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# Complex $[Cd(dafo)_2(tphpo)(CH_3COO)]ClO_4$ (dafo = 4,5-diazafluoren-9-one, tphpo = triphenylphosphine oxide) with chiral metal centers. Helical packing induced by π–π stacking interactions of dafo rings

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## Abstract

The first complex of 4,5-diazafluoren-9-one (dafo) and cadmium: $[Cd(dafo)_2(tphpo)(CH_3COO)]ClO_4$ (triphenylphosphine oxide = tphpo) is a quaternary complex with chiral metal centers and crystallizes in a monoclinic cell with space group $P_2(1)/n$. Cadmium centers with 7-fold coordination adopt a distorted monocapped trigonal prismatic geometry. Two oxygen atoms of acetate and one oxygen atom of triphenylphosphine oxide form the top triangle of the trigonal prism, while three nitrogen atoms from two dafo groups construct the bigger bottom triangle. The last nitrogen atom of dafo groups occupies the monocapped position. Here, dafo molecules display two different coordination patterns, namely unsymmetric and symmetric chelation. Moreover, the interesting linking of screw related cations is fabricated by inter-molecular π–π stacking interactions in the complex.

*Keywords:* 4,5-Diazafluoren-9-one; Quaternary complex of cadmium; Chiral molecule; π–π Stacking interaction

## 1. Introduction

4,5-Diazafluoren-9-one (dafo) is a derivative of 1,10-phenanthroline (phen) and has been expected to be a superior ligand with plentiful coordination chemistry. However, in contrast with 1,10-phenanthroline, dafo forms rather fewer complexes with transition metals. Its Ru (II) and Eu (III) complexes having potential applications in optical field have been studied well [1,2]. Further studies on dafo complexes have discovered that dafo often adopts monodentate coordination or unsymmetric chelation in its copper (II), nickel (II) or cobalt (II) complexes [3–6], unlike complexes of 1,10-phenanthroline where it usually acts as symmetrically chelating ligand. Sindhu Menon and M. N. Rajasekharan first reported two different coordination fashions of dafo in a copper complex [7], and gave the rational explanation that a much larger chelate bite for this ligand (N···N: dafo, 3.00 Å; bipy, 2.62 Å; phen, 2.64 Å) resulting from the presence of a rigid five-numbered ring constrains the symmetrically

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chelating ability of dafo. Herein, we report another example [Cd(dafo)$_2$(tphpo)(CH$_3$COO)]ClO$_4$ (tphpo = triphenylphosphine oxide), where dafo also displays two different chelating coordination styles, one-second as a symmetrically chelating ligand and the other as the unsymmetric.

Apart from adduct of tetrabromocadmate (II) with protonated dafo where dafo just acts as a counter ion [8], from our knowledge, no complex of dafo with subgroup IIB metals has been reported. The title complex is the first complex of dafo with cadmium and also the first complex of triphenylphosphine oxide and cadmium. In the complex, inter-molecular π–π stacking interactions between dafo rings are very strong, which induce the helical linking of cations to be formed in crystal. Moreover, those cadmium centers have chirality owing to coordination environments.

Table 1
Crystal data for complex [Cd(dafo)$_2$(tphpo)(CH$_3$COO)]ClO$_4$

| | | |
|---|---|---|
| Empirical formula | $C_{42}H_{30}CdClN_4O_9P$ | |
| Formula weight | 913.52 | |
| Temperature | 291(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system, space group | Monoclinic, $P2(1)/n$ | |
| Unit cell dimensions | $a = 12.796(3)$ Å | $\alpha = 90°$ |
| | $b = 13.424(3)$ Å | $\beta = 105.21(3)°$ |
| | $c = 24.039(1)$ Å | $\gamma = 90°$ |
| Volume | 3984.6(14) A$^3$ | |
| $Z$, Calculated density | 4, 1.523 Mg/m$^3$ | |
| Absorption coefficient | 0.717 mm$^{-1}$ | |
| $F(000)$ | 1848 | |
| Crystal size | 0.25 × 0.20 × 0.20 mm | |
| Theta range for data collection | 1.65–25.00° | |
| Index ranges | $0 \leq h \leq 15$,<br>$-15 \leq k \leq 15$,<br>$-28 \leq l \leq 27$ | |
| Reflections collected/unique | 9968/6005 [$R(int) = 0.0375$] | |
| Completeness to $2\theta = 25.00$ | 88.57% | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data/restraints/ parameters | 6005/0/524 | |
| Goodness-of-fit on $F^2$ | 0.996 | |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0457$,<br>$wR2 = 0.0776$ | |
| $R$ indices (all data) | $R1 = 0.0958$,<br>$wR2 = 0.0868$ | |
| Largest diff. peak and hole | 0.472 and −0.448 e A$^{-3}$ | |

## 2. Experimental

### 2.1. Equipments and measurements

Elemental analyses were performed with a Carlo–Erba 1106 elemental analyzer. IR spectral was recorded on a FTS-40 infrared spectrophotometer using KBr discs in the 4000–400 cm$^{-1}$regions. Crystal structure was determined on a Rigaku–Raxis-IV X-ray diffractometer.

Table 2
Selected bond lengths (Å) and bond angles (°) for [Cd(dafo)$_2$(-tphpo)(CH$_3$COO)]ClO$_4$

| | |
|---|---|
| *Bond lengths* | |
| Cd1–O5 | 2.324(3) |
| Cd1–O4 | 2.3394(4) |
| Cd1–N4 | 2.398(3) |
| Cd1–O3 | 2.408(3) |
| Cd1–N1 | 2.457(4) |
| Cd1–N2 | 2.478(4) |
| Cd1–N3 | 2.587(4) |
| *Bond angles* | |
| O5–Cd1–O4 | 91.82(2) |
| O5–Cd1–N4 | 75.55(12) |
| O4–Cd1–N4 | 140.27(13) |
| O5–Cd1–O3 | 92.42(12) |
| O4–Cd1–O3 | 54.39(13) |
| N5–Cd1–O3 | 159.92(13) |
| O5–Cd1–N1 | 158.50(12) |
| O4–Cd1–N1 | 103.89(13) |
| N4–Cd1–N1 | 100.09(13) |
| O53–Cd1–N1 | 85.17(13) |
| O5–Cd1–N2 | 85.15(13) |
| O4–Cd1–N2 | 129.68(12) |
| N4–Cd1–N2 | 87.32(12) |
| O3–Cd1–N2 | 75.52(13) |
| N1–Cd1–N2 | 73.54(13) |
| O5–Cd1–N3 | 115.42(12) |
| O4–Cd1–N3 | 80.25(13) |
| N4–Cd1–N3 | 72.17(13) |
| O3–Cd1–N3 | 127.90(13) |
| N1–Cd1–N3 | 82.15(13) |
| N2–Cd1–N3 | 144.85(13) |

### *2.2. Materials and reagents*

Except for 4,5-diazafluoren-9-one being synthesized through the method of literature [6], others were used as purchased from creditable companies without further purification.

### *2.3. Preparation of complex [Cd(dafo)$_2$(tphpo)(CH$_3$COO)]ClO$_4$*

The mixture of Cd(CH$_3$COO)$_2$·4H$_2$O (0.067 g, 0.25 mmol), dafo (0.091 g, 0.5 mmol) and 15 ml absolute ethyl alcohol was put into a 100 ml

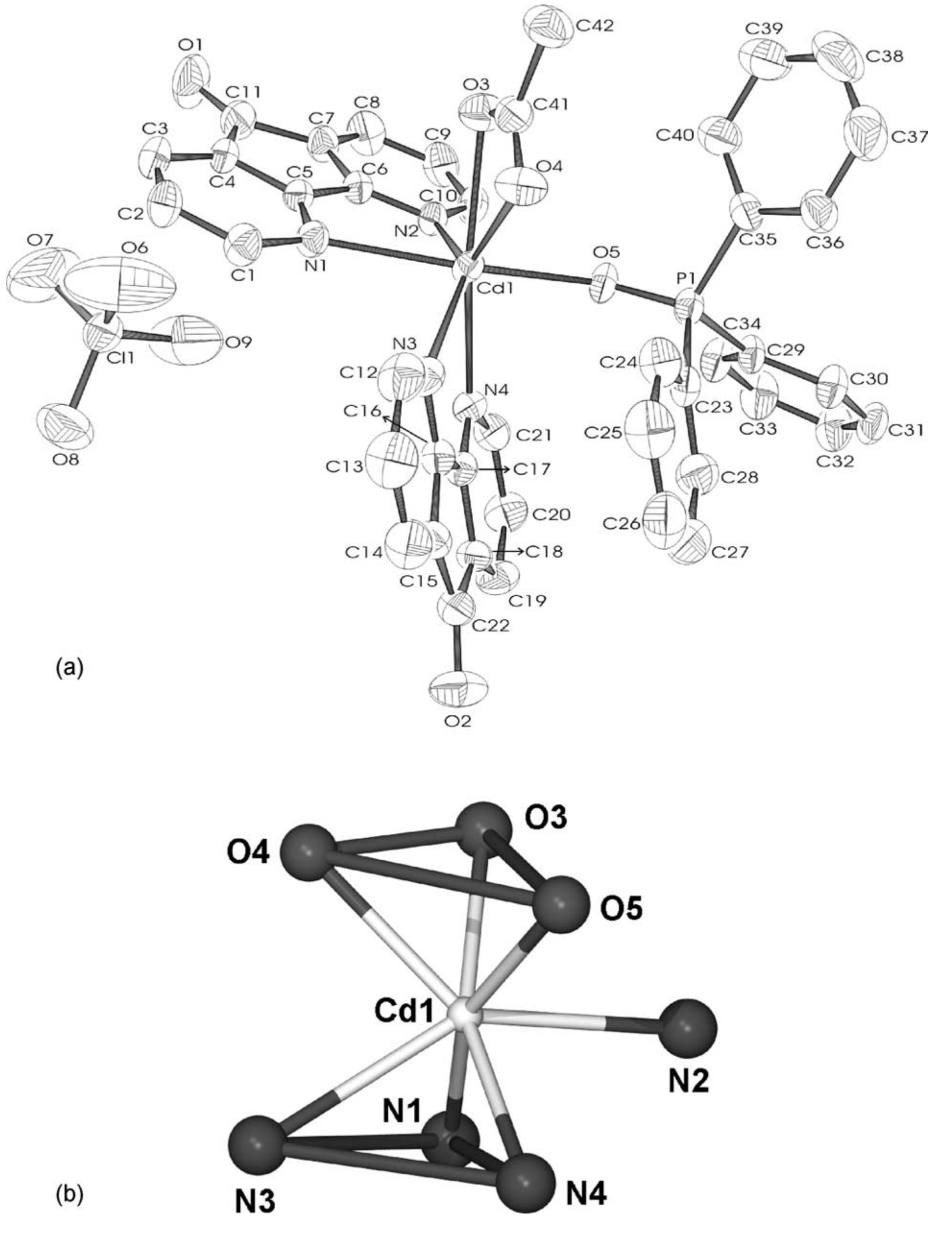

Fig. 1. (a) An ORTEP diagram of the asymmetric unit of complex [Cd(dafo)$_2$(tphpo)(CH$_3$COO)]ClO$_4$ (omitted hydrogen atoms for clarity). (b) Polyhedral representation of the monocapped trigonal prismatic coordination environments around metal centers.

three-necked flask. After being added ten drops of acetic acid, the mixture was heated at refluxed temperature in water-bath for 3 h. Then 2 ml benzene soution of 0.13 g (0.5 mmol) triphenylphine was put into this system which continued to reflux for another 1 h. Two milliliter alcohol solution of 0.122 g (1 mmol) $NaClO_4$ was added to earlier-mentioned system, the mixture was refluxed for final 10 min. After being kept untouched overnight, this mixture was filtrated and the filtrate was let evaporate naturally at room temperature. After half year, yellow needle crystal appeared. Filtrated, washed with ether and dried naturally, pure title complex of 0.16 g was obtained (yield 60%) (Found: C, 55.20; H, 3.28; N, 6.40%. $C_{42}H_{30}CuClN_4O_9P$ requires: C, 55.17; H, 3.28; N, 6.13%). Selected IR spectra: 3441, 3075, 1729, 1592, 1574, 1440, 1414, 1156, 1105, 765, 725, 542 $cm^{-1}$.

### 2.4. X-ray crystallography

A single crystal of dimension $0.25 \times 0.20 \times 0.20$ $mm^3$ was mounted on a Rigaku–Raxis-IV X-ray diffractometer using graphite monochromated Mo $K_a$ ($\lambda = 0.071073$ nm) radiation at 291(2) K. A total of 9968 reflections were measured over the ranges $1.65 \leq 2\theta \leq 25.00$, $0 \leq h \leq 15$, $-15 \leq k \leq 15$, $-28 \leq l \leq 27$, yielding 6005 unique reflections. Raw data were corrected and the structure was solved using the SHELX-97 program. Non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement. The full-matrix least-squares calculations on $F^2$ were applied on the final refinement. The refinement converged at $R1 = 0.0457$ and $wR2 = 0.0776$ values for reflections with $I > 2\sigma(I)$. The unit cell parameters, along with data collection and refinement details were tabulated in Table 1, while other correlated data were also listed in Table 2. Full atomic data are available as a file in CIF format, deposited with the Cambridge Crystallographic Data Center (No. 199387).

## 3. Results and discussion

### 3.1. Synthesis

The title complex was synthesized using fractional step method and its single crystal was obtained through gradual evaporation for half year. Due to exposed to air during the preparation of the title complex, triphenylphosphine was oxidized into triphenylphosphine oxide [9], which is consistent with the results of crystallography and IR spectra.

### 3.2. Crystal structure

X-ray diffraction results show that the title complex is a quaternary complex of cadmium (II) coordinating with dafo, tphpo and acetate. Cadmium centers with 7-fold coordination adopt distorted monocapped trigonal prismatic geometry as shown in Fig. 1(a). Three oxygen atoms of O3,

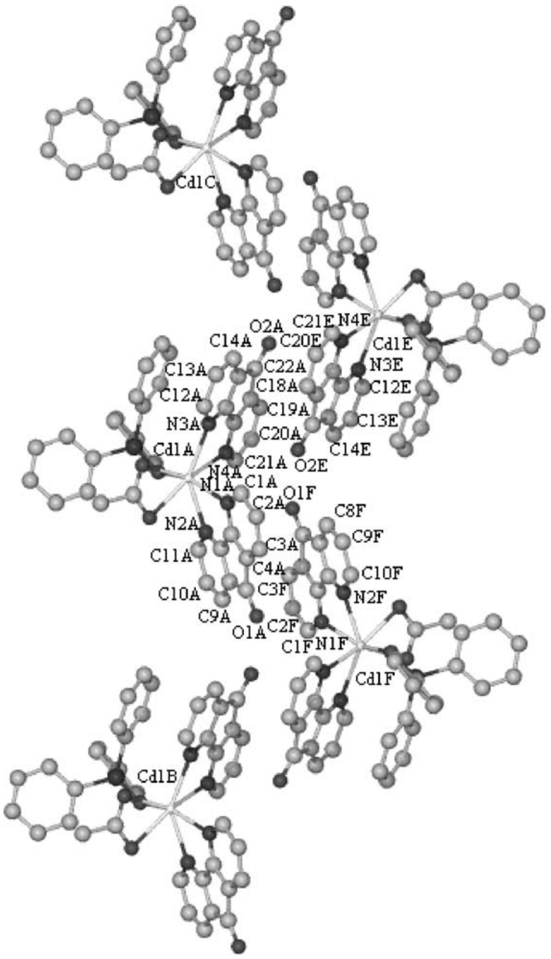

Fig. 2. Helical chains of cations formed by π–π stacking interaction in complex $[Cd(dafo)_2(tphpo)(CH_3COO)]ClO_4$ (viewed down b axis).

O4 and O5 and three nitrogen atoms of N1, N3 and N4 construct top and bottom triangle of trigonal prism, respectively, while N2 from the capped position coordinates to Cd1. From the bond lengths and angles tabulated in Table 2, it can be postulated that the bottom triangle of the prism is larger than the top triangle (see Fig. 1(b)).

In this complex, dafo displays two chelating coordination patterns. Half of the dafo adopt unsymmetrically chelating coordination with Cd1–N3 of 2.587(4) Å and Cd1–N4 of 2.398(3) Å, while the other half adopting symmetrically chelating coordination with Cd1–N1 of 2.457(4) Å and Cd1–N2 of 2.478(4) Å. Acetate ions chelate to cadmium centers, with bond lengths of Cd1–O3 and Cd1–O4 being 2.408(3) and 2.339(4) Å, respectively. Meanwhile, oxygen atom O5 from triphenylphosphine oxide coordinates to Cd1 with bond length of 2.324(3) Å. The symmetry of the metal center $[Cd(dafo)_2(tphpo)(CH_3COO)]^+$ belongs to C1 point group and displays chirality. In crystal cell, however, these four metal centers arrange in internal compensation.

There are two-typed π–π stacking interactions in the crystal as shown in Fig. 2. The distance of phenyl ring C23AC24AC25AC26AC27AC28A and dafo ring C17AC18AC19AC20AC21AN4A ranges from 3.525 to 3.807 Å, indicating weaker intra-molecular π–π stacking interaction that stabilizes the configuration of the title complex. Meanwhile, stronger intermolecular π–π stacking interactions with distance from 3.490 to 3.553 Å offset between adjacent dafo rings of different cations, which conduct discrete cations in helical arrangement (clearly shown in Fig. 2). These helical chains pile up along a axis in the crystal, while perchlorate ions and triphenylphosphine groups occupy cavities between these chains (shown in Fig. 3).

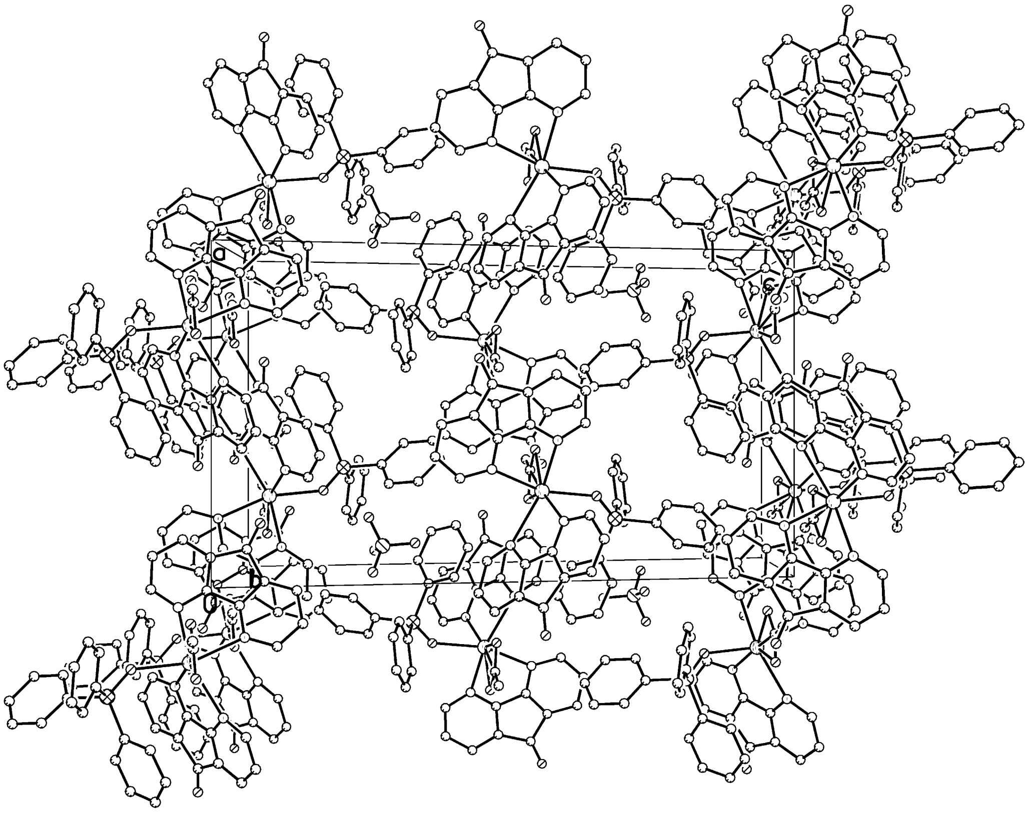

Fig. 3. Crystal packing of complex $[Cd(dafo)_2(tphpo)(CH_3COO)]ClO_4$, occupants of $ClO_4^-$ and $=PPh_3$ in the cavities formed by the helical chains.

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