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Synthesis, Structure, Photoluminescence and Theoretical Study of {(*N,N'*-Dimethyl-4,4'-bipyridinium)[$Cd_2(\mu_2\text{-}Cl)_4Cl_2$]}$_n$ with *N,N'*-Dimethyl-4,4'-bipyridinium Generated *in Situ*

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The title complex, {(*N,N'*-dimethyl-4,4'-bipyridinium)[$Cd_2(\mu_2\text{-}Cl)_4Cl_2$]}$_n$ (**1**), in which the *N,N'*-dimethyl-4,4'-bipyridinium was generated *in situ*, was synthesized *via* hydrothermal reaction. X-Ray diffraction analysis revealed that the structure of **1** consisted of MV^{2+} (MV^{2+} = *N,N'*-dimethyl-4,4'-bipyridinium) cationic moieties and infinite [$Cd_2(\mu_2\text{-}Cl)_4Cl_2$]$_n$ anionic chains. The cadmium atom was bound by one terminal chlorine atom and four μ_2-bridging chlorine atoms, yielding a slightly distorted triangular bipyramid. Photoluminescent investigation revealed that the complex displayed an emission in greenish blue region.

Keywords: Cadmium, Crystal structure, Hydrothermal reaction, *In situ*, Viologen

INTRODUCTION

In the past decade, in situ metal/ligand reactions under hydro(solvo)thermal conditions have attracted increasing attention, due to the *in situ* ligand syntheses leading to the formation of novel coordination complexes with structural diversity or interesting properties for various potential applications [1]. Recently, a variety of novel coordination complexes synthesized *in situ* have been reported, among which many are transition metal complexes that play a very important role in many areas of chemistry and biology [2].

Transition metal complexes containing group 12 (IIB) elements are particularly attractive for many reasons, such as, the variety of coordination numbers and geometries provided by the d^{10} configuration of the IIB metal ions, photoelectric properties, fluorescent properties, and so on.

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Fluorescent materials have been of intense interest for several decades because they have wide-range applications in various fields. Our recent efforts in synthesizing novel group IIB-based complexes have focused largely on the systems with fluorescence. Herein, we report the synthesis, structure, and photoluminescence of {(*N,N'*-dimethyl-4,4'-bipyridinium) [$Cd_2(\mu_2\text{-}Cl)_4Cl_2$]}$_n$ (**1**), which is the first cadmium-containing complex with the in situ generation of the MV^{2+} moiety (MV^{2+} = *N,N'*-dimethyl-4,4'-bipyridinium). The electronic transition in the photoluminescent process of **1** was studied by means of time-dependent density functional theory (TDDFT) calculation.

EXPERIMENTAL

Elemental analyses of carbon, hydrogen and nitrogen were carried out with an Elementar Vario EL III microanalyser. The fluorescent data were collected at room temperature on a computer-controlled JY FluoroMax-3 spectrometer.

The intensity data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) by using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption corrections [3]. The structure was solved by the direct method using the Siemens SHELXTL™ Version 5 package of crystallographic software [4]. The different Fourier maps based on the atomic positions all yielded non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The summaries of crystallographic data and structure analysis are given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Time-dependent density functional theory (TDDFT) calculation was performed, employing the Gaussian03 suite of programs. Calculation of the electronic ground state of **1** was carried out using B3LYP density functional theory. "Double-ζ" quality basis sets was employed for the C, H, N (6-31G) and the Cd and Cl (LANL2DZ). The electron density diagrams of molecular orbital were obtained with the ChemOffice Ultra 7.0 graphics program.

All reactants of A.R. grade were obtained commercially and used without further purification. The complex {(*N*,*N*'-dimethyl-4,4'-bipyridinium)[$Cd_2(\mu_2\text{-}Cl)_4Cl_2$]}$_n$ (**1**) was prepared by mixing $CdCl_2$.2.5H_2O (1 mmol, 228 mg), 4,4'-bipyridine (1 mmol, 156 mg), concentrated HCl acid (1 ml), methanol (2 ml) and distilled water (7 ml) in a 25 ml Teflon-lined stainless steel autoclave and heated at 200 ºC for 10 days. After being slowly cooled to room temperature at 6 ºC h^{-1}, colorless crystals suitable for X-ray analysis were obtained. The yield was 81% (based on cadmium). Anal. Calcd. for $C_{12}H_{16}Cd_2Cl_6N_2$: C, 23.01; H, 2.56; N, 4.47. Found: C, 23.07; H, 2.57; N, 4.49.

RESULTS AND DISCUSSION

As shown in Fig. 1, the X-ray diffraction analysis reveals that the structure of the title complex consists of MV^{2+} cationic moieties and infinite $[Cd_2(\mu_2\text{-}Cl)_4Cl_2]_n$ anionic chains. The cadmium atom is bound by one terminal chlorine atom and four μ_2-bridging chlorine atoms, yielding a slightly distorted triangular bipyramid with two apexes of Cl2 and Cl3 and the mid-plane defined by Cl1, Cl2' and Cl3', respectively. The bond length between the cadmium atom and the terminal chlorine atom Cl1 (Cd1-Cl1 = 2.419(1) Å) is, as was expected, shorter than those of Cd-$Cl_{bridging}$ (2.489(1)-2.761(1) Å). The bond lengths of Cd-Cl are normal and comparable with the

Table 1. Summary of Crystallographic Data and Structure Analysis

Formula	$C_{12}H_{16}Cd_2Cl_6N_2$	Z	1
Formula weight	625.79	$2\theta_{max}$ (º)	50.04
Color	Colorless	Index ranges	$-8 \le h \le 8$, $-8 \le k \le 8$, $-10 \le l \le 11$
Crystal size (mm^3)	0.45 0.33 0.24	Reflections collected	2849
Crystal system	Triclinic	Independent, observed reflections (R_{int})	1549, 1512 (0.0183)
Space group	$P\bar{1}$	$d_{calcd.}$ (g cm^{-3})	2.166
a (Å)	7.166(2)	μ (mm^{-1})	3.047
b (Å)	7.478(3)	T (K)	293(2)
c (Å)	9.284(3)	F(000)	300
α (º)	75.316(6)	$R1$, $wR2$	0.0215, 0.0601
β (º)	85.495(5)	S	1.001
γ (º)	87.840(5)	Largest and Mean Δ/σ	0.001, 0
V (Å^3)	479.7(3)	$\Delta\rho$(max/min) (e/Å^3)	0.658/-0.820

Table 2. Selected Bond Lengths (Å) and Bond Angles (°)

Cd1-Cl1	2.419(1)	Cl1-Cd1-Cl2#1	121.80(3)
Cd1-Cl3	2.489(1)	Cl3-Cd1-Cl2#1	120.43(4)
Cd1-Cl2#1	2.5120(9)	Cl1-Cd1-Cl3#2	94.07(3)
Cd1-Cl3#2	2.704(1)	Cl3-Cd1-Cl3#2	87.06(3)
Cd1-Cl2	2.761(1)	Cl2#1-Cd1-Cl3#2	89.23(3)
Cd1-Cd1#2	3.768(1)	Cl1-Cd1-Cl2	93.64(3)
Cl2-Cd1#1	2.5120(9)	Cl3-Cd1-Cl2	92.90(3)
Cl3-Cd1#2	2.7040(9)	Cl2#1-Cd1-Cl2	83.29(3)
Cl1-Cd1-Cl3	117.77(3)	Cl3#2-Cd1-Cl2	171.30(3)

Symmetry codes: #1-x+3, -y+3, -z+2; #2-x+2, -y+3, -z+2.

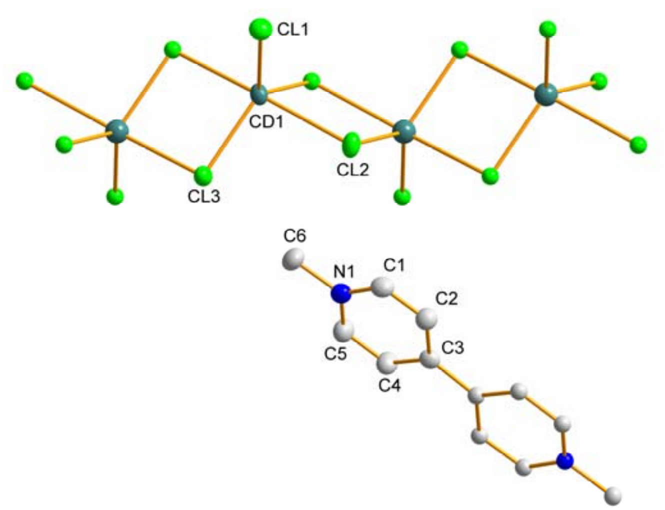


Fig. 1. ORTEP drawing of **1** with 35% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

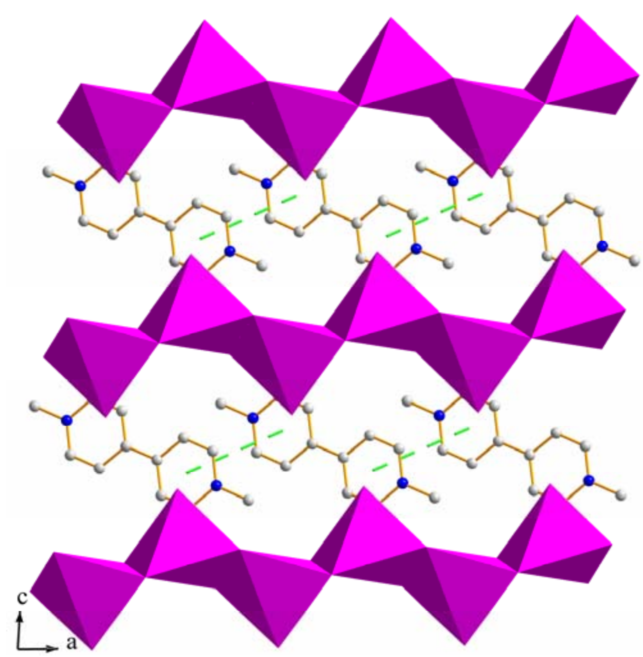


Fig. 2. Packing diagram of **1** with the dashed lines representing π … π interactions.

counterparts found in the literature [5]. The bond angles of Cl-Cd-Cl are in a wide range of 83.29(3)-121.80(3)º. The distance between two neighboring cadmium atoms is 3.768(1) Å, comparable with those documented [6]. The two pyridyl rings of the MV^{2+} moiety are perfectly coplanar with a dihedral angle of 0º.

For the title complex, there are weak π…π stacking interactions (centroid…centroid distance being of *ca*. 4.574 Å) between the MV^{2+} moieties. The cadmium-centered triangular bipyramids edge-share to each other to form a zigzag chain running along [1, 0, 0] direction. The MV^{2+} moieties are located among the $[Cd_2(\mu_2\text{-}Cl)_4Cl_2]_n$ anionic chains. The weak π…π stacking interactions and the electrostatic interactions between the MV^{2+} cationic moieties and the $[Cd_2(\mu_2\text{-}Cl)_4Cl_2]_n$ anionic chains contribute to the stabilization of the crystal packing of the title complex (Fig. 2). The result of the bond valence calculations indicates that the cadmium atom is in +2 oxidation state (Cd1: 2.079) [7]. Due to the fact that all the chlorine atoms are in -1 oxidation state, for the requirement of charge balance, the nitrogen atoms of the MV^{2+} moiety must be protonated, similar to the cases found in other complexes [8].

Unlike the syntheses of other viologen-based complexes, in which the viologen cation is derived from the starting reagent [9], the preparation of **1** resulted in the *in situ* generation of the MV^{2+} dication. This paves the way for the synthesis of viologen-based complexes, and makes the synthesis of viologen comparatively less toxic and more efficient. To the best of our knowledge, this is the second example of the *in situ* generation of the MV^{2+} dication and it is the first cadmium-containing complex with the *in situ* generation of the MV^{2+} dication, although an unprecedented in situ generation of the MV^{2+} dication in the complex of (MV) Bi_2Cl_8 was reported before [10].

The solid-state emission spectra of the title complex were investigated at room temperature. The emission spectrum of the title complex is given in Fig. 3. The fluorescent spectrum study shows that the title complex exhibits a broad and strong greenish blue emission band with a maximum wavelength of 527 nm and a shoulder band at 455 nm upon photo-excitation at 362 nm. The band at 455 nm may be ascribed to the cadmium chloride, because such a band at similar wavelength can be observed in several other cadmium chloride complexes [11], while the band at 527 nm probably results from the MV^{2+} cationic moieties and the anionic chains.

To clarify the nature of the fluorescent emissions of **1**, theoretical computation has been performed on **1**. To avoid the complexity, complex **1** was truncated into a segment of the 1-D {(N,N'-dimethyl-4,4'-bipyridinium)[$Cd_2(\mu_2\text{-}Cl)_4Cl_2$]}$_n$ chain,

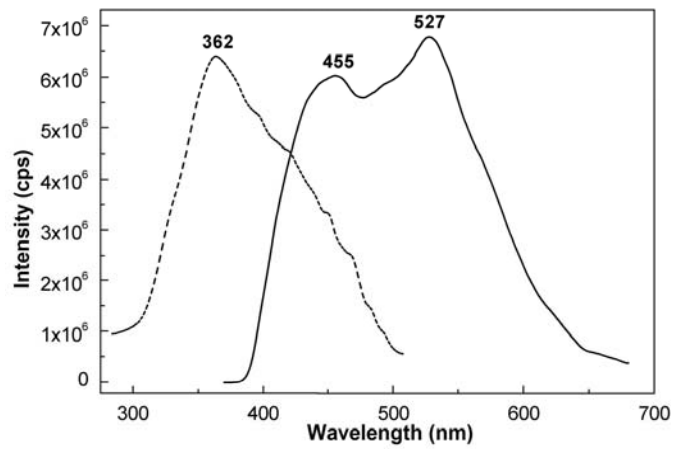
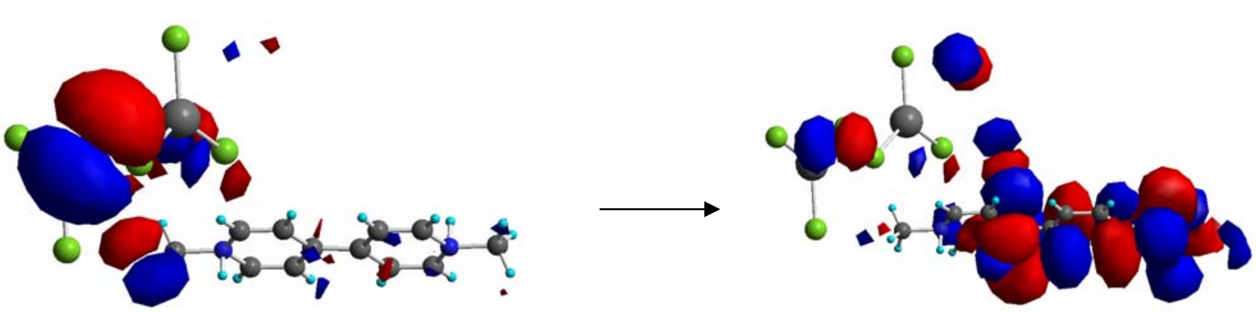


Fig. 3. Solid-state emission and excitation spectra of **1** at room temperature. Solid line: emission spectrum; dashed line: excitation spectrum.

containing one $Cd_2(\mu_2\text{-}Cl)_4Cl_2$entity and one N,N'-dimethyl-4,4'-bipyridinium moiety. The ground state geometry was adapted from the truncated X-ray data. On the basis of this geometry, time-dependent DFT (TDDFT) calculation using the B3LYP functional was performed [12].

Figure 4 depicts the features of the lowest unoccupied (LUMO) and the highest occupied (HOMO) frontier orbitals of **1**. Apparently, the electron densities of the singlet state for the HOMO is located on the cadmium atoms, while that of the LUMO is dominantly distributed on the MV^{2+} moiety and minority on chlorine atoms; this suggests that the emission band of **1** is attributed to the dominant charge transfer from the



HOMO LUMO

Fig. 4. The electron-density distribution of HOMO (left) and LUMO (right) calculated for **1**. The isosurfaces correspond to electronic density differences of -0.015 eÅ^{-3} (blue) and +0.015 eÅ^{-3} (red).

anionic chain to the MV^{2+} cationic moiety and few metal-to-ligand charge transfer (MLCT) (from the HOMO of cadmium atoms to the LUMO of the chlorine atoms). The former probably corresponds to the band at 527 nm and the latter should relate to the band at 455 nm.

In summary, a novel viologen-based complex $\{(N,N'$-dimethyl-4,4'-bipyridinium)$[Cd_2(\mu_2\text{-}Cl)_4Cl_2]\}_n$, in which the *N*,*N'*-dimethyl-4,4'-bipyridinium was generated *in situ*, has been synthesized *via* hydrothermal reaction. Photoluminescent investigation reveals that the complex displays a strong emission in greenish blue region. The scope for the syntheses of new metal halide 4,4′-bipy complexes with novel structures and properties appear to be very large, and further systematic experimental and theoretical investigations on this system are in progress.

SUPPLEMENTARY MATERIALS

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 698571. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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REFERENCES

[1] a) X.M. Chen, M.L. Tong, Acc. Chem. Res. 40 (2007) 162; b) T. Loiseau, L. Beitone, F. Millange, F. Taulelle, D. O’Hare, G.J. Ferey, Phys. Chem. B 108 (2004) 20020; c) J.Y. Lu, Coord. Chem. Rev. 246 (2003) 327.

[2] a) Y.N. Belokon, W. Clegg, R.W. Harrington, M. North, C. Young, Inorg. Chem. 47 (2008) 3801; b) P.D. Benny, G.A. Fugate, A.O. Barden, J.E. Morley, E. Silva-Lopez, B. Twamley, Inorg. Chem. 47 (2008) 2240; c) M.-S. Wang, G.-C. Guo, W.-Q. Zou, W.-W. Zhou, Z.-J. Zhang, G. Xu, J.-S. Huang, Angew. Chem., Int. Ed. 47 (2008) 3565.

[3] Rigaku (2002), CrystalClear Version 1.35, Rigaku Corporation.

[4] Siemens (1994), SHELXTL™ Version 5 Reference Manual, Siemens Energy & Automation Inc., Madison, Wisconsin, USA.

[5] a) F.A. Schroder, J.W. Bats, H. Fuess, E.J.Z. Zehnder, Anorg. Allg. Chem. 499 (1983) 181; b) C.H. Wei, Acta Crystallogr. C 43 (1987) 2295; c) O. Fuhr, D.Z. Fenske, Anorg. Allg. Chem. 626 (2000) 1822.

[6] a) D.-D. Wu, T.C.W. Mak, Acta Crystallogr. C 52 (1996) 526; b) Q.-G. Zhai, X.-Y. Wu, S.-M. Chen, C.-Z. Lu, W.-B. Yang, Cryst. Growth Des. 6 (2006) 2126.

[7] M. O’Keeffe, N.E. Brese, J. Am. Chem. Soc. 113 (1991) 3226.

[8] a) Z. Tang, A.M. Guloy, J. Am. Chem. Soc. 121 (1999) 452; b) L. San Felices, P. Vitoria, J.M. Gutierrez-Zorrilla, L. Lezama, S. Reinoso, Inorg. Chem. 45 (2006) 7748.

[9] a) S. Bonnet, J.-P. Collin, N. Gruber, J.-P. Sauvage, E.R. Schofield, Dalton Trans. (2003) 4654; b) M. Abe, Y. Sasaki, Y. Yamada, K. Tsukahara, S. Yano, T. Yamaguchi, M. Tominaga, I. Taniguchi, T. Ito, Inorg. Chem. 35 (1996) 6724.

[10] G. Xu, G.C. Guo, M.S. Wang, Z.J. Zhang, W.T. Chen, J.S. Huang, Angew. Chem. Int. Ed. 46 (2007) 3249.

[11] a) Y. Xu, W. Bi, X. Li, D. Sun, R. Cao, M.C. Hong, Inorg. Chem. Commun. (2003) 495; b) R.X. Yuan, R.G. Xiong, Y. L. Xie, X.Z. You, S.M. Peng, G.H. Lee, Inorg. Chem. Commun. (2001) 384; c) B.-Y. Lou, R.-H. Wang, Y. Xu, D.-Q. Yuan, Y.-F. Zhou, M.-C. Hong, Chinese J. Struct. Chem. 23 (2004) 747.

[12] a) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785; b) C.C. Wang, C.H. Yang, S.M. Tseng, S.Y. Lin, T.Y. Wu, M.R. Fuh, G.H. Lee, K.T. Wong, R.T. Chen, Y.M. Cheng, P.T. Chou, Inorg. Chem. 43 (2004) 4781.