An unusual Cu(II) polymeric compound with tridentate dehydronated and bidentate neutral ligand bis(pyrimidin-2-yl)amine (=Hdipm) and uncoordinated Hdipm in a complicated H-bonding system. Synthesis, characterization and X-ray structure of {[Cu(dipm)(Hdipm)](Hdipm)(CF$_3$SO$_3$)(C$_2$H$_5$OH)(H$_2$O)}$_n$

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Abstract

A highly unusual polymeric copper(II) compound with formula {[Cu(dipm)(Hdipm)](Hdipm)(CF$_3$SO$_3$)(C$_2$H$_5$OH)(H$_2$O)}$_n$ (in which Hdipm = bis(pyrimidin-2-yl)amine) has been synthesized and characterized by X-ray crystallography, infrared spectroscopy and EPR.

The Cu(II) ion is surrounded by five nitrogen atoms. The basal plane is formed by two nitrogen atoms from a neutral Hdipm ligand and two nitrogen atoms from a dehydronated (dipm)$^-$ ligand with Cu–N distances which vary from 1.990(3) to 2.093(3) Å. The fifth nitrogen atom originate from a neighbouring anionic ligand with a Cu–N distance of 2.183(4) Å, forming a distorted trigonal bipyramidal geometry around the Cu(II) ion. Furthermore the lattice are contains an uncoordinating Hdipm ligand (stacked on other ligands), one triflate anion, one ethanol molecule and one water molecule.

The 2D system of Hydrogen bonds consists of Watson–Crick-type intermolecular double H-bonds between pairs of dipm molecules and H-bonds between the triflate anion, the ethanol and water molecules. The ligand-field and EPR spectra are uneventful and agree with the found coordination geometry. Cu(II) hyperfine splitting remains unresolved.
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1. Introduction

In the field of supramolecular interactions of coordination compounds, not only the direct metal–ligand bonds are of interest, but also hydrogen bonding is of great importance [1–9].

A ligand with interesting hydrogen-bonding properties is the recently developed ligand bis(pyrimidin-2-yl)amine (abbreviated as Hdipm) [10–15]. The Hdipm molecule can both donate and accept hydrogen bonds, and has a more or less linear donor–acceptor array of the A–D–A type (see Scheme 1). This type of array is capable of forming so-called Watson–Crick-type hydrogen bonds, similar to the one reported for the first generation ligand 2-aminopyrimidine [16,17]. So far only a few X-ray crystal structures of Cu(II) compounds with dipm have been published, i.e., [Cu(Hdipm)(CO$_3$)(H$_2$O)](H$_2$O)$_2$ [11], [Cu(Hdipm)$_2$(dicyanamide)(CF$_3$SO$_3$)](C$_2$H$_6$O)$_{1/2}$ [12] [μ-Cl-CuCl(Hdipm)]$_n$ [13], [Cu(Hdipm)$_2$(H$_2$O)$_2$](Hdipm)$_2$(H$_2$O)$_2$(CF$_3$SO$_3$)$_2$ and [Cu(Hdipm)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ [14].

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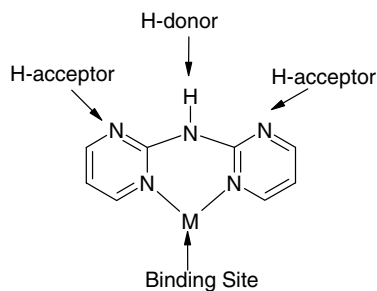
Scheme 1. Scheme of the ligand bis(pyrimidin-2-yl)amine (Hdipm).

In a very recent publication, results were presented with the formato and carboxylato anions revealing mononuclear compounds with the formula $[Cu(Hdipm)(HCOO)_2(H_2O)]$ and $[Cu(Hdipm)(C_2O_4)(H_2O)]$ [15]. In this report, by using acetate in the recipe not the suspected compound with acetate as an anion, but a completely new system, without any acetate anions, but with an anionic ligand (dipm$^-$) was obtained. All the compounds published so far with this ligand contain only the neutral Hdipm ligand.

In the present study the synthesis, crystal structure, characterization of a new Cu(II) compound with formula $\{[Cu(dipm)(Hdipm)](Hdipm)(CF_3SO_3)(C_2H_5OH)(H_2O)\}_n$ has been undertaken. The Cu(II) ion is surrounded by a neutral Hdipm ligand and an anionic dehydronated dipm ligand, which is the first time that this ligand found to be dehydronated, forming a polymeric array, with bridging dipm ligand.

2. Experimental

2.1. Syntheses

The ligand Hdipm was prepared by the method reported in the literature [10]. All other chemicals were used without further purification. The compound was prepared according to the following procedure: 1.2 mmol of the Cu(II) triflate and 1.2 mmol of the ligand were each dissolved in 10 ml of a ethanol/water mixture (1:1). The Cu(II) salt solution was added slowly to the ligand solution and then 1.2 mmol of ammonium acetate dissolved in a ethanol/water mixture was added. The resulting green solution was standing in open air and after about 3 weeks green crystals separated. Yield 35–45%. Elemental Analysis for $C_{27}H_{28}CuF_3N_{15}O_5S$; Found (calc.): 40.3 (40.8) %C, 3.2 (3.5) %H, 26.8 (26.4) %N, 4.2 (4.0) %S.

2.2. Physical techniques

C, H, N determinations were performed on a Perkin Elmer 2400 Series II analyser. X-band powder EPR spectra were obtained on a Jeol RE2× electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. FTIR spectra were obtained on a Perkin Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden

Table 1
Crystallographic data of $\{[Cu(dipm)(Hdipm)](Hdipm)$ $(CF_3SO_3)(C_2H_5OH)(H_2O)\}_n$

Formula	$C_{27}H_{28}CuF_3N_{15}O_5S$
Molecular weight	795.26
Crystal system	Monoclinic
Space group	$P2_1/c$ (no.14)
a (Å)	12.790(2)
b (Å)	30.255(3)
c (Å)	8.644(1)
β (°)	92.17(1)
V (Å^3)	3342.5(7)
Z	4
D_{calc} (g cm^{-3})	1.580
$F(000)$	1628
μ (mm^{-1})	0.796
Crystal size	$0.21 \times 0.04 \times 0.04$
Temperature (K)	173(2)
θ_{min}, θ_{max} (°)	3.02, 23.2
Total data	21085
Total unique data	5810 ($R_{int} = 0.0935$)
No. of refined parameters	478
wR_2[a] (all data)	0.128
R [b]($I > 2\sigma(I)$)	0.056
S	1.01
min. and max. resd. dens. (e/Å^3)	−0.37, 0.50

[a] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.
[b] $R_1 = \sum |F_o| - |F_c| /\sum |F_o|$.

Gate ATR device, using the diffuse reflectance technique (4000–300 cm^{-1}, res. 4 cm^{-1}).

2.3. Crystallography

A crystal from the mother liquid, suitable for structure determination was mounted on a lindemann-glass capillary using the oil-drop technique and transferred into the cold nitrogen stream of a Nonius KappaCCD diffractometer (MoKα radiation, graphite monochromator, $\lambda = 0.71073$). The intensity data were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by direct methods. The programs COLLECT [18], SHELXS-97 [19], SHELXL-97 [20] were used for data reduction, structure solution and structure refinement, respectively. All non-hydrogen atoms were refined anisotropically. All H atoms were introduced at calculated positions and refined with fixed geometry with respect to their carrier atoms. Crystallographic data of the compounds are listed in Table 1.

3. Results and discussion

3.1. Crystal structure of $\{[Cu(dipm)(Hdipm)](Hdipm)(CF_3SO_3)(C_2H_5OH)(H_2O)\}_n$

A plot showing the numbering scheme is given in Fig. 1 and selected bond distances and angles are listed in Table 2. The Cu(II) ion is surrounded by five nitrogen atoms. The basal plane is formed by two nitrogen atoms from a neutral