Unprecedented Change of the Jahn−Teller Axis in a Centrosymmetric Cu^{II} Complex Induced by Lattice Water Molecules − Crystal and Molecular Structures of Bis[bis(3,5-dimethylpyrazol-1-yl)acetato]copper(II) and Its Dihydrate

Bojan Kozlevčar,[a] Patrick Gamez,[a] René de Gelder,[b] Willem L. Driessen,*[a] and Jan Reedijk[a]

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Two copper coordination compounds with the tridentate (NON) ligand bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza) are reported. The central coordination sphere in both compounds is fulfilled by two ligands in [CuL_2]. The ligands are centrosymmetrically oriented around the copper ion, thus forming a *trans*-CuN_4O_2 elongated octahedral chromophore. The atoms in both compounds are not positioned at the same places in the Jahn–Teller-distorted octahedral environment. For compound [CuL_2] (**1**) two nitrogen atoms are located on the longer axis [Cu–N: 2.438(2) Å], while the other two nitrogen atoms [Cu–N: 2.006(2) Å] and the two oxygen atoms [Cu–O: 1.983(2) Å] form the basal plane of the octahedron. The coordination sphere for [CuL_2]·$2H_2O$ (**2**) is composed of four nitrogen atoms [Cu–N: 2.013(3), 2.038(2) Å] that form the basal plane, while the two oxygen atoms are at a longer distance [Cu–O: 2.293(2) Å]. The water molecules in **2** are hydrogen bonded to the non-coordinated carboxylate oxygen atoms, forming bridges between two neighbouring monomeric units and leading to an infinite chain. Significant differences are observed for both compounds by spectroscopic investigations (EPR, IR, ligand field).

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Introduction

Many *trans*-CuN_4O_2 chromophores are reported in the literature with strong nitrogen donor ligands and weaker oxygen donor ligands. For most of them, the Jahn−Teller axis, i.e. the axis with the longest Cu−L bonds, coincides with the O−Cu−O bond in the elongated distorted octahedron.[1,2] A search of the Cambridge Structural Database revealed that in only 9 of the 277 CuN_4O_2 chromophores does the Jahn−Teller axis coincide with one of the N−Cu−N bonds, and there is only one example of a compressed octahedron (four longer and two shorter bonds).[3] No pair of compounds with the same coordinated ligands — one with the O−Cu−O unit as the Jahn−Teller axis and the other with the N−Cu−N as the Jahn−Teller axis — have been reported.[1,2] The absence of isomers is probably due to steric effects of the ligands, which favour only one of the arrangement types in the coordination sphere. With a special ligand shape, different configurations around the central copper ion may be expected. Bearing this in mind, a vicinal tridentate ligand that produces a nitrogen-oxygen-nitrogen (NON) donor set may be of special interest. In this paper, the comparison of two structures of the ligand bis(3,5-dimethylpyrazol-1-yl)acetic acid with copper(II) is presented.

Results and Discussion

Two copper(II) compounds were synthesised with the deprotonated tridentate ligand bis(3,5-dimethylpyrazol-1-yl)-acetic acid (Hbdmpza) in the [CuL_2] coordination sphere. In both cases bdmpza coordinates through two pyrazole nitrogen atoms and one deprotonated carboxylate oxygen atom (NON donor set). Similar coordination complexes are known for other *d*-block metals and bdmpza.[4−7] The ligands are centrosymmetrically arranged around the copper ion, thus forming *trans*-CuN_4O_2 chromophores. Both new copper compounds show an elongated distorted octahedral geometry, however the coordinated atoms do not play the same role. The coordination environment of **1** (Figure 1) is particularly interesting, with the basal plane composed of two nitrogen atoms [Cu−N: 2.006(2) Å] and two oxygen atoms [Cu−O: 1.983(2) Å], and the remaining two coordinated nitrogen atoms forming the Jahn−Teller axis [Cu−N: 2.438(2) Å].

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[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
P. O. Box 9502, 2300 RA Leiden, The Netherlands
Fax: (internat.) +31-71/527-4671
E-mail: driessen@chem.leidenuniv.nl
[b] Department of Inorganic Chemistry, University of Nijmegen,
P. O. Box 9010, 6500 GL Nijmegen, The Netherlands

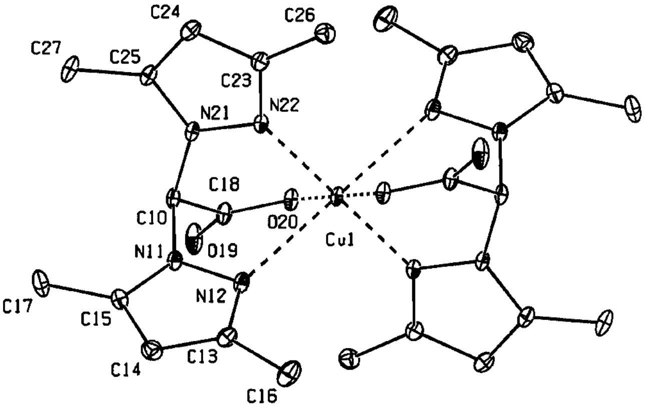

Figure 1. The centrosymmetric structure of **1** with two tridentate scorpionate ligands around the central copper; thermal ellipsoids are drawn at the 10% probability level; all hydrogen atoms have been omitted for clarity.

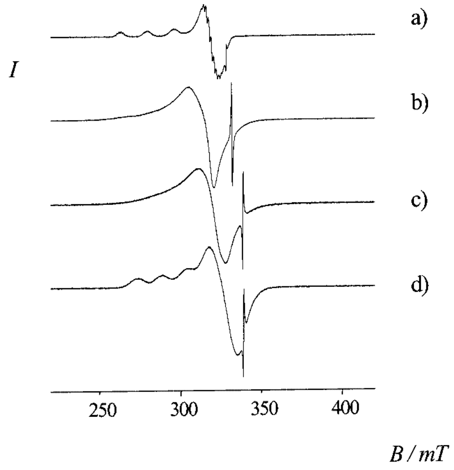

Figure 3. EPR spectra of compounds **1** and **2**, measured under different conditions: a) **1** as a frozen methanol solution at 77 K; b) **1** as a solid at 77 K; c) **1** as a solid at room temp.; d) **2** as a solid at room temp.; the sharp signal closest to 350 mT in all spectra is due to the reference

The more common isomer with the Jahn−Teller axis along the O−Cu−O bonds has also been obtained, but from aqueous solution. In this compound [CuL$_2$]·2H$_2$O (**2**; Figure 2, the basal octahedron plane is composed of four nitrogen atoms [Cu−N: 2.013(3), 2.038(2) Å], while the oxygen atoms are located at a longer distance [Cu−O: 2.293(2) Å]. Such a conformation has also been found in Fe^{II} and Zn^{II} [ML$_2$] analogues.[5] Each water molecule in **2** forms two hydrogen bonds to the noncoordinated carboxylate oxygen atoms [O···H−O:; 2.813(4), 2.868(4) Å], thereby connecting two neighbouring monomeric units and leading to linear chains of octahedra as shown in Figure 2.

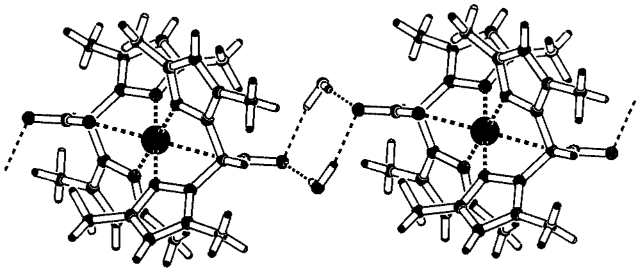

Figure 2. The intermolecular hydrogen-bonding contacts between the coordination octahedra in the structure of the hydrated compound **2**

In the anhydrous compound **1**, a significantly longer C−O distance [1.262(3) Å] is observed for the coordinated carboxylate oxygen atom than for the non-coordinated one [1.214(3) Å]. For the hydrated compound **2**, almost the same C−O distances are observed [1.245(4) and 1.241(4) Å]. These similar C−O bonds for the carboxylate group of **2** are probably due to the binding of both oxygen atoms to a Lewis acid, i.e. to the copper and to a water molecule, while only one carboxylate oxygen is coordinated in **1**.

The solid-state EPR spectrum of compound **1** measured at room temperature shows an isotropic copper(II) signal (Figure 3c). No resolution of $g_{\parallel}$, $g_{\perp}$ or $A_{\parallel}$ is observed, which is indicative of exchange narrowing due to the close distance and dipolar coupling between the Cu ions in the lattice. At 77 K, the spectrum reveals an additional low-intensity $g_{\parallel}$ signal at 260 mT and a small change in the shape of the $g_{\perp}$ signal (Figure 3b). A significantly different feature is observed for the room-temperature solid-state EPR spectrum of **2**. Beside the $g_{\perp}$ signal, a $g_{\parallel}$ signal with three distinctive $A_{\parallel}$ signals is present at lower field (Figure 3d). The value of $A_{\parallel}$ amounts to 15.0 mT, which is typical for a tetragonal Cu centre. The coupling of the *d* electron spin and the nuclear spin results in a hyperfine splitting, and agrees with the anisotropic nature of the coordination sphere that is characteristic of an elongated octahedral geometry. The EPR spectra of frozen methanolic solutions of **1** and **2** are identical (Figure 3a). This is as expected as the water molecules dissociate upon dissolution of **2** in methanol. Solvation of the monomeric complex disrupts the hydrogen-bond network of **2** as the water molecules are probably replaced by methanol molecules. Additional superhyperfine splitting was observed in the frozen solution due to interaction with ^{14}N nuclei from the ligand. Relevant parameters for the solution spectra, which were satisfactorily simulated,[8] are $g_{\parallel} = 2.289$, $g_{\perp} = 2.061$, $A_{\mathrm{Cu}} = 160$ Gs, and $A_{\mathrm{N}} = 15.5$ Gs.

In the region above 3000 cm^{-1} in the vibrational spectra, characteristic bands for H-bonded water O−H stretching vibrations are present only for the hydrated compound **2** (See Figure 4).

The rest of the IR spectra is almost identical for both compounds due to the presence of the same constituents. Exceptions may be found in the regions where the carboxylate group stretching vibrations are expected. Differences are observed at 1650 cm^{-1} for the asymmetric vibration ν_{as}(OOC) and at 1350 cm^{-1} for the symmetric vibration ν_{s}(OOC): the spectrum of the anhydrous compound **1** shows only one band in both areas, while two bands are observed in the spectrum of the solvated compound **2**. In-

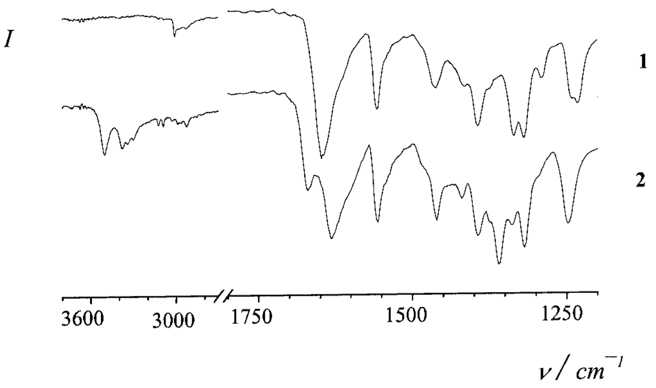

Figure 4. Comparison of two regions in the vibrational spectra of the investigated compounds

terestingly, the stronger $\nu_{as}(OOC)$ band of **2** is shifted towards lower energy and the stronger $\nu_s(OOC)$ band to higher energy relative to the corresponding bands in the spectrum of **1**. Therefore Δ [= $\nu_{as}(OOC) - \nu_s(OOC)$] [9] for **2** is smaller than for **1**. This is related to the typically monodentate carboxylate group in **1** and the pseudo-didentate group in **2**. In the carboxylate group of **1**, more single bond character for the coordinated oxygen atom is present, and more double bond character with the non-coordinated oxygen atom (O=C−O−Cu). The hydrogen bond in **2** attracts the non-coordinated oxygen atom, weakening the double bond (H−O−H···O=C−O−Cu). This is in agreement with the bigger Δ values for monodentate than for didentate carboxylate groups.[9] The IR spectrum of dry **2** is identical to the spectrum of **1**, which is stable under reduced pressure or in diethyl ether.

In the visible part of the electronic spectra, a broad *d−d* band is observed for compounds **1** and **2**. The peak in the spectrum of **1** is found at 13900 cm^{-1}, while in the spectrum of **2** it appears at 15300 cm^{-1}. The difference is in agreement with a weaker tetragonal chromophore CuN_2O_2 in **1** compared to CuN_4 in **2**.

The pair of compounds **1** and **2** clearly represent an unprecedented change of the Jahn−Teller axis induced by water molecules. The two copper complexes prepared show significantly different results in the vibrational, EPR and electronic spectra. The stabilization of **2** by a hydrogen-bonding network modifies the coordination of the ligand around the copper, although steric hindrance would favour the other alternative (complex **1**). The water molecules apparently direct the Cu−O bonds to be in the Jahn−Teller axis of the copper-centred octahedron.

Experimental Section

General Remarks: All reagents and solvents were purchased from commercial sources and used as received. The ligand bis(3,5-dimethylpyrazol-1-yl)acetic acid was prepared from dibromoacetic acid and 3,5-dimethylpyrazole in a basic solution as described in the literature.[5] C,H,N analyses were carried out by the Microanalysis Department of Leiden University. Infrared spectra were recorded on a Perkin−Elmer Paragon 1000 spectrophotometer, equipped with a Golden Gate Diamond ATR as a sample support. X-band EPR spectra were recorded on a JEOL ESR spectrometer, equipped with an Esprit 330 data system, at room temperature and at 77 K, with dpph as an internal reference (g = 2.0036). The ligand field spectra of the solid compounds were recorded in the 300−2000 nm range on a Perkin−Elmer Lambda 900 UV/Vis/NIR spectrometer in the diffuse reflectance mode with MgO as reference.

[CuL_2] (1): A solution of the ligand (25 mg, 0.10 mmol) in acetonitrile (10 mL) was added to copper(II) acetate hydrate (10 mg, 0.025 mmol). Pale-blue crystals started to precipitate from the transparent solution at room temperature in a few hours. They were filtered off the next day and washed with diethyl ether. $C_{24}H_{30}CuN_8O_4$ (558.1): calcd. C 51.7, H 5.42, N 20.1; found C 51.3, H 5.22, N 20.0. IR (solid): $\tilde{\nu}$ = 1645 cm^{-1} (C−O), 1558 (C−N). UV/Vis-NIR (solid): λ_{max} = 13900 cm^{-1}. EPR (solid, room temp.): g = 2.118.

[CuL_2]·$2H_2O$ (2): The ligand (50 mg, 0.20 mmol), dissolved in acidified water (10 mL), was added to copper(II) acetate hydrate (40 mg, 0.10 mmol). Blue crystals started to precipitate from the transparent solution at room temperature after a few hours. They were filtered off next day and dried for 5 minutes on a filter paper. $C_{24}H_{34}CuN_8O_6$ (594.1): calcd. C 48.5, H 5.77, N 18.9; found C 48.5, H 5.46, N 18.9. IR (solid): $\tilde{\nu}$ = 3504 cm^{-1} (O−H), 3381 (O−H), 1669 (C−O), 1634 (C−O), 1558 (C−N). UV/Vis-NIR (solid): λ_{max} = 15300 cm^{-1}. EPR (solid, room temp.): $g_{\parallel}$ = 2.288, $g_{\perp}$ = 2.077, $A_{\parallel}$ = 0.129.

X-ray Crystallography: X-ray data were collected on an Enraf−Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-K_α radiation (0.71073 Å). Crystal data are collected in Table 1. The structure was solved with automated Patterson techniques using DIRDIF/PATTY [10] and refined on F us-

Table 1. Crystal data and structure determination data for the compounds **1** and **2**

Formula	$C_{24}H_{30}CuN_8O_4$ (**1**)	$C_{24}H_{34}CuN_8O_6$ (**2**)
Molecular weight	558.10	594.13
Crystal habit	block	block
Crystal colour	light blue	light blue
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.8946(10)	7.5745(7)
b (Å)	8.7869(13)	8.7165(9)
c (Å)	10.2039(15)	11.1364(12)
α (°)	65.456(16)	69.514(8)
β (°)	83.008(17)	85.676(12)
γ (°)	87.332(13)	89.739(9)
V ($Å^3$)	639.08(18)	686.61(13)
Z	1	1
$D_{calcd.}$ ($g \cdot cm^{-3}$)	1.45	1.44
F(000)	291	311
μ (cm^{-1})	9.0	8.5
Temperature (K)	293	293
θ Min., θ max.	2.55, 27.5	2.7, 27.5
$h/k/l$ range	−10,10/−11,10/−13,0	0,9/−11,11/−14,14
Total reflections	3102	3368
Observed reflections [$I > 2\sigma(I)$]	2815	2447
No. of refined parameters	214	229
Final R, wR [$I > 2\sigma$(I)]	0.032, 0.048	0.047, 0.083
Min. and max. residual density ($e \cdot Å^{-3}$)	−0.34, 0.32	−0.82, 0,71

ing full-matrix least-squares techniques with fl$^{\mathrm{ta}}$L3.4.[11−12] The positions of the non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the Fourier difference maps. The positions of the hydrogen atoms were refined with fixed isotropic displacement parameters. For compound **2** an empirical absorption correction was applied.[13] Geometric calculations and molecular graphics were performed with PLATON.[14]

CCDC-190297 (**1**) and CCDC-190298 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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