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Framework Coordination Polymer Based on the $[Re_3Mo_3S_8(CN)_6]^{6-}$ Heterometallic Cluster Anions and Cd^{2+} Cations

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Abstract—A new coordination polymer, $[Cd(NH_3)_4]_2\{Cd[Re_3Mo_3S_8(CN)_6]\}\cdot 1.5H_2O$ (**I**), was prepared by the reaction between solutions of $Cd(CH_3COO)_2 \cdot 2H_2O$ in aqueous ammonia and $CaK_4[Re_3Mo_3S_8(CN)_6] \cdot 8H_2O$ in water. The crystals are cubic, space group $Fm\bar{3}m$ (Prussian blue structural type); $a = 15.0268(4)$ Å (CIF file CSD no. 431555). According to ESR data, compound **I** is paramagnetic, g-factor is 2.298. Thermal stability investigation by TGA and powder X-ray diffraction showed that elimination of coordinated NH_3 molecules is accompanied by sample amorphization.

Keywords: rhenium, cluster complex, coordination polymer, structure, thermal stability
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INTRODUCTION

The synthesis and investigation of coordination polymers is a vigorously developing research areas of inorganic chemistry during the last decades [1–5]. Compounds with a 3D framework occupy a special place among coordination polymers owing to their thermal and chemical stability and a number of promising properties such as catalysis [6–8], reversible sorption of gases [9–11], and luminescence [12–14]. Mono- and polynuclear transition metal cyano complexes are well known to be suitable as building blocks for the synthesis of framework compounds via coordination to *d*- and *f*-metal cations [15, 16]. One class of framework cyanometallates is known as the Prussian blue type, named after the inorganic pigment existing as two forms, the soluble $KFe^{III}[Fe^{II}(CN)_6] \cdot H_2O$ and insoluble $Fe_4^{III}[Fe^{II}(CN)_6]_3 \cdot H_2O$ ones [17]. The structure of the Prussian blue type compounds can be represented as alternation of octahedrally coordinated units linked by CN groups. This gives rise to a framework with cubic symmetry.

Previously, it was shown that the octahedral transition metal cluster complexes with terminal cyano groups can form coordination polymers, like mononuclear cyano complexes [18–20]. Provided the structural type is retained, the replacement of relatively small mononuclear fragments by large cluster anions usually results in increasing unit cell parameters, which enhances the porosity of the compounds. For the Prussian blue type compounds, the possibility to replace the $[Fe(CN)_6]^{4-}$ group by octahedral cluster anions was demonstrated for $[Re_6Q_8(CN)_6]^{4-}$ [21, 22], $[Nb_6Cl_{12}(CN)_6]^{4-}$ [23], and $[Nb_6Cl_9O_3(CN)_6]^{5-}$ [24].

A recent study of rhenium molybdenum heterometallic chalcogenide clusters resulted in the preparation of a new octahedral cyano cluster anion, $[Re_3Mo_3S_8(CN)_6]^{6-}$ [25], which had 23 cluster valence electrons and was paramagnetic. In combination with the easy preparation and stability, this makes this anion a good building block for the synthesis of coordination polymers. The first studies have demonstrated that the $[Re_3Mo_3S_8(CN)_6]^{6-}$ cluster anion reacts with cationic Zn^{2+} ammonia complexes to give the compound $[Zn(NH_3)_4]_8\{Zn[Re_3Mo_3S_8(CN)_6]_3\} \cdot 8H_2O$, which crystallizes as a new structural type, anti-Prussian blue [26]. The evaporation of ammonia from this compound induces an irreversible structure rearrangement to give the salt $[Zn(NH_3)_4]_2\{Zn[Re_3Mo_3S_8(CN)_6]\} \cdot 2H_2O$, which crystallizes as the Prussian blue structural type.

In this communication, we report the synthesis and X-ray diffraction and thermogravimetric investigations of a new Prussian blue type compound, $[Cd(NH_3)_4]_2\{Cd[Re_3Mo_3S_8(CN)_6]\} \cdot 1.5H_2O$ (**I**).

EXPERIMENTAL

The starting cluster anion salt, $CaK_4[Re_3Mo_3S_8(CN)_6] \cdot 8H_2O$, was prepared by a known procedure [25]. The other reagents were commercial chemicals.

The IR spectra were measured for the powders pressed with KBr on a Bruker Scimitar FTS 2000 spectrometer in the 4000–375 cm^{-1} range. Energy dispersive analysis (EDS) was carried out using a Hitachi TM-3000 electron microscope equipped with a Bruker Nano analyzer. The ESR spectra of powdered samples were measured on a Varian E-109 EPR spectrometer in the X-range at 300 K. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was used as the reference with $g = 2.0036$. Powder X-ray diffraction patterns were measured on a Philips PW 1820/1710 diffractometer (FeK_{α} radiation, graphite monochromator, Si as the external reference). Thermal analysis was performed on a Netzsch TG 209 F1 Iris thermal analyzer in a He flow (80 cm^3 min^{-1}) at a heating rate of 10 K min^{-1}.

Synthesis of complex I. A solution of $Cd(OAc)_2 \cdot 2H_2O$ (100 mg, 0.373 mmol) in concentrated aqueous ammonia was mixed with an aqueous solution of $CaK_4[Re_3Mo_3S_8(CN)_6 \cdot 8H_2O$ (100 mg, 0.062 mmol). The brown precipitate that formed was separated by centrifuging, washed with water, and dried in air. The yield was 90 mg (82%). EDS: found Cd : Re : Mo : S = 3.1 : 3.1 : 2.9 : 7.8. The powder X-ray diffraction pattern was identical to that calculated for **I** with the unit cell parameter $a = 14.950(3)$ Å. The single crystals for X-ray diffraction were obtained by layering, in a narrow tube, a solution of $Cd(OAc)_2 \cdot 2H_2O$ in concentrated ammonia onto a solution of $CaK_4[Re_3Mo_3S_8(CN)_6] \cdot 8H_2O$ in dilute aqueous ammonia. After several days, brown-colored cubic crystals appeared on the tube walls.

Single crystal X-ray diffraction. The single crystal X-ray diffraction data for **I** were collected at 150 K by a standard procedure on a Bruker Apex II Duo automated diffractometer (2D CCD array detector, 150 K, MoK_{α}, $\lambda = 0.71073$ Å, graphite monochromator). The absorption corrections were applied empirically from the equivalent reflection intensities (SADABS) [27]. The structure of **I** was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms (SHELX-2007) [28]. The hydrogen atoms of ammonia were localized geometrically and refined in the riding model. The hydrogen atoms of the water molecules of crystallization were not located. According to EDS data, the metal site occupancies in the cluster core were specified as 50% Mo + 50% Re. The rhenium and molybdenum coordinates and thermal parameters were specified by the EXYZ and EADP instructions.

Crystallographic data: cubic system, space group $Fm\bar{3}m$, $Z = 4$, $a = 15.0268(11)$ Å, $V = 3393.1(4)$ Å^3, ρ(calcd.) = 3.391 g/cm^3, $\mu = 14.082$ mm^{-1}. Crystal size: 0.012 × 0.012 × 0.012 mm. Altogether 14421 reflections were measured (θ from 2.35° to 35.13°), of which 434 were independent and 428 were observable ($I \geq 2\sigma(I)$). The final *R*-factors were $R_1 = 0.0356$, $wR_2 = 0.0918$ for observable reflections and $R_1 = 0.0359$, $wR_2 = 0.0920$ for all independent reflections. The *S*-factor on F^2 was 1.079.

The crystallographic data for **I** were deposited in the inorganic database (Crystal Structure Depot, CSD no. 431555 and can be obtained at URL http://www.fiz-karlsruhe.de/obtaining_crystal_structure_-data.html).

RESULTS AND DISCUSSION

Compound **I** was prepared by the self-assembly reaction between the $[Re_3Mo_3S_8(CN)_6]^{6-}$ cluster anions and Cd^{2+} cations. The independent part of the unit cell comprises one Re/Mo position (coordinates (*x*, 0, 0), 4*m.m* symmetry), one S position (special position), one CN group (C and N coordinates (*x*, 0, 0), 4*m.m* symmetry), framework Cd atom (coordinates (0, 0, 0), $m\bar{3}m$ symmetry), Cd atom of the $[Cd(NH_3)_4]^{2+}$ cation (coordinates (1/4, 1/4, 1/4), $\bar{4}3m$ symmetry), N atom of the NH_3 molecule (special position), and O atom of the H_2O solvation molecule (coordinates (1/4, 0, 1/4), *m.mm* symmetry). The structure of the $[Re_3Mo_3S_8(CN)_6]^{6-}$ cluster anion resembles the structures of the other cyano clusters $[M_6(\mu{-}Q)_8(CN)_6]^{n-}$. The high lattice symmetry leads to a non-distorted octahedral Re_3Mo_3 core in which the Re and Mo atoms are statistically disordered. The M–M distances (2.6357(8)Å) are correlated with the values for previously studied compounds with this cluster anion [25, 26]. The metal core is surrounded by a cube formed by eight bridging S atoms (M–S, 2.427(2) Å). In addition, each metal atom is coordinated to the carbon atom of the terminal CN group (M–C, 2.144(13) Å). Nitrogen of each CN group is coordinated to Cd (Cd–N(CN), 2.339(12) Å), which gives rise to a nearly linear Cd–NC–M group. The Cd atom is also coordinated to six CN groups of different cluster anions, thus forming the Prussian blue type framework (Fig. 1). The structure contains one more Cd^{2+} cation coordinated to four NH_3 molecules (Cd–N, 2.265(12) Å), thus forming a tetrahedral $[Cd(NH_3)_4]^{2+}$ cation located in the structure cavity.

As shown previously, the reaction of the cluster anion and Zn^{2+} cation under similar conditions affords the phase of $[Zn(NH_3)_4]_8\{Zn[Re_3Mo_3S_8(CN)_6]_3\} \cdot 8H_2O$ (**II**), which crystallizes as a new structural type, "anti-Prussian Blue." A typical feature of this structural type is the presence of cluster anions linking the octahedrally coordinated Zn^{2+} units, whereas in the case of cluster-based coordination polymers, the opposite situation is generally observed [26]. The compound is unstable outside the mother liquor and collapses as

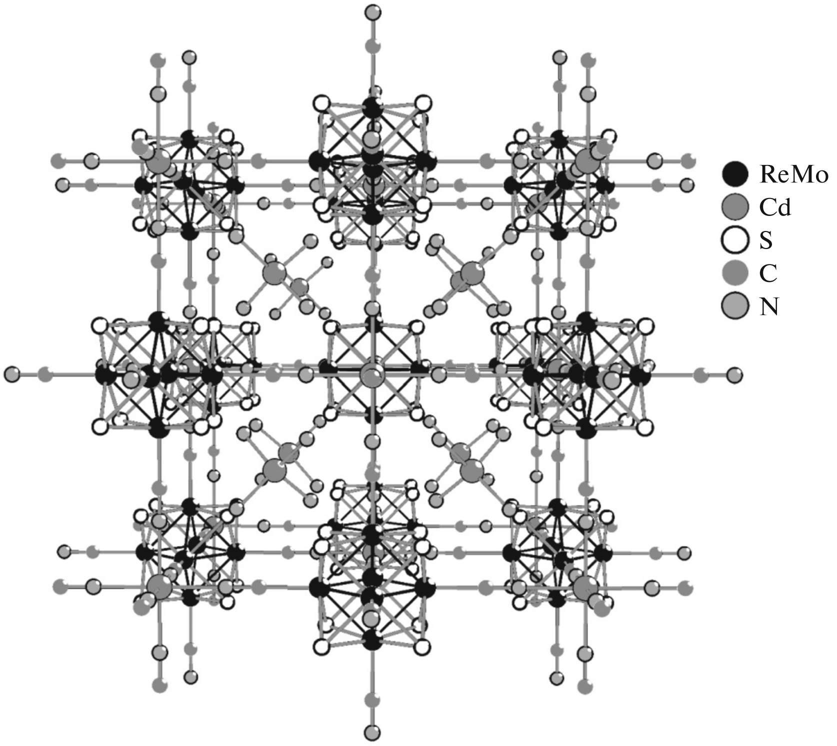

Fig. 1. Structure packing of compound **I**. The H atoms of ammonia and the water molecule of crystallization are omitted.

ammonia is evaporated, resulting in the formation of a classical Prussian blue type structure. In the reaction with Cd^{2+} cations, no formation of other phases besides **I** was detected, which implies that an "anti-Prussian blue" structure with Cd^{2+} cations is unstable. This may be attributable to a large ionic radius of Cd^{2+} and, as a consequence, large unit cell parameter.

The structure of the products of self-assembly of coordination polymers often depends considerably on the reaction conditions. As can be seen from the powder X-ray diffraction data (Fig. 2), in the case of compound **I**, slow mixing of the reactants during layering yields the same phase as fast mixing of solutions. Both phases have the same measured *g*-factor of 2.298. Therefore, the powder of compound **I** can be easily obtained on a preparative scale and studied. An important characteristic of any framework compound is stability upon thermal elimination of the solvent molecules from the framework cavities. Thermogravimetric analysis of a powder of **I** (Fig. 3) demonstrated that all eight NH_3 molecules are removed from the framework in the temperature range of 25–120°C; this corresponds approximately to the loss of 7.5% of the sample weight. The further decrease in the weight by 4.25% in the 120–250°C range indicates the loss of four H_2O molecules per formula unit. The X-ray diffraction study detected only 1.5 H_2O molecules per formula unit; however, additional molecules can occur in partially occupied positions in the cavities. Above 250°C, decomposition of the cluster anion starts; it is accompanied by gradual weight loss up to 900°C, the maximum weight loss rate being observed at 560°C. A powder X-ray diffraction pattern of **I** annealed in an Ar flow at 120°C for 30 min is shown in Fig. 4. It can be seen that removal of ammonia results in the broadening and decrease in intensity of reflections, especially in the long-range region. This attests to disruption of the long-range order and amorphization of the sample at temperatures slightly above 100°C.

Thus, a new compound with a Prussian blue type framework structure was prepared and characterized by single crystal and powder X-ray diffraction and ESR. By powder X-ray diffraction and thermal analysis, it was shown that the compound framework has low stability and already loses crystallinity at 120°C as a result of elimination of coordinated NH_3 molecules.

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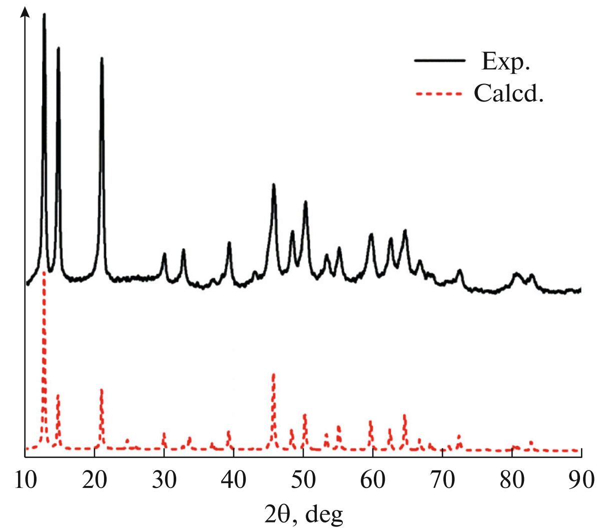

Fig. 2. Experimental powder X-ray diffraction pattern of **I** prepared by mixing of reactant solutions (continuous line) in comparison with the simulated pattern based on the single crystal structure (dashed line).

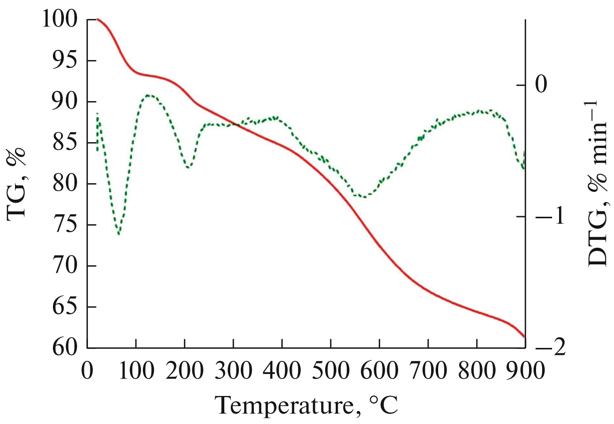

Fig. 3. Thermal analysis curves of compound **I**.

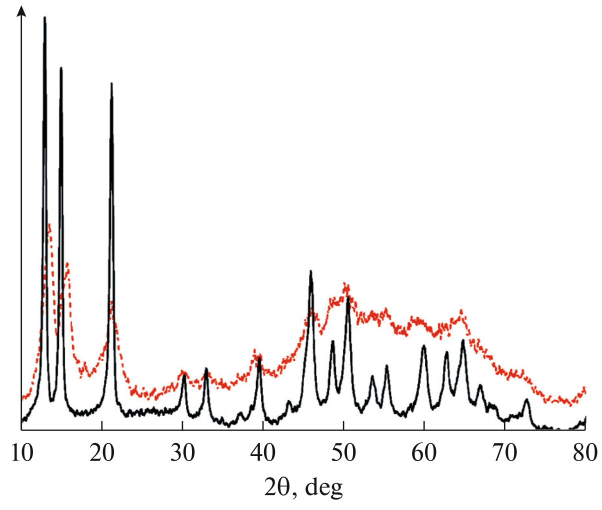

Fig. 4. Powder X-ray diffraction patterns of **I** before annealing (continuous line) and after annealing at 120°C for 30 min (dashed line).

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