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Sulfadiazine/dimethylsulfadiazine transition metal complexes: Synthesis, crystal structures and magnetic properties

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ABSTRACT

Sulfadiazine (Hsulf) and dimethylsulfadiazine (Hdmsulf) were used to assemble divalent transition metal complexes (Cu, Ni or Co). Solvated complexes **1**–**4**, dinuclear **1** (Cu_2), tetranuclear **2** (Ni_4) and **3** (Co_4), and two-dimensional polymeric **4**, were synthesized by controlling the metal ions, ligands and solvents. For complex **1**, two Cu(II) ions are bridged by four N=C—N groups of four $sulf^-$ ligands, while for complex **2**, four Ni(II) ions are alternatively bridged by the pyrimidine rings of four sulfadiazine ligands, forming a neutral square Ni_4 molecule. In complex **3**, four Co(II) ions are bridged by four μ_3-OMe^- groups, yielding a Co_4O_4 cubane. Complex **4** possesses a 2D grid structure with the Co(II) ions bridged by the remote amino groups of the ligand $dmsulf^-$. Magnetic susceptibility measurements show that the desolvated complex (**1d**) exhibits antiferromagnetic coupling between adjacent Cu(II) ions with the $2J$ value of $-90.0\ cm^{-1}$, and the pyrimidine rings transmit weak antiferromagnetic coupling in complex **2**. Complex **3**·$8H_2O$ shows ferromagnetic coupling via the methoxido bridges with the bridging Co—O—Co bond angles of 96–99°. Complex **4** displays a magnetic property for mononuclear cobalt(II) complexes due to the remote separation of Co(II) ions.

1. Introduction

The single-crystal structures of mononuclear sulfadiazine (Hsulf) chelated zinc(II) or copper(II) complexes $[Zn(sulf)_2(NH_3)_2]$ [1,2] and $[Cu(sulf)_2(NH_3)_2]$ [3,4] were first reported as early as 1980s. Then the similar structures of sulfathiazole chelated zinc (II) or copper(II) complexes [5–8] were synthesized in 1990s. In 2001, a one-dimensional dimethylsulfadiazine (Hdmsulf) chelated copper(II) complex $[Cu(dmsulf)_2]\cdot 2H_2O$ [9] was first obtained. In the last decade, a large number of transition-metal complexes based on Hsulf or Hdmsulf were designed and synthesized, such as zinc [10,11], copper [12,13], cobalt [14–17], nickel [18–20] and manganese [21] complexes. It is worth mentioning that Englert and his co-workers have recently found that a coordination Zn—N bond distance in $[Zn(sulf)_2(NH_3)_2]$ obviously changed from 2.4 Å at room temperature to 2.7 Å at low temperature (100 K) [10].

The ligands Hsulf and Hdmsulf possess different coordination modes. For example, Hsulf can coordinate to one metal ion as either a monodentate ligand or a bidentate ligand. Besides, it can bridge two metal ions via pyrimidine ring, or even via remote amino group (Scheme 1). Until now, most of the Hsulf or Hdmsulf coordination complexes are mononuclear [1–4,10–21], and polynuclear [9] or high-dimensional complexes based on Hsulf or Hdmsulf were seldom reported. In this paper, we synthesized a series of dinuclear Cu(II), tetranuclear Ni(II), tetranuclear Co(II) and two-dimensional Co(II) complexes based on Hsulf or Hdmsulf, and characterized their magnetic properties.

2. Experimental

2.1. Materials and synthesis

Sulfadiazine (Hsulf), dimethylsulfadiazine (Hdmsulf), copper chloride dihydrate ($CuCl_2\cdot 2H_2O$), nickel perchlorate hexahydrate ($Ni(ClO_4)_2\cdot 6H_2O$), cobalt acetate tetrahydrate ($Co(CH_3COO)_2\cdot 4H_2O$) and sodium hydroxide (NaOH) were used as received without further purification.

2.1.1. Synthesis of $[Cu_2(sulf)_4]\cdot x$ solvents (**1**)

$CuCl_2\cdot 2H_2O$ (17.0 mg, 0.10 mmol) was dissolved in CH_3CN (4 mL)/H_2O (1 mL), put in one side of an H-tube. Hsulf (50.0 mg, 0.20 mmol) and NaOH (8.0 mg, 0.20 mmol) were dissolved in CH_3CN (4 mL)/H_2O (1 mL), and the solution was put in the other side of the H-tube. The two solutions were connected with CH_3CN.

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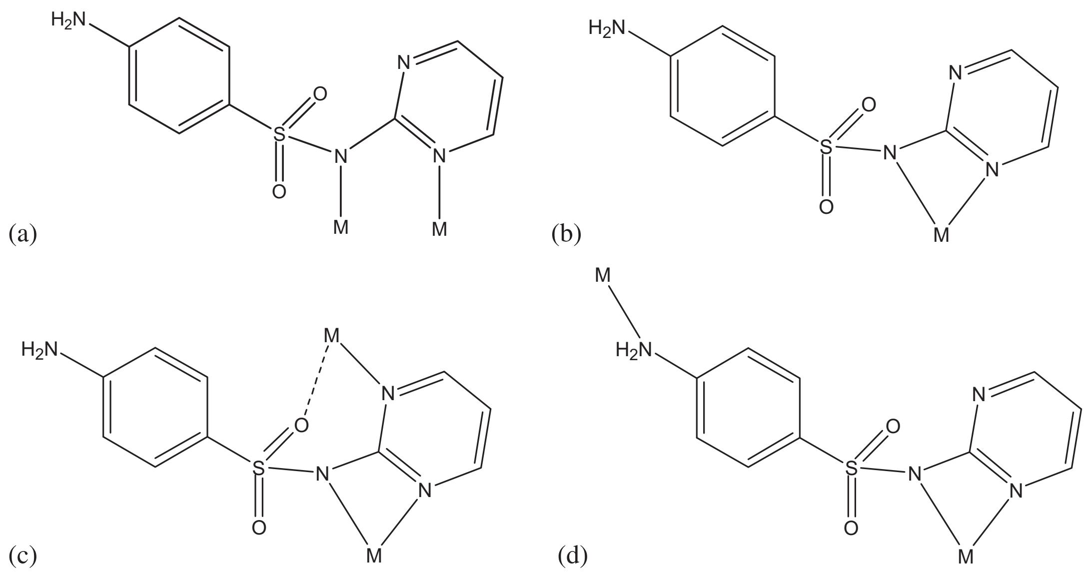

Scheme 1. Coordination modes of Hsulf.

Several days later, black crystals of **1** were obtained. Yield: ca. 20%. The black crystals of **1** were rapidly effloresced in the air, with all solvents taken off, affording desolvated complex **1d**. Main IR bands (cm^{-1}) for complex **1d**: 3449; 3368; 3239; 1634; 1591; 1552; 1503; 1455; 1424; 1278; 1183, ν(S=O); 1127, ν(S=O); 1081; 1017; 1005; 970; 853; 795; 715; 703; 679; 652; 579; 557; 525. *Anal.* Calc. (Found) % for complex **1d**: C, 42.58 (42.93); H, 3.57 (3.07); N, 19.86 (19.64).

2.1.2. Synthesis of $[Ni_4(sulf)_8]\cdot 14H_2O$ (2)

$Ni(ClO_4)_2\cdot 6H_2O$ (36.6 mg, 0.10 mmol) was dissolved in C_2H_5OH (4 mL)/H_2O (1 mL), located at one side of an H-tube. Hsulf (50.0 mg, 0.20 mmol) and NaOH (8.0 mg, 0.20 mmol) were dissolved in C_2H_5OH (4 mL)/H_2O (1 mL), located at the other side of the H-tube. The two sides of H-tube were connected with C_2H_5OH. Several weeks later, blue-green crystals of **2** were obtained. Yield: ca. 20%. The lattice solvents were determined by elemental analysis. Main IR bands (cm^{-1}) for complex **2**: 3358 (br); 2924; 1626; 1596; 1569; 1503; 1450; 1418; 1362; 1271; 1184, ν(S=O); 1139, ν(S=O); 1121; 1091; 1072; 1034; 1015; 991; 832; 798; 681; 586; 554; 523. *Anal.* Calc. (Found) % for complex **2**: C, 38.73 (38.82); H, 4.06 (3.85); N, 18.07 (17.75).

2.1.3. Synthesis of $[Co_4(sulf)_4(OCH_3)_4(CH_3OH)_4]\cdot 4.75CH_3OH$ (3)

$Co(CH_3COO)_2\cdot 4H_2O$ (24.9 mg, 0.10 mmol) was dissolved in CH_3OH (5 mL), located at one side of an H-tube. Hsulf (50.0 mg, 0.20 mmol) and NaOH (8.0 mg, 0.20 mmol) were dissolved in CH_3OH (5 mL), located at the other side of the H-tube. The two sides of H-tube were connected with CH_3OH. Two weeks later, red crystals of **3** were obtained. Yield: ca. 10%. The red crystals of **3** were rapidly effloresced in the air, losing the methanol solvents. The powdered sample absorbed water in the air, affording hydrated complex **3**$\cdot 8H_2O$. Main IR bands (cm^{-1}) for complex **3**$\cdot 8H_2O$: 3382(br); 2928; 2826; 1629, 1596; 1586; 1556; 1503; 1446; 1416; 1356; 1268; 1248; 1183, ν(S=O); 1132, ν(S=O); 1077; 1020; 986; 802; 719; 684; 586; 557; 530. *Anal.* for complex **3**$\cdot 8H_2O$, Calc. (Found) %: C, 35.21 (35.31); H, 4.30 (4.20); N, 14.93 (14.75).

2.1.4. Synthesis of $[Co(dmsulf)_2]\cdot CH_3OH$ (4)

$Co(CH_3COO)_2\cdot 4H_2O$ (24.9 mg, 0.10 mmol) was dissolved in CH_3OH (5 mL), located at one side of an H-tube. Hdmsulf (55.7 mg, 0.20 mmol) and $N(C_2H_5)_3$ (21 μL, 0.15 mmol) were dissolved in CH_3OH (5 mL), located at the other side of the H-tube. The two sides of H-tube were carefully connected with CH_3OH. A week later, purple crystals of **4** were obtained. Yield: ca. 30%. Main IR bands (cm^{-1}) for complex **4**: 3450; 1627; 1599; 1586; 1557; 1498; 1439; 1398; 1378; 1344; 1263; 1183; 1143; 1126; 1079; 1033; 1012; 979; 872; 836; 793; 740; 716; 668; 597; 547. *Anal.* Calc. (Found) % for complex **4**: C, 46.51 (46.80); H, 4.68 (4.71); N, 17.36 (17.17).

2.2. Physical measurements

Single crystal X-ray data were collected on a Rigaku Saturn724+ (2×2 bin mode), Rigaku R-AXIS RAPID IP and Bruker AXS area detector diffractometer. The structures were solved by direct method SHELXS-97 and refined by full-matrix least-squares (SHELXL-2013) on F^2. Hydrogen atoms were added geometrically and refined using a riding model. Due to the serious disorder of the lattice solvents, the SQUEEZE command was used to determine the main structure of complexes **1** and **2**.

IR spectra were performed on Nicolet 7199B infrared spectrometer in the 4000–450 cm^{-1} region, KBr pellet. C, H, N Elemental analyses were characterized on elemental analyzer Elementar Vario EL. Temperature- and field-dependent magnetic susceptibility measurements were carried out on a Quantum Design MPMS SQUID magnetometer from 300 K decreasing to 2 K. Air-dried samples of complexes **1d**, **2**, **3**$\cdot 8H_2O$ and **4** were collected and used for magnetic measurements. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's Tables).

3. Results and discussion

3.1. Synthesis and IR spectra

The direct reaction of the solutions of $CuCl_2\cdot 2H_2O$, $Ni(ClO_4)_2\cdot 6H_2O$ or $Co(CH_3COO)_2\cdot 4H_2O$ with Hsulf/Hdmsulf in the presence of NaOH resulted in rapid precipitation of fine powder. The single crystals of complexes (**1**–**4**) were obtained by slow diffusion of two reaction solutions. The alkali NaOH or $N(C_2H_5)_3$ was exhausted by neutralization of Hsulf/Hdmsulf, yielding complexes **1**–**4** by self