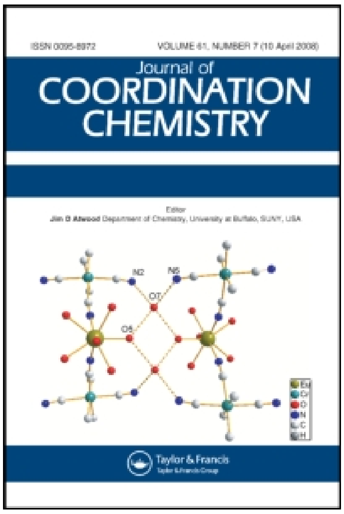

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Crystal structure of a dimeric copper(II) complex with <i>N</i>,<i>N</i>-diethylethylenediamine (dien): a model for the thermally and photoinduced violet forms of the bis(dien)copper(II) cation

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Note

Crystal structure of a dimeric copper(II) complex with *N*,*N*-diethylethylenediamine (dien): a model for the thermally and photoinduced violet forms of the bis(dien)copper(II) cation

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The molecular structure of the violet dimer bis(μ-hydroxo)bis(*N*,*N*-diethylethylenediamine)dicopper(II) perchlorate supports the hypothesis that the photoinduced phase of the monomer bis(*N*,*N*-diethylethylenediamine)copper(II) perchlorate, similar to the corresponding, high temperature, thermally induced phase, features tetrahedral distortion of the square planar coordination.

Keywords: Copper(II); Photochromism; Hydroxide; Dimer; X-ray structure; Thermochromism

The perchlorate, tetrafluoroborate and nitrate salts of bis(*N*,*N*-diethylethylenediamine)copper(II) and nickel(II) are reversibly thermochromic in the solid state above room temperature [1]. For example, the perchlorate salt $[Cu(amine)_2](ClO_4)_2$ (**1**) undergoes a phase transition at 317.6 K from the room temperature, red, triclinic ($P\bar{1}$) phase to a high-temperature, violet, monoclinic ($I2$) phase [2]. Earlier X-ray work [3] showed, and a recent re-investigation [4] confirmed, that in addition to increased disorder in the coordination sphere caused by diagonal puckering of the chelate rings, positional disorder of the ligand chains, and positional/orientational disorder of the perchlorate anions, a crucial feature for the drastic colour change is the tetrahedral distortion of the square planar geometry at the metal centre. Recently, it has been reported that, if excited by UV light at low temperatures, this compound undergoes a photoinduced transition to a violet metastable phase of yet unknown structure [4, 5]. Our attempts to prepare **1** have occasionally resulted in a mixture of red thermochromic and violet non-thermochromic crystals. The results of a structure analysis performed to identify the violet crystals reported here show that they consist of the doubly hydroxo-bridged copper(II) dimer, $[Cu_2(\mu\text{-}OH)_2(amine)_2](ClO_4)_2$ (**2**). The structure of **2**

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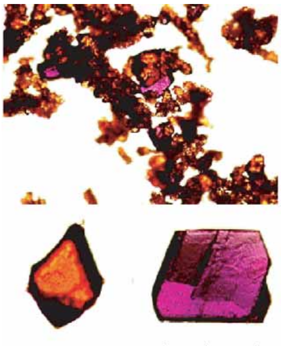
$[Cu(amine)_2]$-$(ClO_4)_2$ $[Cu_2(\mu\text{-}OH)_2$-$(amine)_2](ClO_4)_2$

Figure 1. As-obtained crystal mixture (top) of the red crystals of the monomer and violet crystals of the dimer (bottom) at 298 K.

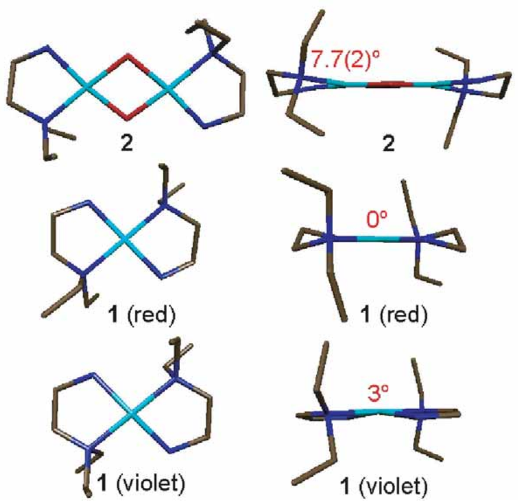

Figure 2. Intramolecular parameters of the dimer **2** and comparison with the low-temperature red phase, **1** (red), and high-temperature violet phase, **1** (violet), of the monomer **1**.

was used to draw some conclusions concerning the structure of the photoinduced phase of **1**.

Compound **2** was obtained in small yield as a side product during the synthesis of **1**. $Cu(ClO_4)_2 \cdot 6H_2O$ (3.705 g) in methanol or ethanol (100 cm^3) was added to a stirred solution of the amine (2.8 cm^3) in the same solvent (50 cm^3). Red thermochromic crystals of $[Cu(amine)_2](ClO_4)_2$ were obtained during several days by slow evaporation of the mixture in a fridge or over concentrated H_2SO_4 in a desiccator at room temperature (the presence of large amounts of water prevents crystallization). Under thermodynamically controlled conditions, or reversed order of addition of the reactants, a small amount of violet parallelepiped crystals was obtained together with the majority of red crystals (figure 1). By careful control of the synthesis and crystallization, it is possible to obtain the pure monomer **1** or increased amounts of the dimer **2**. The violet crystals were stable and did not exhibit any thermochromic properties.

The crystal structure determination of the violet crystals [6] revealed that they are composed of centrosymmetric bis(hydroxo) dimers of the amine complex (figure 2). The perchlorate ion is disordered over two positions around one of the Cl–O bonds. The dimers are hydrogen-bonded to oxygen atoms of the perchlorate ions [7].

The coordination plane in the molecular structure of the cation in the high-temperature violet phase of **1** (figure 2) is distorted, with an angle between the two chelate rings of 3° [4]. Likewise, the interplanar angle in the structure of the violet dimer **2** amounts to 7.7(2)°. On the other hand, the metal atom in the structure of the low-temperature red phase of **1** is positioned on the centre of symmetry, and thus the respective interplanar angle is 0° [3, 4]. Differences in the absorption spectra and colour of red **1** and violet **1** and **2** are drastic, despite the fact that, besides the approach of perchlorate oxygen atoms to the copper ion in **2**, there is only slight tetrahedral distortion of the coordination sphere in the latter two species. This can be taken as indication that the violet form of **1**, which can be produced by UV-excitation of single crystals or powders within the hysteresis region of the low-temperature transition [4], is due to tetrahedral distortion of the coordination sphere of the metal, as was suggested recently by Sato *et al.* [5].

References and notes

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[6] X-ray diffraction data were collected (Mo Kα radiation) with a Siemens SMART diffractometer (*SAINT–Siemens Area Detector Integration* and *SMART–Siemens Molecular Analysis Research Tool*, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA (1996)) equipped with a CCD detector. The structure was solved by direct methods (A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli. *J. Appl. Crystallogr.*, **27**, 435 (1994)) and refined on F^2 (G.M. Sheldrick. *SHELXL-97. Structure Refinement Program*, University of Göttingen, Germany (1997)) with all non-H atoms anisotropic and H atoms as riding bodies on respective non-H atoms. $T = 295(2)$ K, $\lambda = 0.71073$ Å, triclinic, space group $P\bar{1}$, $a = 7.370(1)$ Å, $b = 8.081(1)$ Å, $c = 10.853(1)$ Å, $\alpha = 111.494(2)$, $\beta = 91.212(3)$, $\gamma = 97.244(2)^{\circ}$, $V = 595.1(1)$ Å^3, $Z = 1$, $\rho_{\mathrm{calc}} = 1.648\ \mathrm{Mg\,m^{-3}}$, $\mu = 2.063\ \mathrm{mm^{-1}}$, crystal size $0.25 \times 0.16 \times 0.10\ \mathrm{mm^3}$, θ for data collection: 2.0 to 27.5°, reflections collected/unique: 4269/2698 [$R(\mathrm{int}) = 0.015$], $T_{\mathrm{max/min}} = 0.8202/0.6265$, refinement full-matrix least-squares on F^2, data/restraints/parameters 2698/118/145, $GOF = 0.941$, $R_1 = 0.046$, $wR_2 = 0.122$ ($I > 2\sigma(I)$), R_1(all data) $= 0.058$, wR_2 (all data) $= 0.126$, Largest difference peak/hole $0.82/-0.38\ \mathrm{e}$ Å^{-3}. Crystallographic data for the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with file number CCDC 290492 and can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

[7] Selected geometrical parameters: d/Å: Cu1–O1 = 1.908(3), Cu1–O1$^{\mathrm{i}}$ = 1.909(3), Cu1–N1 = 1.970(3), Cu1–N2 = 2.047(3), Cu1–Cu1$^{\mathrm{i}}$ = 2.9634(8), Cl1–O5′ = 1.394(5), Cl1–O3 = 1.395(5), Cl1–O5 = 1.428(5), Cl1–O2 = 1.431(3), Cl1–O4′ = 1.431(5), Cl1–O3′ = 1.458(5), Cl1–O4 = 1.462(5), O1–Cu1$^{\mathrm{i}}$ = 1.909(3), N1–C1 = 1.468(5), N2–C3 = 1.467(7), N2–C2 = 1.483(5), N2–C5 = 1.549(7), C1–C2 = 1.494(6), C3–C4 = 1.458(10), C5–C6 = 1.423(8); angles/°: O1–Cu1–O1$^{\mathrm{i}}$ = 78.1(1), O1–Cu1–N1 = 173.3(1), O1–Cu1–N2 = 100.2(1), O1$^{\mathrm{i}}$–Cu1–N1 = 95.9(1), O1$^{\mathrm{i}}$–Cu1–N2 = 172.9(2), N1–Cu1–N2 = 86.1(1).