Synthesis, Crystal Structure and Luminescent Property of Cd (II) Complex with \(N\)-Benzenesulphonyl-\(L\)-leucine

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Abstract: A new trinuclear Cd (II) complex \([\text{Cd}_3(\text{L})_6(2,2\text{-bipyridine})_3]\) \((\text{L} = \text{N-phenylsulfonyl-} \text{L-leucinato})\) has been synthesized and characterized by elemental analysis, IR and X-ray single crystal diffraction analysis. The results show that the complex belongs to the orthorhombic, space group \(P2_12_12_1\) with \(a = 16.877(3)\) Å, \(b = 22.875(5)\) Å, \(c = 29.495(6)\) Å, \(\alpha = \beta = \gamma = 90^\circ\), \(V = 11387(4)\) Å\(^3\), \(Z = 4\), \(D_c = 1.416\) \(\mu\text{g}\cdot\text{m}^{-3}\), \(\mu = 0.737\) \(\text{mm}^{-1}\), \(F(000) = 4992\), and final \(R_1 = 0.0390\), \(\omega R_2 = 0.0989\). The complex comprises two seven-coordinated Cd (II) atoms, with a N\(_2\)O\(_5\) distorted pentagonal bipyramidal coordination environment and a six-coordinated Cd (II) atom, with a N\(_2\)O\(_4\) distorted octahedral coordination environment. The molecules form one dimensional chain structure by the interaction of bridged carboxylato groups, hydrogen bonds and \(\pi-\pi\) interaction of 2,2-bipyridine. The luminescent properties of the Cd (II) complex and \(N\)-Benzenesulphonyl-\(L\)-leucine in solid and in CH\(_3\)OH solution also have been investigated.

Keywords: \(N\)-Benzenesulphonyl-\(L\)-leucine; trinuclear Cd (II) complex; synthesis; crystal structure; luminescent property

1. Introduction

Investigation of the inorganic-organic hybrid materials with carboxylate ligands has gained considerable attention during the last decade due to their attractive structures and promising potential applications for catalysis, gas storage, magnetic, luminescence materials [1–7]. Structural studies have
shown that the organic ligands containing multi-oxygen and nitrogen atoms can coordinate with metal ions in different ways, resulting in the formation of various metal-organic frameworks with specific topologies and useful properties. The Cd (II) complexes have gained considerable attention due to their luminescent properties [4]. We have been exploring the preparation of inorganic-organic hybrid materials by combining metal ions and organic ligands containing multi-oxygen and nitrogen atoms. We have now synthesized a new hybrid material, \([\text{Cd}_3(L)_6(2,2\text{-bipyridine})_3]\) \([L= \text{N-phenylsulfonyl-L-leucinato}\). The luminescent properties of the Cd (II) complex and \(\text{N-Benzencesulphonyl-L-leucine}\) in solid and in \(\text{CH}_3\text{OH}\) solution also have been investigated.

2. Results and Discussion

2.1. IR Spectra

The \(\nu_{as}(\text{COOH}), \nu_s(\text{COOH})\) and \(\nu\ (\text{C}=\text{N})\) vibrations of free ligand are at \(1,659\ \text{cm}^{-1}\) and \(1,436\ \text{cm}^{-1}\) and \(1,587\ \text{cm}^{-1}\), respectively. For the Cd (II) complex, they shift to \(1,587\ \text{cm}^{-1}, 1,402\ \text{cm}^{-1}\) and \(1,552\ \text{cm}^{-1}\), respectively, which suggest that the oxygen atoms of \(\text{COO}^-\) and the nitrogen atoms of 2,2-bipyridine coordinate to Cd (II) ions [8]. The difference between the \(\nu_{as}(\text{COO}^-)\) and \(\nu_s(\text{COO}^-)\) band is \(185\ \text{cm}^{-1}\), indicating a bidentate carboxylate moiety, consistent with the X-ray structural analysis. The new band at \(419\ \text{cm}^{-1}\) is assigned to the \(\nu\ (\text{Cd-O})\) vibration.

2.2. Structure Description

The molecular structure and molecular packing arrangement are shown in Figures 1 and 2, respectively. Figure 3 shows the coordination environment of the Cd (II) atom. From Figures 1 and 3, we can see that two coordination environments of the Cd (II) atoms exist in the complex. The first coordination environment of the Cd (II) atom [Cd1, Cd3] is a distorted pentagonal bipyramidal coordination environment with five oxygen atoms from the \(\text{N-phenylsulfonyl-L-leucinato}\) ligand, two nitrogen atoms from 2,2-bipyridine. The second coordination environment of the Cd (II) atom [Cd2] is a distorted octahedral coordination environment with four oxygen atoms from the \(\text{N-phenylsulfonyl-L-leucinato}\) ligand, two nitrogen atoms from 2,2-bipyridine. The carboxylates have three coordination ways of in the Cd (II) complex (Figure 4). The distances of the Cd-O bonds and Cd-N bonds are in the range of \(2.244(3)–2.450(4)\ \text{Å}\) and \(2.329(4)–2.366(4)\ \text{Å}\), respectively. The aromatic rings of 2,2-bipyridine in the complex are nearly parallel, the dihedral angle and distance between ring 1 (containing N71 and N72) and ring 2 (containing N81 and N82) are \(7.8(3)^\circ\) and \(3.846(4)\ \text{Å}\), ring 2 (containing N81 and N82) and ring 3 (containing N91 and N92) are \(6.2(3)^\circ\) and \(3.886(4)\ \text{Å}\). The hydrogen bonds and \(\pi-\pi\) interaction of 2,2-bipyridine rings help to stabilize the structure. The bond lengths of Cd-O are similar to the Cd-O bond lengths reported previously [9,10]. The aromatic rings in the molecules do not show any unusual features, and the bond lengths and bond angles are within the range of normal values.
**Figure 1.** The molecular structure of the Cd (II) complex.

![Molecular structure of Cd (II) complex](image1)

**Figure 2.** The molecular packing arrangement of the Cd (II) complex.

![Molecular packing arrangement of Cd (II) complex](image2)
2.3. Luminescent Properties

Previous studies have shown that the Cd (II) complexes exhibit luminescent properties [11]. Hence, we investigated the luminescent properties of the Cd (II) complex in the solid-state and in CH$_3$OH solution (1.06 × 10$^{-5}$ mol L$^{-1}$) at room temperature. The emission spectra of the Cd (II) complex are shown in Figure 5. In the solid state, the Cd (II) complex displays strong luminescent emission bands at 442 nm when excited at 335 nm. And in CH$_3$OH solution, the Cd (II) complex displays strong luminescent emission bands at 457 nm when excited at 335 nm. For excitation wavelengths between 280 and 420 nm, there is no obvious emission observed for the N-benzenesulphonyl-L-leucine ligand. Compared with the emission maximum of the Cd (II) complex in methanol solution, the emission maximum of the Cd (II) complex in solid was blue shifted, which may be due to the quenching effect of the methanol solvent.
Figure 5. The emission spectrum of the Cd (II) complex. The excitation and emission slit widths were 5 nm.

3. Experimental Section

3.1. Materials and Methods

The N-benzenesulphonyl-L-leucine ligand was prepared according to the method reported in the literature [5]. Other chemicals were of reagent grade and were used without further purification.

Carbon, hydrogen and nitrogen analyses were obtained using an Elementar Vario III EL elemental analyzer. Infrared spectra were recorded on a Nicolet AVATAR 360 FTIR spectrophotometer with KBr in the range of 400 cm\(^{-1}\)–4000 cm\(^{-1}\). Mass spectrum was performed on a VG ZAB-HS Fast-atom bombardment (FAB) instrument. Excitation and emission spectra were obtained on a PE LS-55 spectrometer at room temperature. X-ray diffraction data of the Cd (II) complex was collected on a Bruker smart CCD diffractometer.

3.2. Synthesis of Cd (II) Complex

A methanolic solution of 0.5 m mol (0.1543 g) cadmium nitrate tetrahydrate was added to a solution containing 1.0 m mol (0.2710 g) of N-benzenesulphonyl-L-leucine and 1.0 m mol (0.04 g) of sodium hydroxide in 10 mL CH\(_3\)OH. The mixture was continuously stirred for 2 h at refluxing temperature. The mixture was cooled at room temperature, and was collected by filtration. By evaporation in air at room temperature, a single crystal suitable for X-ray determination was obtained from methanol solution after 15 days. Elementary analysis: calcd for C\(_{102}\)H\(_{120}\)Cd\(_3\)N\(_{12}\)O\(_{24}\)S\(_6\): C, 50.42; H, 4.94; N, 6.92%; found: C, 50.77; H, 4.58; N, 6.73%. IR \(v\)\(_{\text{max}}\) (cm\(^{-1}\)): \(v\)\(_{\text{as}}\) (COO\(^-\)):1,587 cm\(^{-1}\), \(v\)\(_{\text{s}}\) (COO\(^-\)):1402 cm\(^{-1}\), \(v\) (-SO\(_2\)-NH-): 3,249 cm\(^{-1}\), 1,320 cm\(^{-1}\),1,156 cm\(^{-1}\), \(v\) (C=N): 1,552 cm\(^{-1}\), \(v\) (Cd-O):419 cm\(^{-1}\).
3.3. X-Ray Crystallography

Single crystal X-ray diffraction data were collected on a Bruker smart CCD diffractometer at 153(2) K using graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å). The structure was solved by the direct method and refined with full-matrix least-squares techniques using SHELXL-97 [12]. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were put in calculated positions. Molecular graphics were drawn with the program package SHELXTL-97 crystallographic software package [13]. The main crystal data of the collection and refinement details of the Cd (II) complex are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

| Crystallographic parameter | Crystallographic data |
|----------------------------|-----------------------|
| Formula                    | C_{102}H_{120}Cd_{3}N_{12}O_{24}S_{6} |
| Formula weight             | 2427.66               |
| Crystal system             | Orthorhombic          |
| Space group                | P2_12_12_1            |
| a (Å)                      | 16.877(3)             |
| b (Å)                      | 22.875(5)             |
| c (Å)                      | 29.495(6)             |
| Z                          | 4                     |
| F(000)                     | 4992                  |
| Temperature (K)            | 153(2)                |
| V (Å^3)                    | 11387(4)              |
| Calculated density (µg·m^{-3}) | 1.416                 |
| Crystal size (mm^3)        | 0.24 × 0.20 × 0.12    |
| µ (mm^{-1})                | 0.737                 |
| S                          | 1.060                 |
| −20 ≤ h ≤ 20               |                       |
| −26 ≤ k ≤ 27               |                       |
| −35 ≤ l ≤ 34               |                       |
| Reflections collected/unique | 20023/17894           |
| R_1, wR_2 [all data]       | 0.0452, 0.1029        |
| R_1, wR_2 [I > 2σ(I)]      | 0.0390, 0.0989        |
| Largest diff. peak and hole (e·Å^{-3}) | 1.213–1.250 |
Table 2. Selected bond lengths (Å) and angles (°) for the Cd (II) complex.

| Bonds               | Bond parameter | Bonds               | Bond parameter |
|---------------------|----------------|---------------------|----------------|
| Cd1-O31             | 2.241(3)       | Cd2-O41             | 2.386(3)       |
| Cd1-N71             | 2.329(4)       | Cd2-O32             | 2.408(3)       |
| Cd1-O22             | 2.331(3)       | Cd3-O42             | 2.244(3)       |
| Cd1-O11             | 2.331(4)       | Cd3-O52             | 2.310(3)       |
| Cd1-N72             | 2.366(4)       | Cd3-N91             | 2.330(4)       |
| Cd1-O12             | 2.450(4)       | Cd3-N92             | 2.347(5)       |
| Cd2-O21             | 2.253(3)       | Cd3-O62             | 2.360(4)       |
| Cd2-O51             | 2.263(3)       | Cd3-O61             | 2.420(4)       |
| Cd2-N81             | 2.335(4)       | -                   | -              |
| Cd2-N82             | 2.341(4)       | -                   | -              |

O31-Cd1-N71         161.91(14) O41-Cd2-N81  78.30(13)
O31-Cd1-O22         92.09(14) O41-Cd2-N82  116.50(13)
N71-Cd1-O22         84.39(14) O21-Cd2-O32  89.06(12)
O31-Cd1-O11         94.74(16) O51-Cd2-O32  81.05(12)
N71-Cd1-O11         100.64(17) N81-Cd2-O32  120.38(13)
O11-Cd1-O22         133.05(13) O32-Cd2-N82  78.95(13)
O31-Cd1-N72         102.03(15) O32-Cd2-O41  160.16(12)
N71-Cd1-N72         70.04(15) O42-Cd3-O52  94.83(13)
N72-Cd1-O22         137.92(14) N91-Cd3-O42  106.22(15)
O11-Cd1-N72         85.50(15) N91-Cd3-O52  133.77(15)
O31-Cd1-O12         99.51(15) O42-Cd3-N92  168.28(15)
N71-Cd1-O12         97.17(16) N92-Cd3-O52  80.53(14)
O12-Cd1-O22         78.55(13) N91-Cd3-N92  70.57(16)
O11-Cd1-O12         54.50(14) O42-Cd3-O62  91.90(15)
N72-Cd1-O12         135.80(15) O52-Cd3-O62  135.51(13)
O21-Cd2-O51         103.84(12) N91-Cd3-O62  85.27(16)
O21-Cd2-N81         97.39(14) O62-Cd3-N92  98.95(16)
O51-Cd2-N81         150.20(14) O61-Cd3-O42  100.38(13)
O21-Cd2-N82         153.49(14) O61-Cd3-O52  81.03(12)
O51-Cd2-N82         97.58(13) N91-Cd3-O61  132.21(14)
N81-Cd2-N82         69.58(14) O61-Cd3-N92  89.58(15)
O21-Cd2-O41         81.37(11) O62-Cd3-O61  54.52(13)
O51-Cd2-O41         84.41(12) -                   -               

4. Conclusions

In summary, by selecting the Cd (II) ion as a knot, and N-phenylsulfonyl-L-leucinato and 2,2-bipyridine as a building block, a new complex [Cd₃(L)₆(2,2-bipyridine)₃] has been synthesized and structurally characterized. The complex comprises two seven-coordinated Cd (II) atoms, with a N 2O5 distorted pengonal bipyramidal coordination environment and a six-coordinated Cd (II) atom, with a N2O4 distorted octahedral coordination environment. The molecules form a one dimensional chain structure by the interaction of bridged carboxylato groups and π-π interaction of 2,2-bipyridine. The Cd (II) complex exhibited fluorescence in solid and in CH₃OH. Based on those results, a series of new Cd (II) complex could be designed and synthesized to optimize the luminescent properties.
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Supplementary Material

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No.CCDC 890837. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

References

1. Tian, L.J.; Yang, H.J.; Zheng, X.L.; Ni, Z.H.; Yan, D.M.; Tu, L.L.; Jiang, J.Z. Synthesis, structural characterization and cytotoxic activity of diorganoyin (IV) complexes of N-(5-halosalicylidene)tryptophane. *Appl. Organometal. Chem.* **2009**, *23*, 24–31.
2. Kusrini, E.; Saleh, M.I.; Adnan, R.; Yulizar, Y.; Shiong, N.S.; Fun, H.K.; Abdullah, M.A.A.; Mamat, M.; Zaaba, N.K.; Majid, W.H.A. Structural, optical electrical properties of europium picrate tetraethylene glycol complex as emissive material for OLED. *J. Luminesc.* **2012**, *132*, 91–99.
3. Tang, Y.Z.; Zhou, M.; Yang, Y.M.; Wang, X.W.; Huang, S. Synthesis, crystal structure and characterization of olsalazine complex. *J. Synth. Cryst.* **2011**, *40*, 1083–1086.
4. Lu, W.G.; Jiang, L.; Feng, X.L.; Lu, T.B. Three 3D coordination polymers constructed by Cd(II) and Zn(II) with imidazole-4,5-dicarboxylate and 4,4′-bipyridyl building blocks. *Cryst. Growth Des.* **2006**, *6*, 564–571.
5. Tai, X.S.; Wei, N.; Wang, D.H. Synthesis, crystal structure and luminescent property of Mg (II) complex with N-benzenesulphonyl-L-leucine and 1,10-phenanthroline. *Materials* **2012**, *5*, 558–565.
6. Wang, L.F.; Hu, Y.X.; Zhang, W.W.; Ren, X.M. Solvothermal synthesis, crystal structure and photoluminescence property of a coordination polymer based on 1,1′-ethylenbenzene-3,3′,5,5′-tetracarboxylate. *China J. Inorg. Chem.* **2011**, *27*, 542–546.
7. Tai, X.S.; Feng, Y.M.; Wang, L.T.; Tan, M.Y. Synthesis, structure characterization and luminescent properties of ternary zinc acetate complex with 4-aminohippuric acid and 1,10-phenanthroline ligand. *Polish J. Chem.* **2009**, *83*, 1099–1104.
8. Nakamoto, K. *Infrared and Ramen Spectra of Inorganic and Coordination Compounds*, 3rd ed.; John Wiley and Sons: New York, NY, USA, 1978; Volume 1, pp. 359–368.
9. Liu, D.; Li, N.Y. Poly[di-μ-1,2-bis(pyridine-4-yl)-ethene-N,N’-tetrakis(4-iodobenzoato-O,O′)] dicadmium. *Acta Cryst.* **2012**, *C68*, m21–m23.
10. Jian, F.F.; Xiao, H.L.; Sun, P.P.; Zhao, P.S. Crystal structure and characterization of the dinuclear Cd(II) complex [Cd(H2O)2(o-HOC6H4COO)]2. *Molecules* **2004**, *9*, 876–882.
11. Tao, J.; Yin, X.; Wei, Z.B.; Huang, R.B.; Zheng, L.S. Hydrothermal syntheses, crystal structures and photoluminescent properties of three metal-cluster based coordination polymers containing mixed organic ligands. *Eur. J. Inorg. Chem.* **2004**, *1*, 125–133.

12. Sheldrick, G.M. *SHELXL-97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

13. Sheldrick, G.M. *SHELXTL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

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