most significant differences in the molecular units are seen in the axial Cu–O bonds. No other properties of the two isomers have yet been reported. The aim of the present work is to evaluate the differences in the isomers in more detail.

Experimental

Preparative study. Bis(1,3-diaminobutane)copper(II) perchlorate was prepared as described earlier.⁵ In the earlier crystallographic study the single crystals were picked up from a mixture containing both forms. In the present investigation the compound was recrystallised from two different solutions resulting in pure isomers. The blue–violet isomer was obtained from cold water and the red–violet isomer from hot ethanol.

Spectral study. The electronic spectra were measured on a Beckman DK 2A ratio recording spectrophotometer. The IR spectra of the isomers were recorded on a Perkin Elmer model 125 spectrophotometer. Nujol mull techniques were applied for all the measurements. The ESR spectra of the powdered samples were run on a Varian model E4 spectrometer at ambient temperature.

Magnetic study. The magnetic susceptibility measurements were made at 0.8 T in the temperature range 70–310 K in a helium atmosphere with a Faraday-type magnetometer (Oxford Instruments Ltd.). Hg[Co(NCS)₄] served as the standard.⁶ All data were corrected for diamagnetism by making use of Pascal's constants.⁷

[†] To whom correspondence should be addressed

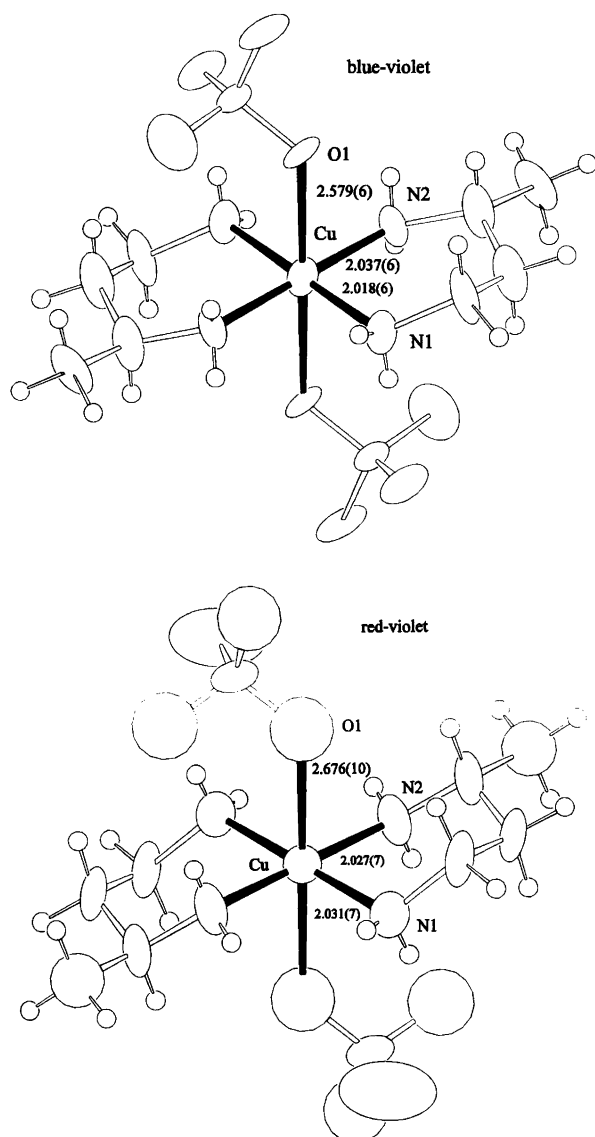


Fig. 1. The two isomeric complex units of bis(1,3-diaminobutane)copper(II) perchlorate.

Results and discussion

The IR bands of the two isomers with their tentative assignments are given in Table 1. There are numerous differences in the spectra. The assignments of the bands due to perchlorate ion are based upon the results reported in Ref. 8. These bands have generally higher intensity for the blue-violet isomer than for the red-violet isomer.

The strong absorptions at 1095–1060 cm^{-1} (blue-violet isomer) and at 1110–1060 cm^{-1} (red-violet isomer) can be assigned to the non-degenerate symmetric bending frequency of ClO_4^- . Usually the bands are broad. In the range 950–905 cm^{-1} the bands can be assigned to the non-degenerate Cl–O1 [O1 refers to the oxygen coordinated to the copper(II) ion] symmetrical stretching frequency ν_2 . The absorption band at 1175 cm^{-1} can be assigned to the Cl–O1 antisymmetrical bending fre-

Table 1. Tentative assignments of the bands in the IR spectra of the blue-violet and red-violet isomers of bis(1,3-diaminobutane)copper(II) perchlorate.

Blue-violet isomer	Red-violet isomer	Assignment
3300 sp	3310 s	$\nu_{\text{as}} \text{NH}_2$
3245 s	3245 m, sp	$\nu_{\text{as}} \text{NH}_2$
3140 w	3145 w	$\nu_{\text{str}} \text{NH}_2$
2720 w	2720 w	CH_2 str
1584 vs	1600 m, 1578 m	NH_2 sci
1392 m		CH_2 wag
1312 m, 1295 w	1312 w, 1285 w	CH_2 twi
1260 m, 1232 s	1245 w, 1220 w	NH_2 wag
1175 s	1175 m	$\nu_4 \text{Cl-O1}$
1095 s, 1060 s	1110 s, 1060 s	$\nu_3 \text{ClO}_4^-$
1040 m	1045 w	$\nu_1 \text{ClO}_4^-$
970 w	965 w	CC str
950 m	947 m	$\nu_2 \text{Cl-O1}$
926 w	926 w	$\nu_2 \text{Cl-O1}$
912 s	905 w	$\nu_2 \text{Cl-O1}$
872 m	870 w	CH_2 rock
790 w, 718 m	790 w, 718 m	NH_2 rock
665 s	670 m	$\nu_3 \text{ClO}_4^-$
615 vs, sp	615 vs	$\nu_5 \text{ClO}_4^-$
570 w	570 w	Ring skeletal

vs, very strong; s, strong; m, medium; w, weak; sp, splitting.

quency ν_4 , and those at 1040 and 1045 cm^{-1} (blue-violet and red-violet isomers, respectively) to the non-degenerate ClO_4^- symmetrical stretching frequency ν_1 of monodentately coordinated perchlorate group. The bands at 665 and 670 cm^{-1} (blue-violet and red-violet isomers, respectively) are due to the non-degenerate ClO_4^- symmetrical bending frequency ν_3 ; those at ca. 615 cm^{-1} , which is split in the blue-violet isomer, to the ClO_4^- antisymmetrical bending frequency ν_5 . The band positions of perchlorate groups in the two isomers indicate a weak coordination of the groups to the Cu(II) ion, which is somewhat stronger for the blue-violet isomer. This is in good agreement with the results of the single-crystal structure determination, where the blue-violet isomer has a slightly shorter axial Cu–O bond. Moreover, there must be hydrogen bonding involved. In the two isomers the degeneracy of a perchlorate anion has been entirely removed, which cannot be explained by coordination alone.⁹

The absorption bands in the range up to 3200 cm^{-1} show only slight differences and can be assigned to the asymmetric valence vibrations of the amino groups. The far-IR spectra exhibit bands at 353 and 430 cm^{-1} for the blue-violet isomer and at 350 and 428 cm^{-1} for the red-violet isomer, which can be assigned to $\nu(\text{Cu-N})$. The $\nu(\text{Cu-O})$ bands are at 475 and 490 cm^{-1} (blue-violet isomer) and 482 cm^{-1} (red-violet isomer). The differences between the positions of the bands are in agreement with the observed structures.

The electronic spectra of the blue-violet and red-violet isomers exhibit wide, nearly symmetrical bands at 18.58×10^3 and $18.86 \times 10^3 \text{ cm}^{-1}$, respectively. The corresponding maximum reported for $[\text{Cu}(\text{bdn})_2]^{2+}$ in aqueous solution is at $17.70 \times 10^3 \text{ cm}^{-1}$.³ These bands can be

Table 2. Tetragonalities and d-d transitions of some CuN₄O₂ chromophores.

Compound	T*	d-d transition/ 10 ³ cm ⁻¹	Ref.
Red isomer	0.758	18.86	This work
Blue isomer	0.786	18.58	This work
CUTOSY	0.785	18.18	11
CUMEIO	0.814	17.90	12
CUBENT	0.825	17.20	13

* T refers to tetragonality; $T = R_s/R_l$, where R_s = the average value for the equatorial Cu-N bond lengths and R_l = the axial Cu-O bond length. CUTOSY = *trans*-di(4-methylbenzenesulfonato-O)bis(1,3-diaminopropane-*N,N'*)copper(II); CUMEIO = *trans*-di(3-iodobenzoato-O)bis(1,3-diaminopropane-*N,N'*)copper(II); CUBENT = *trans*-di(benzoato-O)bis(1,3-diaminopropane-*N,N'*)copper(II).

assigned to the d-d transitions of a copper(II) ion in elongated tetragonal octahedral surroundings.¹⁰ The 'blue-shift' of the d-d band of the red-violet isomer indicates somewhat greater tetragonal distortion than for the blue-violet isomer. This again accords with the single-crystal X-ray determination, as seen in Table 2. The lower value for the aqueous solutions is probably due to a species in which one or two water molecules are coordinated to the Cu(II) ion.

The ESR spectra of the powdered samples of the isomers are different. While the blue-violet isomer shows a typical axial spectrum, where $g_{\parallel} > g_{\perp}$ ($g_{\perp} = 2.05_6$; $g_{\parallel} = 2.17_2$; $g_{av} = 2.09_5$), the red-violet isomer exhibits a pseudo-isotropic spectrum with $g_i = 2.080$. This is in accordance with the different canting of the axial directions within the unit cell of both isomers.¹⁴

The axial bonding in copper(II) complexes has been the subject of a number of investigations. The concept of 'semi-coordination' was introduced by Brown *et al.* to describe a long axial distance between a copper(II) ion and a weakly coordinated anion. The axial interaction was said to produce small distortions in a coordinated anion, which, however, can be detected by IR spectroscopy.¹⁵ Later on, d-s mixing has been used as a rationale to explain the axial elongation in pseudo-octahedral copper(II) complexes.¹⁶⁻¹⁹

We report here the extended Hückel calculations for the two isomers. Because the positions of the hydrogen atoms were not determined, they were placed at their ideal positions. The calculations were carried out with a CACAO program.²⁰ The results are given in Tables 3 and 4.

As expected, the unpaired electron is on the $d_{x^2-y^2}$ orbital in both isomers. There is significant contribution of 4s mixing in the d_{z^2} MO, as suggested by Vanquickenborne.¹⁹ Also the energy level of the MO is lower for the red isomer. This accords with the observed electronic spectra. The clearest differences in the compositions are seen in these d_{z^2} orbitals. In the blue-violet isomer there is significant contribution from the axial oxygen atoms; the Cu contribution is smaller in the blue-violet isomer. The contribution from the oxygen in the red-violet isomer is almost negligible. The weak semi-coordination in the red-violet isomer is seen also in the IR bands of the perchlorate anion. Since the geometry of an anion is unaffected by (semi-) coordination alone (also hydrogen bonds may have an effect), we suggest that extended Hückel analysis would be a better method to establish the existence of axial bonding in *trans*-CuL₂L'₂-type complexes.

The net charges on the central Cu(II) ion in the blue-violet and red-violet isomers are 0.279 and 0.291 electrons, respectively (Table 4). This accords well with the difference in the axial bond lengths and the suggestion made earlier.⁴ The excess of positive charge on the Cu(II) ion is reflected in the increased negative charge on the coordinated nitrogen atoms. The total charges on the nitrogen atoms of the blue-violet and red-violet isomers are -1.570 and -1.400 *e*, respectively.

The magnetic behaviour of the isomers obeyed the Curie-Weiss law with $C = 0.388(6)$ and $\Theta = 6(1)$ for the blue-violet isomer and $C = 0.365(5)$ and $\Theta = 7(1)$ for the red-violet isomer. The increased axial distance results in compression in the equatorial direction and accordingly increased ligand field. It is also expected that the orbital motion of the unpaired electron would be quenched more by the increased ligand field. This in turn causes reduced orbital magnetism in the red-violet isomer and consequently a smaller value of the Curie constant.

Table 3. Description of molecular orbitals, with metal AO contributions from the 3d orbitals of Cu(II). The percentage figures are the contributions of copper, oxygen, nitrogen and 4s AO to the respective MO.

	Cu (%)	O (%)	N (%)	4s (%)	Energy/eV
Blue isomer HOMO $d_{x^2-y^2}$	36	< 1	56	< 1	-10.932
Blue isomer d_{z^2}	68	12	4	7	-13.475
Blue isomer d_{yz}	68	< 1	6	< 1	-13.708
Blue isomer d_{xz}	91	< 1	2	< 1	-13.855
Blue isomer d_{xy}	94	< 1	< 1	< 1	-13.926
Red isomer HOMO $d_{x^2-y^2}$	37	< 1	56	< 1	-10.927
Red isomer d_{z^2}	49	2	6	6	-13.513
Red isomer d_{yz}	66	< 1	4	< 1	-13.813
Red isomer d_{xz}	92	< 1	2	< 1	-13.871
Red isomer d_{xy}	79	< 1	< 1	< 1	-13.907

Table 4. Net charges for the main non-hydrogen atoms in the two isomers.

Atom	Net charge	
	Blue-violet isomer	Red-violet isomer
Cu	0.279	0.291
N1	-0.349	-0.343
N2	-0.436	-0.357
O1	-1.232	-1.225

The Weiss constants are not zero and seem to indicate interactions between the copper(II) cations. However, according to X-ray crystal studies, no magnetic pathway is evident.⁵ Further investigations of crystal structure and magnetic measurements at low temperatures are in progress.

References

- (a) Murphy, B. P. *Coord. Chem. Rev.* 124 (1993) 63; (b) Wilkinson, G., Gillard R. D. and McCleverty J. A. (Eds.) *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon Press, Oxford 1987, p. 553; (c) Gazo, J., Bersuker, I. B., Garaj, J., Kabesova, M., Kohout, J., Langfelderova, H., Melnik M., Serator, M. and Valach, F. *Coord. Chem. Rev.* 19 (1976) 253.
- (a) Ferrer, S., Haasnoot, J. G., Reedijk, J., Muller, E., Biagini-Cingi, M., Manotti-Manfredi, A. M., Ugozzoli F. and Foglia, C. *J. Chem. Soc., Dalton Trans.* (1992) 3029; (b) Melnik, M. *Coord. Chem. Rev.* 47 (1982) 239.
- Klixbüll Jørgensen, Chr. *Acta Chem. Scand.* 10 (1956) 887.
- Lever, A. B. P. and Mantovani, E. *Inorg. Chim. Acta* 5 (1971) 429.
- Pajunen, A., Smolander, K. and Belinskij, I. *Suomen Kem., Sect. B45* (1972) 317.
- Bünzli, J.-C. G. *Inorg. Chim. Acta* 36 (1979) L413.
- Pascal, P. *Ann. Chim. Phys.* 19 (1910) 5.
- Hathaway, B. J. and Underhill, E. A. *J. Chem. Soc.* (1961) 3091.
- Ebsworth, E. A. V., Rankin, D. W. H. and Cradock, S. *Structural Methods in Inorganic Chemistry*, Blackwell Scientific Publications, Worcester, 1987, p. 217.
- Hathaway, B. J. *Struct. Bonding* 57 (1984) 55.
- Sundberg, M. R. and Sillanpää, R. *Acta Chem. Scand.* 47 (1993) 1173.
- Sundberg, M. R. and Sillanpää, R. *Acta Chem. Scand.* 46 (1992) 34.
- Sundberg, M. R. and Klinga, M. *Inorg. Chim. Acta* 105 (1985) 115.
- Hathaway, B. J. and Billing, D. E. *Coord. Chem. Rev.* 5 (1970) 143.
- Brown, D. S., Lee, J. D., Melsom, B. G. A., Hathaway, B. J., Procter, I. M. and Tomlinson, A. A. G. *Chem. Commun.* (1967) 369.
- Yamatera, H. *Acta Chem. Scand. Ser. A33* (1979) 107.
- Gerloch, M. *Inorg. Chem.* 20 (1981) 638.
- Burdett, J. K. *Inorg. Chem.* 20 (1981) 1959.
- Ceulemans, A., Beyens, D. and Vanquickenborne, L. G. *Inorg. Chim. Acta* 61 (1982) 199.
- Mealli, C. and Proserpio, D. M. *J. Chem. Educ.* 67 (1990) 399.

Received January 20, 1995.