Inorganica Chimica Acta 391 (2012) 201–205

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Three new multinuclear motifs in Cu(II)-pyrazolate chemistry

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ARTICLE INFO

Article history:
Received 30 April 2012
Received in revised form 25 May 2012
Accepted 28 May 2012
Available online 5 June 2012

Keywords:
Cu(II) complexes
Pyrazolate ligands
Multinuclear assemblies

ABSTRACT

Combining the tendencies of copper(II)-pyrazolato complexes to form trinuclear or oligonuclear rings with its coordination plasticity, three new structural motifs have been recognized: An hexanuclear assembly of two triangular Cu_3-units held together by a single H-bond (**1**); a dodecanuclear structure composed of triangular and linear-chain units (**2**); and an octanuclear ring encapsulating two glycerate trianions (**3**) have been structurally characterized by single crystal X-ray diffraction.

1. Introduction

Polynuclear Cu(II) complexes are of interest to biological chemists and magnetochemists alike. They make up the active centers of several oxidase enzymes [1–3], while early fundamental theories of magnetostructural relationships have been developed through the study of the magnetic exchange among the $S = 1/2$ centers of polynuclear Cu(II)-complexes [4]. The manner in which polynuclear Cu complexes manage the addition or elimination of electrons, leading to various "flavors" of mixed valency, is intimately connected to the structural organization of the multicopper core and its supporting ligands [5–9]. Therefore, the discovery of novel structural motifs enriches the continuing search for new phenomena.

Our laboratory has worked on the systematic structural and accompanying magnetic and electrochemical manipulation of triangular Cu-pyrazolate complexes of the general formula $[Cu_3(\mu_3\text{-}E)(\mu\text{-}4\text{-}R\text{-}pz)_3X_3]^z$ where E = OH, OMe, OEt, O, $(Cl)_2$ and $(Br)_2$, R = H, Cl, Br, NO_2, Me, CHO and COOEt, X = Cl, Br, MeCOO, SCN, NCO and py, z = +, −, 2− [10–18] (Scheme 1A–C). We have studied the effect of Cu–E–Cu angles on their magnetic properties, as well as the mechanism of spin relaxation in the E = $(Cl)_2$ complexes [11,19]. We have also shown a systematic shift of the one-electron oxidation $E_{1/2}$-values of the E = O complexes with the variation of their X-ligands [18]. Finally, we have discovered that when the terminal X-ligands are removed, the triangular Cu-pyrazolato ring opens up and reorganizes itself into larger $[Cu(\mu\text{-}OH)(\mu\text{-}pz)]_n$ rings forming supramolecular assemblies (Scheme 1D) [12]. We and others have shown that larger polynuclear Cu-pyrazolato complexes – e.g., hexanuclear, nonanuclear – as well as infinite polymeric structures can be assembled via covalent or H-bonding interactions between Cu_3-units [17,20,21]. Some Cu_6- and Cu_8-pyrazolate rings have also been reported [21–24].

In the course of our synthetic endeavors, along with the intended products, we have in some instances serendipitously structurally characterized some unexpected, nevertheless interesting polynuclear complexes that fell outside the scope of our research project at the time. Recognizing that some of these materials may be legitimate targets of systematic synthetic efforts in the future, we describe here the crystal structures of three such complexes: a hexanuclear assembly held together by a single H-bond between Cu_3-units (**1**), a dodecanuclear complex with a mixed ligand set (**2**), and an octanuclear ring encapsulating two adventitious glycerolate anions (**3**).

2. Experimental

2.1. Materials and methods

$Cu(CF_3SO_3)_2$ (anhydrous), $Cu(OH)_2$ (stabilized tech.) pyrazole (98%), 3,5-dimethylpyrazole (97%), pyridine (>99%) and benzoic acid (98%) (all Sigma–Aldrich) and NaOH (Fluka) were purchased and used as received. Solvents were purified according to standard techniques [25].

2.2. Synthesis

2.2.1. $[Cu^{II}_3(\mu_3\text{-}OH_{0.5})(\mu\text{-}pz)_3(pzH)_3]_2(CF_3SO_3)_3$ (**1**) and $[Cu^{II}_{12}(\mu_3\text{-}OH)_2(\mu\text{-}OH)_4(\mu\text{-}pz)_{16}(NCO)_2]\cdot 4H_2O$ (**2**)

$Cu(CF_3SO_3)_2$ (114 mg, 0.31 mmol), NaNCO (18.6 mg, 0.27 mmol), pzH (19.8 mg, 0.29 mmol), and NaOH (17.3 mg,

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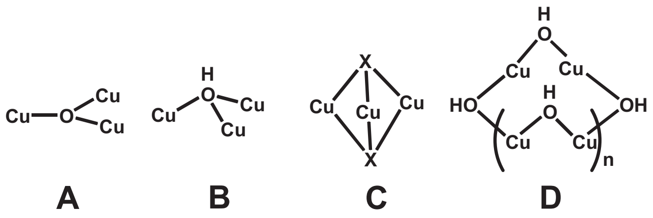
http://dx.doi.org/10.1016/j.ica.2012.05.027



Scheme 1.

0.43 mmol) were mixed in 15 mL water. After stirring at ambient temperature for 1 h, 10 mL of CH_2Cl_2 was added and stirred for an additional 1.5 h. The organic layer was collected using a separatory funnel. Several X-ray quality blue crystals of **1** and **2** were isolated through the slow evaporation of the solvent.

*2.2.2. [$Cu^{II}_8(\mu_5\text{-glyc})_2$ (μ-3,5-$Me_2pz)_8$(3,5-$Me_2pzH)_2(PhCOO)_2$] (**3**)*

$Cu(OH)_2$ (48.8 mg, 0.5 mmol), PhCOOH (122.1 mg, 1.0 mmol dissolved in 2 mL MeOH) 3,5-Me_2pzH (48 mg, 0.5 mmol), and NEt_3 (69.7 μL, 0.5 mmol) were stirred in 10 mL acetonitrile for 5 days and the filtrate was allowed to slowly evaporate, yielding several crystals of **4** after 4 weeks. A blue plate-like crystal was analyzed to be **3**. Glycerate trianions ($C_3H_5O_3{}^{3-}$) in the complex have been scavenged from the stabilizer of the starting $Cu(OH)_2$ material.

2.3. Crystallography

X-ray diffraction data were collected at room temperature from crystals mounted atop a glass fiber with a Bruker AXS SMART 1K CCD diffractometer, Mo-Kα radiation [26]. Data were corrected for Lorentz and polarization effects [27]. The structures were solved employing the SHELXTL-direct methods refined by full-matrix least squares methods on F^2 [28]. Crystallographic details are summarized in Table 1.

In **1**, one H-bonded H-atom (H1A) was fixed at an equidistant position from O1 and O1A (DFIX), and its thermal parameters were fixed to be similar to other riding H-atoms in the molecule (ISOR). In **2**, one metal-atom (Cu(6)) and one pyrazole ring (N(16)–N(17)–C(24)–C(25)–C(26)) were crystallographically disordered over two positions (50% each) across the mirror plane bisecting the molecule. This required the application of bond restraints (N(16)–N(17), C(23)–H(23) and C(100)–O(1W)) to overlapping components of the disorder model. The methanolic proton of the interstitial solvent molecule could not be refined to satisfaction and was omitted from the refinement. Subsequently, the unaccounted for electron density was removed using the SQUEEZE routine available with the PLATON suite [29]. SQUEEZE was also applied to **3** to remove electron densities of disordered solvent molecules that could not be refined.

3. Results and discussion

3.1. Synthesis

In efforts to manipulate the physicochemical properties of trinuclear Cu-pyrazolato complexes, $[Cu_3(\mu_3\text{-}E)(\mu\text{-}4\text{-}R\text{-}pz)_3X_3]^{n-}$, by systematic variation of the ancillary ligands X, we have successfully employed metathetical and self-assembly approaches. The reaction of $Cu(ClO_4)_2$, pzH, NaOH, NaNCO and $(PPN)(CF_3SO_3)$ yielded the expected $[PPN][Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(NCO)_3]$ crystalline material as the major reaction product [30]. Here, a similar reaction involving $Cu(CF_3SO_3)_2$, pzH, NaOH and NaNCO yielded visually distinguishable single crystals of **1** and **2**.

We have previously described some spectacular supramolecular assemblies of [*cis*-Cu(μ-OH)(μ-pz)]$_n$-rings, n = 6, 8, 9, 12 and 14, synthesized from $Cu(OH)_2$, the latter prepared from $CuSO_4$ and NaOH and used *in situ*. Similar [*trans*-Cu(μ-OH)(μ-3,5-Me_2-pz)]$_n$-rings, n = 6 and 8, have been reported by others [22,24]. In a modified procedure, we used here 3,5-Me_2-pzH and commercially available, technical grade $Cu(OH)_2$, isolating single crystals of the octacanuclear complex **3**, which surprisingly contained two encapsulated glycerolate anions. The supplier of $Cu(OH)_2$ informed us that "an organic, non-phosphate stabilizer" used in the synthesis of this reagent is present in less than 1% quantities in the market product. Even though the suppliers of the reagent could not divulge proprietary information on the stabilizer used in their manufacturing process, glycerol has been known as a stabilizer in this process for over five decades [31–33]. Further attempts to produce **3** using the same synthetic procedures or using stoichiometric or excess amounts of glycerol have, so far, been unsuccessful.

Table 1
Crystal data for compounds **1**–**3**.

Compound	1	2	3
Formula	$C_{39}H_{43}Cu_6F_9N_{24}O_{11}S_3$	$C_{52}H_{62}Cu_{12}N_{34}O_{10}$	$C_{70}H_{92}Cu_8N_{20}O_{10}$
f_w (amu)	1672.39	2085.84	1881.96
Size (mm^3)	0.12 × 0.12 × 0.11	0.09 × 0.07 × 0.06	0.16 × 0.11 × 0.04
Crystal System	Trigonal	Monoclinic	Triclinic
Space group	$P\bar{3}1c$ (No. 163)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a (Å)	13.789(7)	25.921(5)	14.402(2)
b (Å)	13.789(7)	18.758(4)	18.496(2)
c (Å)	17.998(12)	15.948(3)	18.766(3)
α (°)	90	90	106.245(3)
β (°)	90	103.004(4)	106.116(3)
γ (°)	120	90	105.183(3)
V ($Å^3$)	2963(3)	7555(3)	4286.9(10)
Z	2	4	2
ρ_{calc} ($g\ cm^{-3}$)	1.964	1.834	1.458
μ (mm^{-1})	2.367	3.377	2.007
Total data	15074	24639	20359
Unique data	2172	8583	9869
θ (°)	2.05–27.64	1.35–28.31	1.22–28.30
Goodness of fit (GOF) on F^2	0.987	0.946	1.008
R indices [$I > 2\sigma(I)$]	0.0646	0.0838	0.1194
R indices (all data)	0.1516	0.2042	0.2166
Maximum and minimum transition	0.7678 and 0.7841		0.7453 and 0.5245
Largest difference in peak and hole ($e\ Å^{-3}$)	0.711 and −1.122	2.406 and −0.667	0.971 and −0.818