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Synthesis and Characterization of a New Cadmium Framework Based on 2,5-Dimethyl-1,3,4-Thiodiazole and Dicyanamide Anion

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RESEARCH ARTICLE

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ABSTRACT

Using the 2,5-dimethyl-1,3,4-thiodiazole (L) ligand and bridging dicyanamide anion, a new Cd^{II} complex [Cd_{0.5}(L)(H₂O)(cyanourea)] [Cd(N(CN)₂(H₂O)]_n (**1**) has been synthesized and characterized by X-ray single crystal diffraction. The fundamental structural unit of the title complex contains two Cd^{II} centers, two neutral free L ligands, two bridging dca anions, one bridging cyanourea ligand and three terminal coordinated aqua molecules. It is noted that the cyanourea ligands are not used as the starting materials and formed from dicyanamide simply by hydrolysis. To the best of our knowledge, cyanourea represents the first example to participate in the coordination of metal ions in coordination chemistry up to now.

INTRODUCTION

In recent years, great interest has been shown in transition metal dicyanamide (dca) coordination polymers because of their novel structural topologies and interesting magnetic properties^[1-19]. A versatile ligand, dca can act in mono-, bi- ($\mu_{-1,3}$ and $\mu_{-1,5}$) and tri- ($\mu_{-1,3,5}$) dentate coordination modes to bridge transition metal ions to form various networks with different magnetic properties. Although there are several examples with only dca as bridges, most of them containing other co-ligands to form the framework structure. These co-ligands are very important since not only they can influence the structures of the framework, they can also play a role in the magnetic coupling in some cases. When co-ligands were introduced, a large number of novel networks have been obtained and characterized. 1,2,4-Triazole and its derivatives are very interesting ligands because they combine the coordination geometry of both pyrazole and imidazole with regard to the arrangement of their three heteroatoms. In our previous studies, a series of new functional complexes were formed based on 1,2,4-triazole bridging ligands and its derivatives, which have the potential possibility of coordinating with metal ions to fulfill the coordination requirements of clusters^[20-28]. These coordination polymers varying from one- three-dimensional have been formed via triazole-bridged trinuclear Cd^{II}, Cu^{II}, Ni^{II} and tetranuclear Ag^I clusters as second building units (SBUs). Because both these N,N'-linkage ligands such as 1,2-diazoles and 1,2,4-triazoles are very versatile ligands that are able to connect a wide range of inter-metallic separations through two close adjacent N donors^[29,30]. In recent reports, we employ 2,5-dimethyl-1,3,4-thiodiazole (L) as building block to obtain a series of Ag^I, Cu^{II}, Ni^{II} complexes^[20]. As a continuation of our systematic contribution on this interesting subject, with the help of L and bridging ligands dicyanamide anions, a new Cd^{II} coordination polymer [Cd_{0.5}(L)(H₂O)(cyanourea)][Cd(N(CN)₂(H₂O)]_n (**1**) was isolated and its crystal structure was determined via single-crystal X-ray diffraction. Photo-luminescent results of complex **1** exhibit strong fluorescent emission bands in the solid state and in solution at ambient temperature.

EXPERIMENTAL

Materials and synthesis

All the starting reagents and solvents were commercially available and used without further purification. Analyses for C, H, and N were carried out with a Perkin-Elmer analyzer. IR spectra were measured on a TENSOR 27 OPUS (Bruker) FT-IR spectrometer using KBr pellets in the 4000-400 cm^{-1} range.

Preparation of 1: A mixture of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0419 g, 0.1 mmol) and L (0.0114 g, 0.1 mmol) was stirred for ca. 30 min in H_2O (10 mL). Then, $\text{NaN}(\text{CN})_2$ (0.0178 g, 0.2 mmol) in water (10 mL) was added slowly to the above solution with further stirring for 30 min, and the resultant colorless solution was filtered at room temperature. Block colorless single-crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvents after two months. The yield was 60% based on L. Anal. Calc. for $\text{C}_{10}\text{H}_{12}\text{Cd}_{1.5}\text{N}_{11}\text{O}_3\text{S}$ (534.96): C, 22.45; H, 2.26; N, 28.80%. Found: C, 22.38; H, 2.20; N, 28.86%. **FT-IR** (KBr): $\tilde{\nu}$ =3015 (w), 2245 (s), 1611 (s), 1389 (m), 1290 (s), 807 (s), 570 (m) cm^{-1} .

Caution: Although no problems were encountered in this study, transition-metal perchlorate complexes are potentially explosive and should be handled with proper precautions.

X-Ray crystallography and structure solution

Determination of the unit cell and data collection were performed on an APEX II CCD area detector equipped with a graphite crystal monochromated Mo-K α radiation ($k=0.71073 \text{ \AA}$) at 293(2) K with crystal size 0.18 mm \times 0.17 mm \times 0.16 mm. Semi-empirical absorption corrections were applied using the SADABS program. The structures of complexes were solved by direct methods and successive Fourier difference syntheses (SHELXS-97) [31,32]. Hydrogen atoms were generated geometrically and initially located in a difference Fourier map. The final agreement factor values are $R_1=0.0220$, $\omega R_2=0.0578$ ($I>2\sigma$), $R_1(F_o)=\sum ||F_o|-|F_c||/|F_o|$, $\omega R_2(F_o^2)=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. Further details of the structure analysis of complex **1** are given in **Table 1**. CCDC reference number 999732 (**1**) contains the supplementary crystallographic data. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

Table 1. Crystallographic data and structure refinement summary for complex **1**. a: $R=\sum ||F_o|-|F_c||/|F_o|$; b: $\omega R=[\sum w(|F_o|^2-|F_c|^2)^2/\sum w|F_o|^2]^{1/2}$.

	1
Formula	$\text{C}_{10}\text{H}_{12}\text{Cd}_{1.5}\text{N}_{11}\text{O}_3\text{S}$
M (g mol ⁻¹)	534.97
Crystal system	Triclinic
Space group	P-1
Temperature	173(2)
a (Å)	8.3989(7)
b (Å)	9.9601(8)
c (Å)	10.8284(9)
α (°)	86.054(2)
β (°)	85.5370(10)
γ (°)	86.9540(10)
V (Å ³)	899.91(13)
Z	1
F(000)	522
ρ_{calc} (Mg m ⁻³)	1.974
μ (mm ⁻¹)	1.942
Data/restraints/params	3156/0/243
GOF on F ²	1.057
R_1^a ($I = 2\sigma(I)$)	0.0216
ωR_2^b (all data)	0.0512

RESULTS AND DISCUSSION

Structural description of $[\text{Cd}_{0.5}(\text{L})(\text{H}_2\text{O})(\text{Cyanourea})][\text{Cd}(\text{N}(\text{CN})_2(\text{H}_2\text{O}))_N]_N$ (**1**)

Complex **1** crystallizes in the triclinic crystal system with P-1 space group. As shown in **Figure 1**, one of the two crystallographically independent Cd cations is located on a center of inversion, whereas the second obviously occupy a general position. The fundamental structural unit of **1** contains two Cd^{II} centers (Cd1 and Cd2), two neutral free L ligands, two bridging dca anions, one bridging cyanourea ligand and three terminal coordinated aqua molecules. It is noted that the cyanourea ligands are not used as the starting materials and formed from dicyanamide simply by hydrolysis. To the best of our knowledge, cyanourea represents the first example to participate in the coordination of metal ions in coordination chemistry up to now. In **1**, Cd1 is coordinated with four nitrogen atoms, two of which come from two cyanourea ligands (N9 and N9A), and the others from two L

ligands. Two oxygen atoms from two water molecules complete a distorted octahedral geometry. Cd2 is also six-coordinate with four nitrogen atoms from four dca ligands (N3, N5A, N6 and N8A). One nitrogen atom of cyanourea ligand and one oxygen atom from one aqua ligand are involved in the coordination of Cd^{II} to constitute CdN₅O donor set. All the Cd-N bond lengths and Cd-O bond lengths fall into the normal range. 1D double chain connects Cd^{II} center ions to 2D layer through cyanourea ligand, as illustrated in **Figure 2**. Selected bond lengths and angles for complex **1** are presented in **Table 2**.

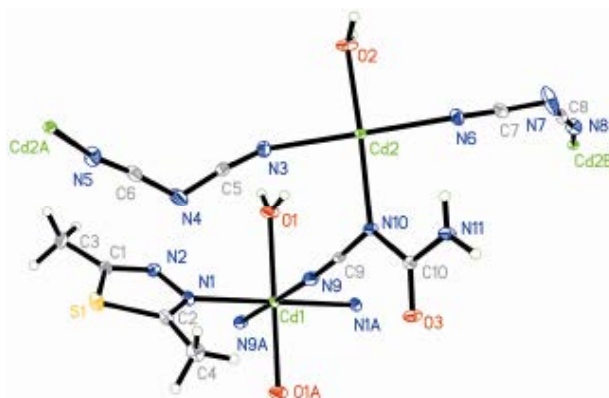


Figure 1. The fundamental structural unit of **1**.

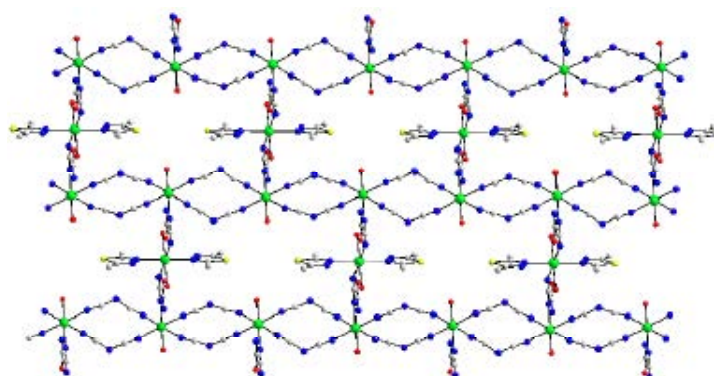


Figure 2. The 2D layer structure of **1** containing a 1D [Cd(dca)₂] chains. Green, Cd; red, O; gray, C; blue, N; yellow, S.

Table 2. Selected bond lengths/Å and angles/° for **1**. Symmetry transformations used to generate equivalent atoms: #1 -x + 2, -y + 2, -z; #2 -x + 1, -y + 1, -z; #3 -x + 1, -y + 2, -z + 1.

Cd(1)-N(9)#1	2.249(2)	Cd(1)-O(1)	2.339(2)	Cd(1)-N(1)	2.345(2)
Cd(2)-O(2)	2.2578(18)	Cd(2)-N(5)#2	2.283(2)	Cd(2)-N(6)	2.309(2)
Cd(2)-N(3)	2.386(3)	N(9)#1-Cd(1)-N(9)	180.0	N(9)#1-Cd(1)-O(1)	98.39(8)
N(9)-Cd(1)-O(1)	81.61(8)	N(9)-Cd(1)-O(1)#1	98.39(8)	N(9)#1-Cd(1)-N(1)	90.15(8)
N(9)-Cd(1)-N(1)	89.85(8)	O(1)-Cd(1)-N(1)	87.68(8)	O(1)#1-Cd(1)-N(1)	92.32(8)
N(9)#1-Cd(1)-N(1)#1	89.85(8)	N(9)-Cd(1)-N(1)#1	90.15(8)	O(1)-Cd(1)-N(1)#1	92.32(8)
O(1)#1-Cd(1)-N(1)#1	87.68(8)	O(2)-Cd(2)-N(5)#2	87.36(8)	O(2)-Cd(2)-N(6)	90.85(8)
N(5)#2-Cd(2)-N(6)	93.70(9)	O(2)-Cd(2)-N(8)#3	86.66(8)	N(5)#2-Cd(2)-N(8)#3	172.12(9)
N(6)-Cd(2)-N(8)#3	91.51(8)	O(2)-Cd(2)-N(10)	174.65(7)	N(5)#2-Cd(2)-N(10)	96.82(8)
N(6)-Cd(2)-N(10)	92.20(8)	O(2)-Cd(2)-N(3)	87.60(8)	N(5)#2-Cd(2)-N(3)	89.57(9)
N(6)-Cd(2)-N(3)	176.32(8)	N(8)#3-Cd(2)-N(3)	85.07(9)	N(10)-Cd(2)-N(3)	89.09(8)

Luminescent properties

Inorganic-organic hybrid coordination polymers have been investigated for fluorescent properties and for potential applications as luminescent materials, such as light-emitting diodes [33]. Owing to their ability to affect the emission wavelength and strength of organic materials, the syntheses of inorganic-organic coordination polymers by the judicious choice of conjugated organic spacers and transition-metal centers can be an efficient method for obtaining new types of photo-luminescent materials, especially for d¹⁰ systems [34]. Because complex **1** are air stable and can retain their structural integrity at room temperature for a considerable length of time and are insoluble in common organic solvents, however they are very soluble in DMSO solutions. Therefore in the present work, the luminescent properties of complex **1** in the solid state and in DMSO solutions have been investigated.

In the solid state, the emission spectra are shown in **Figure 3**, complex **1** exhibit strong fluorescent emissions with a broad emission maximum at 430 nm. Compared with the fluorescent emission of L in the solid state [20], the emission band of **1** is blue-shifted. As is discussed in the previous literature [35], a wide range of π-conjugated organic molecules are commonly used as linkers due to their rigidity, and the majority of them are based on rigid backbones functionalized with multi-carboxylate groups

or heterocyclic groups for metal ligand coordination. Usually, the fluorescence emission from organic ligands is similar to their emission behavior in solution, corresponding to the transition from the lowest excited singlet state to the singlet ground state, and the transitions are either $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ in nature. However, the fluorescence properties such as maximum emission wavelength of organic linkers in the solid metal-organic frameworks are often different from those of the free molecules. The solid-state fluorescent emission band of **1** should be assigned to ligand-to-metal charge transfer in nature. In comparison with free ligand, the effective enhancement of these fluorescent bands in **1** may be due to the coordination of L to Cd(II) centers increasing the ligand conformational rigidity, thereby reducing the non-radiative decay of the intraligand ($\pi \rightarrow \pi^*$) excited state.

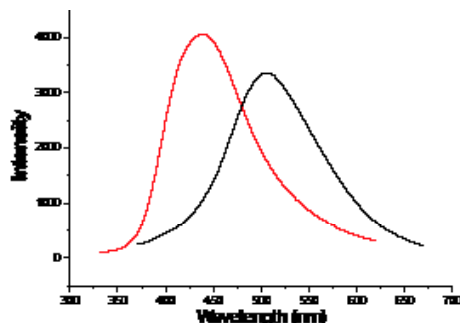


Figure 3. Emission spectrum of complex **1** in the solid state (red) and in the DMSO solution (black) at room temperature.

At room temperature, complex **1** in DMSO solutions are luminescent and show a broad emission maximum at 510 nm. However, the free ligand L is not emissive in DMSO^[20]. As has been discussed previously, $[\text{Au}_2\text{Ag}(\mu\text{-mes})_2(\mu\text{-dppy})](\text{ClO}_4)$ [dppy=1,2-bis(di-3-pyridylphosphano)-ethane] also displayed a similar strong luminescent emission maximum at ca. 524 nm in a DMSO solution at room temperature^[36]. The strong luminescent emission bands can be correlated with the existence of Cd^{II} ions in DMSO solutions.

In conclusion, a 2D layer Cd^{II} complex based on 2,5-dimethyl-1,3,4-thiadiazole (L) and bridging ligand $\text{NaN}(\text{CN})_2$ was synthesized and structurally characterized. The fundamental structural unit of the title complex contains two Cd^{II} centers, two neutral free L ligands, two bridging dca anions, one bridging cyanourea ligand and three terminal coordinated aqua molecules. It is noted that the cyanourea ligands are not used as the starting materials and formed from dicyanamide simply by hydrolysis. To the best of our knowledge, cyanourea represents the first example to participate in the coordination of metal ions in coordination chemistry up to now. 1D double chain connects Cd^{II} center ions to a 2D layer through cyanourea ligand. Further syntheses and structures with L ligand are also under way in our laboratory.

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