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Sorption−Desorption Behavior of Bispyrazolato−Copper(II) 1D Coordination Polymers

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In the past decade, polymeric metal diazolates, such as pyrazolates and imidazolates, have been extensively studied[1] and have been shown to possess a few interesting functional aspects, ranging from spin-crossover behavior,[2] thermal, optical, dielectric,[3] and anticorrosive[4] properties, and even relevant antifungal activity.[5] Their structures ranged from cyclic oligomers of different nuclearities up to chains, layers, or three-dimensional networks,[1b] and the presence of polymorphic systems was often evidenced.[6] More recently, other diazaheterocyclic ligands (such as hydroxypyrimidines) have been employed, which showed new interesting structural features and a rich host−guest chemistry.[7]

During our continuous studies on the synthesis, structural, and catalytic properties of metal pyrazolates, $M(pz)_n$, with a number of ancillary ligands, we obtained, from copper acetate and pyrazole MeCN solutions, an insoluble pink material (**4c** in Table 1). This synthesis was found to be quantitative and highly reproducible (also employing different copper carboxylates), and the product, *manipulated in air*, was eventually characterized by DSC, TG, and IR as a hydrated $Cu(pz)_2$ species, **1**.[8]

Our ab initio X-ray powder diffraction (XRPD) structural determination (see Figure 1) confirmed the purported $Cu(pz)_2 \cdot H_2O$ formulation and showed the presence of bispyrazolate−copper(II) 1D polymers (see Figure 2), with the pz moieties bridging in the common *N,N′-exo*bidentate mode (Cu⋯Cu 3.64 Å).[9] Noteworthy, the Cu(II) ions are in a square-planar environment of four nitrogen atoms, *only very weakly* perturbed by the presence of two "axial" Cu⋯O contacts, defining a heavily elongated octahedron (Cu⋯O ca. 2.91 Å). The unusual color of this copper polymer is thus determined mainly by the stereochemistry of the CuN_4 chromophore, as in *truly* square-planar complexes, with the water molecules (apparently) not influencing the spectroscopic properties (vide infra). At variance, the related anhydrous species α-$Cu(pz)_2$, **2**, studied by Storr and co-workers back in 1991,[10] possesses a deep green color, pseudo-tetrahedral copper ions, and a completely different arrangement of the pz ligands (Figure 2).

Upon gentle heating, water is quantitatively lost from **1**, and a *new* (beige) $Cu(pz)_2$ species (β-phase, **3**) is formed. Ab initio XRPD (Figure 1) showed it to be a true polymorph of **2**, containing collinear chains of copper ions as well, but maintaining the square-planar arrangement found in the precursor **1**, with slightly inflated intermetallic interactions (Cu⋯Cu 3.70 Å).[11] By heating **3** above 200 °C, a greenish hue is observed, but **2** is *not* formed since a significant reorganization of the Cu−N bonds would be required. Indeed, **2** was prepared by a completely different (high-temperature) synthesis from Cu shots, molten pyrazole, and bubbling O_2.[10,12] Worthy of note, species **3** is stable at room temperature only in the absence of moisture or other small molecules with Lewis basic character; for example, within a few minutes (during cooling in air), **2** restores the polycrystalline hydrated phase **1**, or if exposed to *vapors* of NH_3, $MeNH_2$, CH_3CN, pyridine, MeOH, or EtOH, the corresponding solvates (**4a**−**f**) are formed.[13,14]

Table 1 shows the reaction details and the unit cells for species **1**−**4**, which nicely show the formation of monosolvates and the interchain location of these clathrated molecules. Species **4a**−**f** can easily restore **3** upon vacuum pumping or gentle heating, thus allowing the quantitative recovery of **1**.[15] Other small molecules were tested, but we found that I_2, Me_3N, Me_2NH, CO_2, CS_2, CO, THF, PhCN, and EtBr are not absorbed.

A special concern was actually raised by the unusual location and bonding properties of the water molecules in **1**; too far from the Cu(II) ions to be considered as apical ligands in a Jahn−Teller distorted d^9 CuN_4O_2 environment, and not supporting the *pink* color of **1**, the water molecules were initially considered as possibly misplaced (i.e., disordered), eventually affording a 1D polymer of pentacoordinated Cu(II) ions. Although our XRPD data do not possess the required resolution for rejecting (or validating) this hypothesis, the fortunate occurrence of the NH_3 and CH_3CN *isomorphous* (**4a** and **4c**) compounds (with nearly identical structural features; see Table 1) indicates that pentacoordinate ions must be excluded on the basis of geometrical considerations (e.g., the size and shape of CH_3CN), and that these ligands bind in similar ways, through their lone pair(s) interacting with two adjacent Cu atoms. As confirmed by the sharp ν(OH) IR bands above 3500 cm^{-1}, the water H atoms do not interact with the surrounding pz moieties (estimated $H_w \cdots N,C > 2.7$ Å), thus suggesting that the driving forces in the formation of **1** are the weak, but non-negligible, Cu−O bonds.

In all of these materials, the crystal packing of parallel $Cu(pz)_2$ bundles can be subdivided into three classes: the rhombic *Cmcm* motif, as in **1**, **4a**,**c**,**d**, and α-$Ni(pz)_2$,[16] **5**; the oblique $P2_1/m$ packing (as in **3** and β-$Ni(pz)_2$,[16] **6**); and the pseudo-hexagonal *Ibam* packing found in a number of pseudo-tetrahedral metal−pyrazolates (**2**,[10] $Fe(pz)_2$,[17] $Zn(pz)_2$, and $Cd(pz)_2$[18]). Noteworthy, the isostructural $Ni(pz)_2$ phases do not show any tendency to water sorption−removal, thus suggesting that the Cu(II) ions in the square-planar environment of **3** are more acidic than the Ni(II) ones in **6**, and are, possibly, very promising catalytic sites. Such acidity is definitely absent in **2** (*the thermodynamically stable, denser, phase*), where a more isotropic distribution of ligands is found.

Preliminary magnetic measurements for species **1**, **3**, and **4** at room temperature showed values in the 1.4−1.6 μ_B range, thus

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Table 1. Synoptic Collection of $Cu(pz)_2$-Based (and related) Species, with Their Partial Crystallographic Data

species	composition	reagent[a]	reaction time	color	*a* (Å)	*b* (Å)	*c* (Å)	*β* (deg)	space group	*V* (Å^3)	ref
1	$Cu(pz)_2 \cdot H_2O$	H_2O	2 min	pink	16.96	6.24	**7.28**[b]	90	*Cmcm*	770	this work
2	α-$Cu(pz)_2$			green	7.92	11.49	**7.78**	90	*Ibam*	708	*c*
3	*β*-$Cu(pz)_2$	**1**, 130 °C		beige	9.05	**7.40**	5.60	99.5	$P2_1/m$	370	this work
4a	$Cu(pz)_2 \cdot NH_3$	NH_3	20 min	blue	17.06	6.33	**7.24**	90	*Cmcm*	783	this work
4b	$Cu(pz)_2 \cdot MeNH_2$	$MeNH_2$	3 h[d]	blue					n.a.		this work
4c	$Cu(pz)_2 \cdot MeCN$	MeCN	24 h	pink	16.06	8.23	**7.20**	90	*Cmcm*	952	this work
4d	$Cu(pz)_2 \cdot$pyridine	pyridine	24 h	blue	14.23	11.28	**7.25**	90	*Pmnm*[e]	1164	this work
4e	$Cu(pz)_2 \cdot MeOH$	MeOH	24 h	pink					n.a.		this work
4f	$Cu(pz)_2 \cdot EtOH$	EtOH	48 h	brown					n.a.		this work
5	α-$Ni(pz)_2$			yellow	16.68	6.49	**6.94**	90	*Cmcm*[f]	751	*g*
6	*β*-$Ni(pz)_2$			yellow	8.97	**6.97**	6.02	98.5	$P2_1/m$[f]	372	*g*

[a] When omitted, the starting material is **3**. [b] Bold characters refer to 2× (M···M) vectors. [c] From ref 10. [d] **3** was allowed to react with $MeNH_2$ vapors from a 2 M solution of $MeNH_2$ in THF. [e] A proper subgroup of *Cmcm*. [f] Note the isostructural features of the **1**/**5** and **3**/**6** pairs. [g] From ref 16.

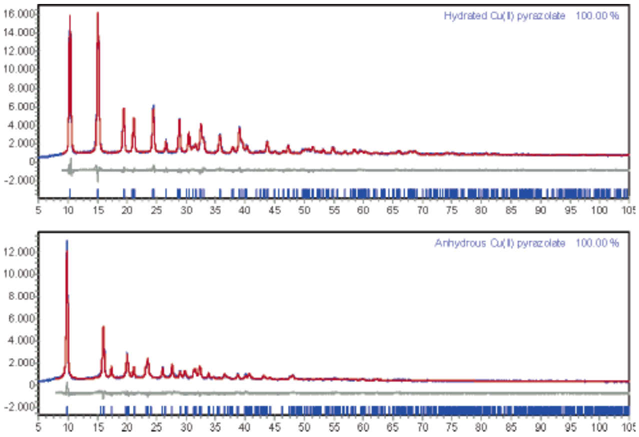

Figure 1. Rietveld refinement plots for **1** (top) and **3** (bottom), with peak markers and difference plots. Horizontal scale: 2*θ*, vertical scale, counts.

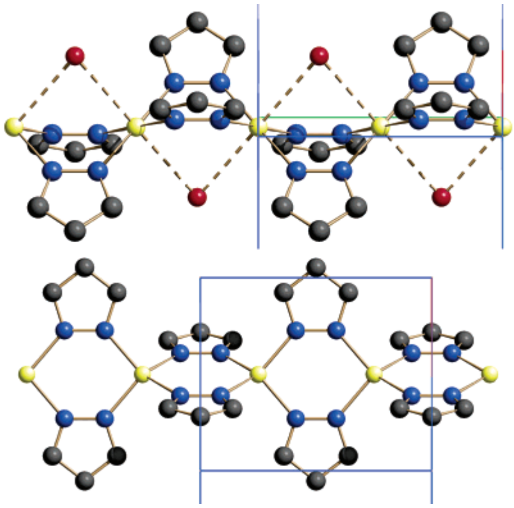

Figure 2. 1D $Cu(pz)_2$ chains in **1** (top) and **2**[10] (bottom), with a trace of their unit cells. Weakly bound H_2O molecules [Cu···O 2.913(4) Å] in red. In **1**: Cu−N 2.037(4), N−N 1.348(7), N−C1 1.368(6), C1−C2 1.381(6) Å, N−Cu−N 88.0(2)−92.0(2)°. The structure of **3** is substantially similar to that of **1**, with the obvious removal of the H_2O molecules. In **3**: Cu−N 2.00−2.07(2) Å, N−Cu−N 86.9(5)−93.1(5)°.

indicating the occurrence of weak coupling among the adjacent Cu(II) ions. Extensive structural, kinetic, catalytic, spectroscopic, and magnetic studies are underway, aiming to fully characterize the unusual properties of these systems.

Supporting Information Available: CIF files for **1** and **3**. Synthesis, spectral, and analytical data for **1**, **3**, and **4a**−**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) If other copper salts (e.g., $CuCl_2 \cdot 2H_2O$ or $CuSO_4 \cdot 5H_2O$) are employed (*in the same experimental conditions*), different species are obtained, thus indicating the templating effect of carboxylates in the formation of **1**, as if the preorganization of oligomeric species by the (typically) bridging RCO_2^- moieties favored a novel reaction path, not normally accessible if inorganic salts are used: Davey, R. J.; Allen, K.; Blagden, N.; Cross, I.; Lieberman, H. F.; Quayle, M. J.; Righini, S.; Seton, L.; Tiddy, G. J. *Cryst. Eng. Commun.* **2002**, *4*, 257.

(9) Crystal data for **1**: $C_6H_8CuN_4O$, fw 215.70 g mol^{-1}, orthorhombic, *Cmcm*, $a = 16.960(1)$, $b = 6.2360(3)$, $c = 7.2829(3)$ Å, $V = 770.3(7)$ Å^3, $Z = 4$; $\rho_{calc} = 1.859$ g cm^{-3}, μ (Cu Kα) = 36.4 cm^{-1}, $R_{wp} = 0.045$, $R_{Bragg} = 0.015$ for 4801 data collected in the 9−105° range.

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(11) Crystal data for **3**: $C_6H_6CuN_4$, fw 197.69 g mol^{-1}, monoclinic, $P2_1/m$, $a = 9.055(1)$, $b = 7.4010(6)$, $c = 5.5970(4)$ Å, $\beta = 99.476(7)°$, $V = 370.0(1)$ Å^3, $Z = 2$, $\rho_{calc} = 1.774$ g cm^{-3}, μ (Cu Kα) = 36.2 cm^{-1}, $R_{wp} = 0.056$, $R_{Bragg} = 0.014$ for 4851 data (8−105° range, $T = 130$ °C). No solvent-accessible space found (Spek, A. L. *J. Appl. Cryst*. **2003**, *36*, 7).

(12) Actually, *pure* **2** can be prepared employing freshly precipitated **4c** and slow heating to ca. 195 °C (3°/min, XRPD evidence).

(13) In a typical sorption experiment, ca. 200 mg of **1** was weighed into an open vial and deposited into a 25 mL Schlenk tube, which was then evacuated; a small amount of the reagent was then introduced through a serum cap (liquids) or a faucet (gases) and the vial occasionally shaken. Reaction times were in the minutes to days range, depending on the species (see Table 1).

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(15) Only the H_2O and NH_3 solvates were found to be stable in air at rt; the other solvates showed fast exchange (in the minutes to a few hours time scale) with air moisture, thus hampering complete (and meaningful) XRPD data collections in flat-plate configuration.

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