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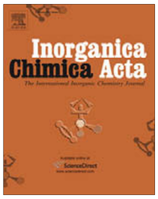

Cu/Cd heterometallic solids with the $[Cu(Hdea)(H_2dea)]_2{}^{2+}$ motif (H_2dea = diethanolamine): Exchange interactions through hydrogen bonding

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ABSTRACT

The novel hybrid composites $[Cu(Hdea)(H_2dea)]_2[CdX_4]$, X = Br (**1**), I (**2**) have been prepared in reactions of zero-valent copper with cadmium halide in air-exposed solution containing the corresponding ammonium salt and diethanolamine (H_2dea). X-ray crystallographic analysis reveals ionic solids of non-symmetric H-bonded dimeric $[Cu(Hdea)(H_2dea)]_2{}^{2+}$ cations and perhalocadmate anions. Further hydrogen bonding joins the dimers into 'zig-zag' like tetramers with copper–copper distances of about 5 Å for **1** and forms columns of the dimeric cations propagated along the *b* axis in **2** (copper–copper separations within the column are of ~4.5 and 6 Å). In the crystal structure of **1**, tetrahedral $CdBr_4{}^{2-}$ anions alternate with cationic tetramers in three dimensions, whereas $CdI_4{}^{2-}$ anions form sheets parallel to the *ab* plane in **2**. The exchange interactions between paramagnetic centres in the solid state, revealed by the triplet EPR spectra measured at X-band frequency, occur along the Cu–OH···O–Cu pathways, being mediated by hydrogen bonds established between OH and alkoxo groups of diethanolamine ligands.

1. Introduction

Hybrid composites, in which the inorganic and organic components are present as separate phases (host–guest solids, cation–anion salts), provide a basis for creating two-network materials where each network furnishes distinct physical properties [1]. Advances in preparation of organic–inorganic composites will depend on the development of convenient synthetic techniques to more effectively model these and related systems so that structural character of both components of the hybrids can reliably be controlled. Detailed studies of the intermolecular interactions present in new solids, with particular attention paid to the interphase between the two molecular networks, provide important opportunities for the development of organic–inorganic hybrid microelectronic technologies [2].

Organic–inorganic halometalate salts have attracted much attention due to interesting and potentially useful magnetic, electrical and optical properties offered by hybrid perovskite systems [3]. In organic–inorganic layer perovskites, it is generally thought that the hydrogen bonding capability of the organic (primary ammonium) cations promotes the observed structures [4]. A possible templating effect was also assigned to the entrained $[Cu(en)_2]^{2+}$ cations present in the compound $[\{Cu(en)_2\}_2Cu_7Cl_{11}]$ [5]. The proven utility of hydrothermal synthesis for incorporating organic components in composite materials has made it a routine technique in synthetic preparations of hybrid solids [6]. A number of cadmium halides charge balanced by protonated organoamines or transition-metal complex cations prepared in hydrothermal media or concentrated hydrochloric acid solution has been reported [7].

Our synthetic approach that employs inactivated metal powders and metal oxides to prepare metal complexes in mild conditions (in solution, in open air, moderate heating, normal pressure) has proven to be a powerful tool in the search for heterometallic structures with new properties [8]. The reactions of copper powder and cadmium oxide or zinc oxide and cadmium iodide with ethylenediamine and NH_4X (X = Br, I) in non-aqueous solvent afforded copper/zinc ethylenediamine-halocadmates in high yield [9]:

$$\begin{aligned} &Cu^0 + 2CdO + 2en + 4NH_4X + 1/2O_2 + Solv \\ &\quad \rightarrow [Cu(en)_2CdX_4] \cdot Solv + 4NH_3 + 2H_2O, \end{aligned} \tag{1}$$

where X = Br, I; Solv = dmso, dmf

$$\begin{aligned} &2ZnO + CdI_2 + 3en + 4NH_4I \\ &\quad \rightarrow [Zn(en)_3]_2[CdI_4]I_2 + 4NH_3 + 2H_2O \end{aligned} \tag{2}$$

The replacement of en with an amino alcohol (diethanolamine) in the reaction (1) led to the formation of a ferromagnetic compound containing tetracopper cations with bromocadmate and bromide anions and solvent molecules [10]:

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$$4\mathrm{Cu}^0 + \mathrm{CdO} + 6\mathrm{NH_4Br} + 4\mathrm{H_2dea} + 2.5\mathrm{O_2} + 3\mathrm{dmf} \rightarrow [\mathrm{Cu_4(NH_3)_4(Hdea)_4}][\mathrm{CdBr_4}]\mathrm{Br_2} \cdot 3\mathrm{dmf} \cdot \mathrm{H_2O} + 2\mathrm{NH_3} + 4\mathrm{H_2O} \quad (3)$$

The subtle interactions that control formation of compounds in such conditions and their architectural characteristics may be rationalized after the event, but can rarely be predicted in advance. Thus, under the same experimental conditions but using $\mathrm{CdX_2}$ instead of CdO, two new solids containing the H-bonded $[\mathrm{Cu(Hdea)(H_2dea)}]_2{}^{2+}$ dimers and perhalocadmate anions, $[\mathrm{Cu(Hdea)(H_2dea)}]_2[\mathrm{CdX_4}]$, X = Br (**1**), I (**2**) were isolated. In this paper the synthesis, crystal structures, EPR studies of the two compounds are described, and exchange interactions between copper centres are rationalized on the basis of the structural findings.

2. Experimental

2.1. Materials and general methods

All chemicals were of reagent grade and used as received. All experiments were carried out in air. Elemental analyses were performed by atomic absorption spectroscopy for metals by the Department of Chemistry, National Taras Shevchenko University of Kyiv and by the microanalytical service at the Faculty of Chemistry, University of Wroclaw for C, H and N. The halide contents were determined using titration with silver nitrate (Volhard method). The infrared spectra (4000–400 $\mathrm{cm^{-1}}$) were recorded on KBr pellets with a UR-10 spectrophotometer. X-band EPR spectra were recorded on a Bruker ESP 300E (Bruker, Rheinstetten, Germany) spectrometer equipped with a Bruker NMR gaussmeter ER 035M and a Hewlett–Packard microwave frequency counter HP 5350B.

2.2. Syntheses of $[\mathrm{Cu(Hdea)(H_2dea)}]_2[\mathrm{CdX_4}]$, X = Br (**1**), I (**2**)

Copper powder (0.16 g, 2.5 mmol), $\mathrm{CdBr_2 \cdot 4H_2O}$ (0.86 g, 2.5 mmol) and $\mathrm{NH_4Br}$ (0.54 g, 5 mmol) or $\mathrm{CdI_2}$ (0.91 g, 2.5 mmol) and $\mathrm{NH_4I}$ (1.45 g, 5 mmol), methanol (20 mL) and diethanolamine (1 mL) were heated to 50–60 °C and magnetically stirred in a flask until total dissolution of $\mathrm{Cu^0}$ was observed (40–60 min). After the addition of *i*-PrOH, microcrystals suitable for X-ray analysis were obtained from the resulting dark-blue solutions after 1–2 months. They were collected by filter-suction and dried *in vacuo*. Mass collected: 1.06 g, yield 42.7 (**1**); 1.8 g, yield 61.4% (**2**). *Anal.* Calc. for $\mathrm{C_{16}H_{42}Br_4CdCu_2N_4O_8}$ (977.65): C, 19.65; H, 4.33; N, 5.73; Cu, 13.00; Cd, 11.50; Br, 32.69. Found: C, 19.5; H, 4.2; N, 5.7; Cu, 12.9; Cd, 11.8; Br, 32.6%. IR (KBr pellet, $\mathrm{cm^{-1}}$): 3470br, 3145s,

Table 1
Crystallographic data and relevant data referring to the structure solution and refinement.

Compound	**1**	**2**
Empirical formula	$\mathrm{C_{16}H_{42}Br_4CdCu_2N_4O_8}$	$\mathrm{C_{16}H_{42}I_4CdCu_2N_4O_8}$
Formula weight	977.66	1165.65
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	9.374(1)	15.100(1)
b (Å)	11.826(1)	10.633(1)
c (Å)	14.428(2)	21.252(2)
α (°)	78.227(3)	90
β (°)	84.441(3)	103.095(3)
γ (°)	84.251(3)	90
U (Å^3)	1553.1(3)	3323.5(5)
Z	2	4
μ ($\mathrm{mm^{-1}}$)	7.223	5.658
Measured reflections	38279	53453
Unique reflections (R_{int})	11049 (0.065)	12030 (0.049)
Observed reflections [$I > 2\sigma(I)$]	6490	8167
Final R indices for observed reflections	R_1 = 0.0436 wR_2 = 0.0909	R_1 = 0.0292 wR_2 = 0.0552
R indices (all data)	R_1 = 0.0885 wR_2 = 0.1003	R_1 = 0.582 wR_2 = 0.0609

Table 2
Selected bond distances (Å) and angles (°) for **1**[a].

Cd–Br(1)	2.5980(6)	Cu(1)–O(13)	1.958(3)
Cd–Br(2)	2.6031(6)	Cu(1)–O(14)	2.652(3)
Cd–Br(3)	2.5964(6)	Cu(2)–N(21)	2.050(4)
Cd–Br(4)	2.5548(6)	Cu(2)–O(21)	2.547(4)
Cu(1)–N(11)	2.054(3)	Cu(2)–O(22)	1.953(3)
Cu(1)–O(11)	1.926(3)	Cu(2)–N(22)	2.037(3)
Cu(1)–O(12)	2.404(3)	Cu(2)–O(23)	1.910(3)
Cu(1)–N(12)	2.033(4)	Cu(2)–O(24)	2.564(4)
Cu(1)···Cu(2)	4.8215(9)	Cu(1)···Cu(2)^1	6.8629(3)
Cu(1)···Cu(1)^1	4.9753(9)		
Br(1)–Cd–Br(2)	109.53(2)	N(12)–Cu(1)–O(13)	84.8(1)
Br(1)–Cd–Br(3)	105.80(2)	N(12)–Cu(1)–O(14)	75.4(1)
Br(1)–Cd–Br(4)	112.72(2)	O(13)–Cu(1)–O(14)	106.2(1)
Br(2)–Cd–Br(3)	109.34(2)	N(21)–Cu(2)–O(21)	74.4(1)
Br(2)–Cd–Br(4)	107.38(2)	N(21)–Cu(2)–O(22)	84.4(1)
Br(3)–Cd–Br(4)	112.04(2)	N(21)–Cu(2)–N(22)	103.1(1)
N(11)–Cu(1)–O(11)	84.1(2)	N(21)–Cu(2)–O(23)	171.1(1)
N(11)–Cu(1)–O(12)	77.7(1)	N(21)–Cu(2)–O(24)	81.1(1)
N(11)–Cu(1)–N(12)	103.3(2)	O(21)–Cu(2)–O(22)	99.9(1)
N(11)–Cu(1)–O(13)	171.6(1)	O(21)–Cu(2)–N(22)	90.3(1)
N(11)–Cu(1)–O(14)	78.3(1)	O(21)–Cu(2)–O(23)	100.3(1)
O(11)–Cu(1)–O(12)	104.1(2)	O(21)–Cu(2)–O(24)	149.2(1)
O(11)–Cu(1)–N(12)	170.4(2)	O(22)–Cu(2)–N(22)	168.8(2)
O(11)–Cu(1)–O(13)	88.1(2)	O(22)–Cu(2)–O(23)	89.5(1)
O(11)–Cu(1)–O(14)	100.6(1)	O(22)–Cu(2)–O(24)	96.0(1)
O(12)–Cu(1)–N(12)	83.7(1)	N(22)–Cu(2)–O(23)	83.9(1)
O(12)–Cu(1)–O(13)	101.4(1)	N(22)–Cu(2)–O(24)	77.2(1)
O(12)–Cu(1)–O(14)	143.3(1)	O(23)–Cu(2)–O(24)	106.1(1)

[a] Symmetry operations: ^{1} $2 - x, 1 - y, -z$.

Table 3
Selected bond distances (Å) and angles (°) for **2**[a].

Cd–I(1)	2.7843(3)	Cu(1)–O(13)	1.936(2)
Cd–I(2)	2.8270(4)	Cu(1)–O(14)	2.907(2)
Cd–I(3)	2.7549(4)	Cu(2)–N(21)	2.030(3)
Cd–I(4)	2.7814(4)	Cu(2)–O(21)	1.942(2)
Cu(1)–N(11)	2.009(3)	Cu(2)–O(22)	2.449(2)
Cu(1)–O(11)	1.935(2)	Cu(2)–N(22)	2.020(3)
Cu(1)–O(12)	2.526(2)	Cu(2)–O(23)	1.987(2)
Cu(1)–N(12)	2.018(3)	Cu(2)–O(24)	2.539(2)
Cu(1)···Cu(2)	4.4647(5)	Cu(2)···Cu(2)^1	5.8661(6)
Cu(2)···Cu(1)^1	6.0819(5)	Cu(2)···Cu(2)^2	5.8661(6)
I(1)–Cd–I(2)	108.47(1)	N(12)–Cu(1)–O(13)	84.1(1)
I(1)–Cd–I(3)	113.35(1)	N(12)–Cu(1)–O(14)	71.33(8)
I(1)–Cd–I(4)	104.80(1)	O(13)–Cu(1)–O(14)	110.03(8)
I(2)–Cd–I(3)	107.85(1)	N(21)–Cu(2)–O(21)	86.7(1)
I(2)–Cd–I(4)	104.06(1)	N(21)–Cu(2)–O(22)	75.62(9)
I(3)–Cd–I(4)	117.66(1)	N(21)–Cu(2)–N(22)	99.9(1)
N(11)–Cu(1)–O(11)	86.8(1)	N(21)–Cu(2)–O(23)	169.0(1)
N(11)–Cu(1)–O(12)	76.2(1)	N(21)–Cu(2)–O(24)	84.35(9)
N(11)–Cu(1)–N(12)	99.6(1)	O(21)–Cu(2)–O(22)	106.28(9)
N(11)–Cu(1)–O(13)	176.0(1)	O(21)–Cu(2)–N(22)	170.9(1)
N(11)–Cu(1)–O(14)	72.8(1)	O(21)–Cu(2)–O(23)	90.16(9)
O(11)–Cu(1)–O(12)	97.87(9)	O(21)–Cu(2)–O(24)	98.26(8)
O(11)–Cu(1)–N(12)	172.8(1)	O(22)–Cu(2)–N(22)	81.58(9)
O(11)–Cu(1)–O(13)	89.58(9)	O(22)–Cu(2)–O(23)	95.18(8)
O(11)–Cu(1)–O(14)	107.82(8)	O(22)–Cu(2)–O(24)	147.03(7)
O(12)–Cu(1)–N(12)	86.92(9)	N(22)–Cu(2)–O(23)	84.51(9)
O(12)–Cu(1)–O(13)	102.58(9)	N(22)–Cu(2)–O(24)	76.34(9)
O(12)–Cu(1)–O(14)	138.04(7)	O(23)–Cu(2)–O(24)	106.60(8)

[a] Symmetry operations: ^{1} $-x, y - 1/2, 3/2 - z$; ^{2} $-x, y + 1/2, 3/2 - z$.