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Anion influences on the solid state coordination chemistry of copper–bispyrazole materials

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ABSTRACT

The reactions of the p-xylene-bridged and methylene-bridged bipyrazolyl ligands 1,4-bis[(3′,5′-dimethyl-1H-pyrazole-4′-yl)methylene]benzene ($xdpH_2$) and bis[(3′,5′-dimethyl-1H-pyrazole-4′-yl)]methane ($mdpH_2$) with the appropriate copper salt have provided eight unique members of the Cu/bipyrazole/X system with X = Cl^-, Br^-, I^- and SO_4^{2-}. The anionic component of $[Cu(xdpH_2)(H_2O)]Cl\cdot H_2O$ (**1**·H_2O) acts as a simple charge-compensating counterion. In contrast, the anionic units of $[Cu(xdpH_2)Cl_2]$·2DMF (**2**·2DMF), $[Cu(xdpH_2)Cl_2(DMF)]$·DMF (**3**·DMF), $[Cu_2(xdpH_2)_2Br_2]$ (**4**), $[Cu(mdpH_2)Br_2]$ (**5**), $[Cu_4(xdpH_2)_4I_4]$ (**6**), $[Cu_2(xdpH_2)_2(SO_4)]\cdot H_2O$ (**7**·H_2O) and $[Cu_2(xdpH_2)_2(SO_4)]\cdot 2H_2O$ (**8**·$2H_2O$) are involved in bonding to the copper sites. Compounds **1**, **4**, and **6**–**8** contain Cu(I) sites while compounds **2**, **3**, and **5** are polymers of Cu(II). Compounds **1**–**5** and **7** are one-dimensional, while **8** is two-dimensional and **6** is three-dimensional. Considering the $\{Cu_4I_4\}$ clusters of **6** as nodes, the structure is a fivefold interpenetrated framework with individual networks adopting the common $\{3^3.12^3\}$ topology in Schlafli notation.

1. Introduction

One significant focus of solid state coordination chemistry is the design of materials composed of metal or metal cluster centers connected through di- or polytopic ligands. Such materials are characterized by unique structural chemistry and applications to areas that include sorption, catalysis, optical materials and magnetism [1–8].

Through the efforts of investigators such as Yaghi [9–11], Ferey [12,13], Kitagawa [14,15], Clearfield [16] and others [17–22], metal organic frameworks constructed from polyfunctional carboxylate, polypyridyl and organophosphonate ligands have witnessed significant development. In addition to these ligand types, polyazoheteroaromatic ligands such as imidazole, pyrazole, triazole, tetrazole and their derivatives have also been exploited for their ability to bridge multiple metal sites and to provide superexchange in the design of materials with interesting magnetic properties [23–37].

In our investigations of coordination polymers, we focused on aspects of materials incorporating triazolate and tetrazolate ligands and their derivatives [38–55]. By introducing tethering groups between the azolate units, considerable flexibility in spatial dimensions, as well as a significant expansion in the structural chemistry of the coordination polymers, could be achieved (Scheme 1). Based on our observations of the structural chemistry of metal-phenyl-bis tetrazole and aminophenyl-tetrazole complexes, we expanded our investigations to the related bis-pyrazole chemistry.

The pyrazole ligand itself can act as a monodentate ligand or upon deprotonation as a monodentate or an *endo*-bidentate (η^2) or an *exo*-bidentate bridging ligand (η^1–η^1) [56–60]. The coordination chemistry of multi-dimensional structures may be expanded through the design of bitopic rod-like bispyrazoles such as 4,4′-bipyrazole, which has been used in the construction of a number of meal organic frameworks [61–71]. However, further expansion of this chemistry may be achieved by insertion of tethering groups of variable lengths and functionalities, as previously noted for tetrazole-based materials [48]. As an extension of the metal–pyrazole and metal–bispyrazole chemistry, we have investigated a series of one-, two- and three-dimensional materials of copper incorporating the methylene-[bis-(1H-pyrazol-4′-yl)]($mdpH_2$) and xylyl-[bis-(3′-5′-dimethyl-1H-pyrazol-4′-yl)] ($xdpH_2$) ligands. Since we had previously noted for the Cu/triazole/X system, where X is an anionic component such as cyanide, halide, or an inorganic oxide, that anion identity dramatically influenced the structure and properties of the composite materials, variations in anion identity for the Cu/bispyrazole/X system were explored for X = Cl^-, Br^-, I^- and SO_4^{2-}. Since the ligands may be present in the neutral form or as the deprotonated pyrazolate, reaction conditions were chosen so as to favor neutral ligand modality. Under these conditions, seven copper-based coordination polymers of $xdpH_2$ were isolated

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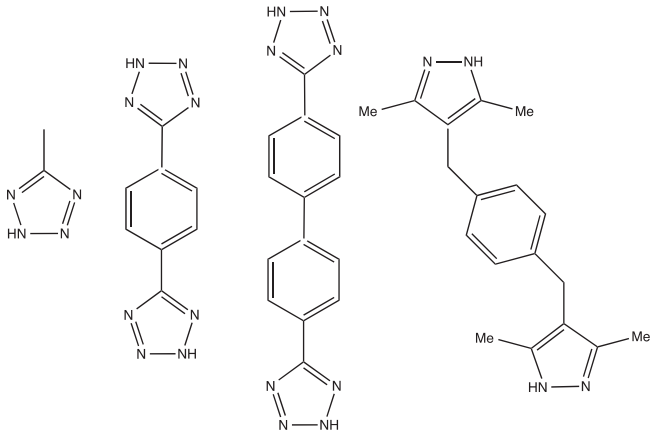

Scheme 1. The tetrazole ligand, tethered bis-tetrazole ligands and the bis-pyrazole ligand $xdpH_2$ of this study.

and structurally characterized: the one-dimensional $[Cu(xdpH_2)(H_2O)]Cl$(**1**), $[Cu(xdpH_2)Cl_2]\cdot 2DMF$ (**2**·2DMF), $[Cu(xdpH_2)Cl_2(DMF)]\cdot DMF$ (**3**·DMF), $[Cu_2(xdpH_2)_2Br_2]$ (**4**), and $[Cu_2(xdpH_2)_2(SO_4)]\cdot H_2O$ (**7**·H_2O); the two-dimensional $[Cu_2(xdpH_2)_2(SO_4)]\cdot 2H_2O$ (**8**·$2H_2O$); and the three-dimensional $[Cu_4I_4(xdpH_2)]$ (**6**). A single example incorporating the mdpH ligand, $[Cu(mdpH_2)_2Br_2]$ (**5**) was isolated.

2. Experimental

2.1. General procedures

All chemicals were used as obtained without further purification with the exception of bis-[(3′,5′-dimethyl-1H-pyrazole-4′-yl)]methane ($mdpH_2$) and 1,4-bis-[(3′,5′-dimethyl-1H-pyrazole-4′-yl)methylene]benzene ($xdpH_2$) which were synthesized in a similar fashion to the literature method [72–75]. Copper salts were purchased from Sigma–Aldrich. All syntheses were carried out in 23-mL poly(tetrafluoroethylene)-lined stainless steel containers under autogeneous pressure. The pH values of the solutions were measured prior to and after heating using pHydrion vivid 1-11® pH paper. Water was distilled above 3.0 MΩ in-house using a Barnstead Model 525 Biopure Distilled Water Center.

2.2. Synthesis of $[Cu(xdpH_2)(H_2O)]Cl\cdot H_2O$ (**1**·H_2O)

A solution of copper(II) chloride (0.064 g, 0.48 mmol), xylyl-bis(3,5-dimethylpyrazole) (0.200 g, 0.68 mmol), HF (48%, 0.1 mL) and H_2O (10.0 g, 556 mmol) in the mole ratio 1.0:1.42:5.8:1160 was stirred briefly before heating to 150 °C for 48 h. Yellow crystals of **1** were isolated in 40% yield. IR (KBr pellet, cm^{-1}): 3209 (m, N–H), 3018 (m), 2913 (m), 1578 (w, C=C + C=N), 1511(w, C=C + C=N). *Anal.* Calc. for $C_{18}H_{26}ClCuN_4O_2$: C, 50.3; H, 6.05; N, 13.0. Found: C, 50.0; H, 6.23; N, 12.9%.

Table 1
Summary of crystallographic data for the structures of $[Cu(xdpH_2)(H_2O)]Cl\cdot H_2O$ (**1**), $[Cu(xdpH_2)Cl_2]\cdot 2DMF$ (**2**·2DMF), $[Cu(xdpH_2)Cl_2(DMF)]\cdot DMF$ (**3**·DMF), $[Cu_2(xdpH_2)_2Br_2]$ (**4**), $[Cu(mdpH_2)_2Br_2]$ (**5**), $[Cu_4(xdpH_2)_4I_4]$ (**6**), $[Cu_2(xdpH_2)_2(SO_4)]\cdot H_2O$ (**7**·H_2O) and $[Cu_2(xdpH_2)_2(SO_4)]\cdot 2H_2O$ (**8**·$2H_2O$).

	1	**2**	**3**	**4**
Empirical formula	$C_{18}H_{26}ClCuN_4O_2$	$C_{24}H_{36}Cl_2CuN_6O_2$	$C_{24}H_{36}Cl_2CuN_6O_2$	$C_9H_{11}BrCuN_2$
Formula weight	429.42	575.03	575.03	290.65
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	13.388(3)	86874(7)	12.8466(5)	4.5776(6)
b (Å)	29.031(6)	8.7747(7)	14.4677(6)	9.2930(11)
c (Å)	4.771(1)	9.3138(7)	14.4823(6)	11.987(1)
α (°)	90.	87.585(1)	90.	82.200(2)
β (°)	102.010(4)	82.471(1)	94.35(1)	84.840(2)
δ (°)	90.	73.597(1)	90.	76.620(2)
V (Å^3)	1813.5(6)	675.21(9)	2683.9(2)	490.6(1)
Z	4	2	4	2
D_{calc} (g cm^{-3})	1.573	1.414	1.423	1.968
μ (mm^{-1})	1.373	1.039	1.046	6.249
T (K)	98(2)	98(2)	98(2)	98(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
R_1[a]	0.0667	0.0324	0.0319	0.0413
wR_2[b]	0.1819	0.0831	0.0829	0.1100
	5	**6**	**7**	**8**
Empirical formula	$C_{14}H_{16}Br_2CuN_8$	$C_9H_{11}CuIN_2$	$C_{36}H_{46}Cu_2N_8O_5S$	$C_{36}H_{48}Cu_2N_8O_6S$
Formula weight	519.70	337.64	829.94	847.98
Crystal system	monoclinic	tetragonal	monoclinic	orthorhombic
Space group	$P2_1/c$	$I4_1/a$	$C2/c$	$Fddd$
a (Å)	7.180(1)	15.4451(4)	17.897(3)	4.5151(5)
b (Å)	14.241(3)	15.4451(4)	17.983(3)	26.511(3)
c (Å)	8.879(2)	17.1881(9)	14.680(3)	61.100(6)
α (°)	90.	90.	90.	90.
β (°)	103.428(4)	90.	127.56	90.
δ (°)	90.	90.	90.	90.
V (Å^3)	883.1(3)	4100.2(3)	3745.6(1)	7313.5(13)
Z	2	16	4	8
D_{calc} (g cm^{-3})	1.955	2.188	1.472	1.537
μ (mm^{-1})	5.777	5.096	1.245	1.278
T (K)	98(2)	98(2)	98(2)	98(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
R_1[a]	0.0418	0.0253	0.0449	0.0629
wR_2[b]	0.0875	0.0603	0.0958	0.1554

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$.

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