Self-Assembly of Two Novel Cadmium(II) Complexes: One from Tripodal Imine−Phenol Ligand and the Other from In situ Partial Degradation of Dipolar Imine−Phenol Ligand

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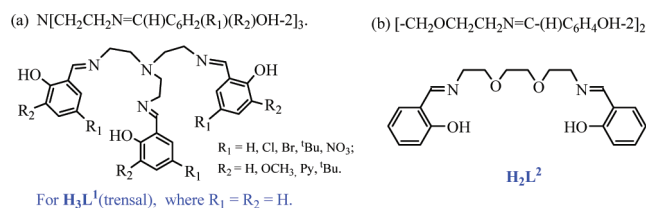
ABSTRACT: Through different synthetic strategies, two novel cadmium(II) complexes have been synthesized and characterized. The first mesocate complex $Cd_3L^1_2$ (**1**) with S_6 symmetry based on tris[(2-salicylaldeneimino)ethyl]-amine (H_3L^1 or H_3trensal) is constructed from the self-assembly of Cd^{2+} ion and two chiral building block units, Δ- and Λ-[Cd(trensal)]$^-$, in which the coordination numbers of six and seven for Cd(II) ions are rarely found in one discrete compound without any auxiliary ligand. However, under the same reaction conditions, $CdL^3(H_2O)(NO_3)$ (**2**) with N_3O_4 donors is obtained from Cd^{II} coordination induced partial hydrolysis of dipolar imine−phenol Schiff base ligand N,N'-bis(salicylidene)-3, 6-dioxa-1,8-diaminooctane (H_2L^2), which provides the first example of hydrated Cd^{II} salt promoting partial degradation of the imine−phenol ligand. The strong fluorescence emission of **1** makes it a potentially useful photoactive material for its high thermal and chemical stability.

Metallosupramolecular chemistry has witnessed many developments over the past two decades to an important and still growing field of research.[1] Supramolecular aggregates of different shapes were obtained by use of well-designed organic ligands in combination with appropriate metal ions or metal complex fragments.[2] Especially, the use of tripodal/dipolar imine−phenol Schiff base ligands of general formula $N[CH_2CH_2N=C(H)C_6H_3(R_1)(R_2)OH-2]_3/[-CH_2OCH_2CH_2N=C-(H)C_6H_4OH-2]_2$ (Scheme 1) to promote the self-assembly of discrete and well-defined metallosupramolecular architectures has by now become a significant synthetic strategy, mainly because these ligands have made profound contributions to the development of catalysis, magnetism, optics, molecular architectures, and materials chemistry.[3] Thus, various discrete structures have been constructed, and among those are the ML (M = d/p or f-metals) mononuclear,[3,4] M_2L_2 (M = d/p or f-metals) dinuclear,[3] M_3L_2 (M = homo-p or f or hetero-f/d metals) trinuclear[4,5] and $M_4(\mu^3$-O)$_2L_2$ (M = $Mn^{II, III}$)[4,6] tetranuclear species with high symmetry. Surprisingly, the homotrinuclear metal compounds M_3L_2 (M = transition metals) as a mesocate (Δ + Λ) containing tripodal imine−phenol Schiff base ligands H_3trensal (H_3L^1) with S_6 symmetry have remained unexploring in comparison with other reported high-symmetry discrete complexes. On the other hand, Cu^{II}-, Sn^{II}- and Zn^{II}-catalyzed partial hydrolysis of tripodal ligands $N[CH_2CH_2N=C(Me)C_6H_4OH-2]_3$ or $N[CH_2CH_2N=CHC_6H_3(R)-OH-2]_3$ (R = H, 3-OCH_3, 5-Br, or 5-NO_2) have been well-documented in the literature.[7]

Divalent metal Cd^{2+} with such tripodal/dipolar ligands has, in contrast, received less attention up to now.

Recently, several well-defined and characterized discrete molecular aggregates containing the tripodal ligands with benzimidazolyl arms have been constructed by us.[8] The flexible C_3-symmetric tripodal ligand such as tris(1-benzimidazolylethyl)amine can encapsulate one or two metal ions with the two tripodal ligands exhibiting double-propeller-like topology (with each tripodal ligand exhibiting an independent propeller sense).[8] Moreover, the flexible dipolar ligands with two terminal phenol groups give several novel tetranuclear copper(II) and lanthanide compounds.[9] As a continuation of our earlier investigations, we report herein the syntheses

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Scheme 1. Relative (a) Tripodal or (b) Dipolar Imine-Phenol Schiff Base Ligands

(a) $N[CH_2CH_2N=C(H)C_6H_2(R_1)(R_2)OH-2]_3$.

(b) $[-CH_2OCH_2CH_2N=C-(H)C_6H_4OH-2]_2$

R_1 = H, Cl, Br, ^tBu, NO_3;
R_2 = H, OCH_3, Py, ^tBu.

For H_3L^1(trensal), where $R_1 = R_2 = H$.

H_2L^2

and characterizations of two novel Cd^{II} complexes $Cd_3L^1_2$ (**1**) and $CdL^3(H_2O)(NO_3)$ (**2**) [H_2L^3 = 2-((2-(2-(2-aminoethoxy)ethoxy)ethylimino)-methyl)phenol]. The main novelty of this work is that (a) as far as we know, the mesocate $Cd_3L^1_2$ (**1**) with S_6 symmetry based on tris[(2-salicylaldeneimino)ethyl]amine (H_3L^1) featured mainly in its heptadentate propeller-like N_4O_3 coordination mode is first constructed from the self-assembly of Cd^{2+} ion and the chiral building block units Δ- and Λ-[Cd(trensal)]$^-$, in which the coordination numbers of six and seven for Cd(II) ions are rarely found in one discrete compound without any secondary ligand; and (b) in our continuing study of 3d and 4f metal complexes with dipolar Schiff base ligands, $CdL^3(H_2O)(NO_3)$ (**2**) with N_3O_4 donors is the first example from hydrated Cd(II) salt promoting partial hydrolysis of the imine−phenol Schiff base ligand.

The reaction of $Cd(NO_3)_2·nH_2O$ with H_3L^1 or H_2L^2 in methanol solution at room temperature for 6 h afforded pale yellow crystals **1** and **2**,[10,11] respectively. The IR spectra of two complexes show that there are all small red shifts appear in ν(C=N), ν(C−O), and ν(C−N) compared with the free H_3L^1 or H_2L^2 values, indicating N and O atoms of ligand H_3L^1 or H_2L^3 ligated to central metal Cd^{II} ions. In addition, the very wide band for ν (O−H) at 3409 cm^{-1} in the ligand H_3L^1 as compared to the disappearance in the compound **1** coincides with the analytical result of the single-crystal stucture of $Cd_3L^1_2$ (**1**). However, a broad stretching bond at 3412 cm^{-1} in compound **2** is mainly attributed to the destruction of the Schiff base ligand (H_2L^2) to form a NH_2 group, which provides N−H bonds. To examine the thermal stability of the complexes, we carried out the thermogravimetric (TG) analyses of **1** and **2** from 20 to 800 °C. It can be seen from the TG curve of compound **2** that one water molecule was lost in the approximate temperature from 118 to 135 °C (calcd 4.06%, found 4.12%). A complicated decomposition reaction then took place when the heating continued.

a)

b)
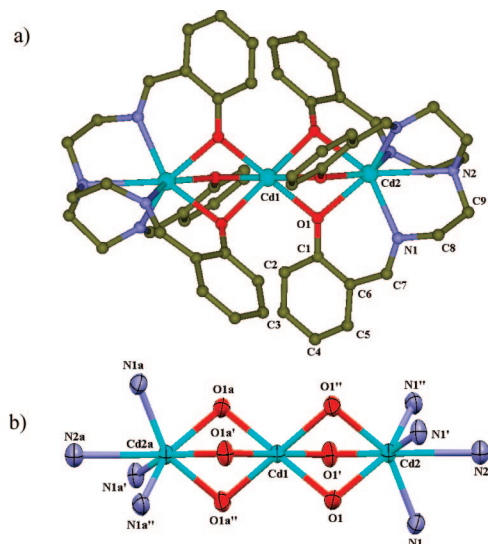
Figure 1. (a) Molecular structure of trinuclear compound **1**. Selected bond distances: Cd1−O1 2.278(2), Cd2−O1 2.331(2), Cd2−N1 2.311(2), Cd2−N2 2.695(2) Å. Hydrogen atoms are omitted for clarity. (b) Thermal ellipsoid plot (30% probability level ellipsoids) viewed perpendicular to the C_3 axis; the noncoordinating atoms remote from the central metal ions were omitted for clarity.

The preliminary thermogravimetric analysis of $Cd_3L^1_2$ (**1**) shows no weight loss below 320 °C and the coordination framework decomposition up to a temperature of 345 °C (see the TG curve in the Supporting Information S1).

Single-crystal structural analysis showed that the neutral tricadmium complex $Cd_3L^1_2$ (**1**) is a five-component molecular aggregate consisting of a linear arrangement tricadmium core, in which three Cd(II) atoms exist in dissimilar environments, and two trensal^{3-} ligands with different helical chirality (Δ or Λ) as shown in Figure 1. Two terminal Cd^{II} atoms are bound by all of the nitrogen atoms and phenolate oxygens of $(L^1)^{3-}$ and are seven-coordinate mono-capped octahedrons with N_4O_3 donor sets, giving one Δ-$[CdL^1]^-$ and one Λ-$[CdL^1]^-$ unit defined by the C_3 helical configurations of $(L^1)^{3-}$ and the NO chelate conformations. The central Cd^{II} atom shows six-coordinate distorted octahedral geometry ligated by six phenolate oxygen atoms from two $[CdL^1]^-$ units, where each $[CdL^1]^-$ unit acts as a tridentate ligand to the central Cd^{II} atom. Such coordination numbers of six and seven around Cd(II) ions are rarely found in one discrete compound **1** without any auxiliary ligand.[12] The C_3 axis passes through the two apical tertiary amino nitrogen atoms (N2, N2a) and the three cadmium atoms (Cd2, Cd1, Cd2a) with a symmetry center in the central Cd1 atom, so that the Cd_3L_2 has S_6 symmetry. All Cd−N and Cd−O bond distances show no remarkable features and closely resemble those in literature,[13] and selected bond distances are listed in Figure 1. Viewed down the C_3 axis direction, two staggered trensal^{3-} ligands present the right- and left-handed propeller appearance, respectively, and form the canonical six-blade propeller with the smallest steric hindrance and the stablest conformation (Figure 2). As each trensal^{3-} ligand possesses three phenoxo oxygen atoms lying on the edge of the coordination spheres of [Cd(trensal)]$^-$ motifs, which are potential bridging coordination atoms, it is possible in principle to self-assemble two secondary building units (SBUs) [Cd(trensal)]$^-$ species by employing Cd^{2+} ion with flexible and variable coordination behavior into three different conformational trinuclear complexes $Cd_3L^1_2$ (ΔΔ, ΔΛ, ΛΛ), finally only the meso-compound with double-propeller-like topology (where each tripodal ligand exhibiting a different Δ or Λ mode propeller sense) was obtained. Alternatively, the mesocate trinuclear compound $Cd_3L^1_2$ may be also prepared by metal template synthesis from tris(aminoethyl)-amine, salicylaldehyde and cadmium(II) perchlorate. The potential
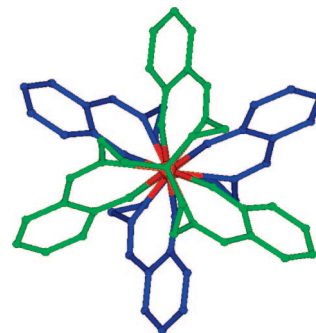
Figure 2. Top view of the mesocate (Δ + Λ conformation, Δ blue, Λ green) trinuclear $Cd_3(trensal)_2$ with S_6 symmetry.
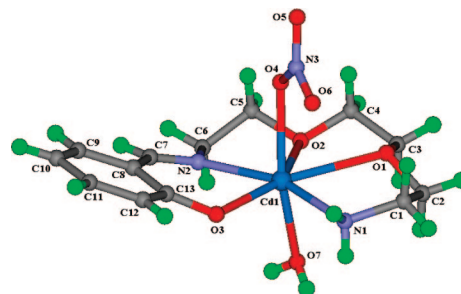

Figure 3. Coordination environment of the central cadmium ion in $Cd^{II}L^1(H_2O)(NO_3)$ (**2**). Selected bond lengths (Å) and angles (deg): Cd1−N1 2.298(2), Cd1−N2 2.317(2), Cd1−O3 2.274(2), Cd1−O7 2.342(2), Cd1−O4 2.350(2), Cd1−O2 2.602(2), Cd1−O1 2.624(2), O1−Cd1−N1 68.85(8), O1−Cd1−O2 62.46(8), O1−Cd1−O7 85.90(7), O1−Cd1−O4 78.88(8), O2−Cd1−N2 68.03(8), N2−Cd1−O3 79.04(7), N1−Cd1−O3 81.20(7).

enantioselective assembly route is illustrated in Scheme S2 (Supporting Information S2).

As compared with tripodal imine−phenol Schiff base ligand H_3L^1, the reaction of $Cd(NO_3)_2 \cdot nH_2O$ with dipolar imine−phenol ligand 2-((2-(2-(2-aminoethoxy)ethoxy)ethyl-imino)methyl)phenol (H_2L^2) (cif file and molecular structure for H_2L are presented in Supporting Information S3−S4) under the same reaction conditions gives one unexpected $CdL^3(H_2O)(NO_3)$ (**2**), the crystal structure of which is presented in Figure 3. The result reveals that one imine bond in the dioxa-imine phenol ligand H_2L^2 is degraded into NH_2 group and that one salicylaldehyde is thrown away, giving the almost closed complex **2**. We could find that the central cadmium atom is seven-coordinated as a distorted pentagonal bipyramidal geometry with N_2O_3 pentagonal plane constructed by new ligand $(L^3)^-$, one water molecule and one nitrate occupying the axial positions below and above the pentagon-planar, respectively. Moreover, intermolecular hydrogen bonding interactions (N−H···O, O−H···O, and C−H···O) result in the formation of 3D supramolecular network (see Supporting Information S5), which contribute to the additional stability of the structure.

The imine−phenol Schiff base ligands are normally not considered to be liable to hydrolysis considering the stronger intramolecular hydrogen bonds, despite the presence of a C=N linkage. To further assess the extent to which ligand H_2L^2 is prone to hydrolysis, we refluxed ligand H_2L^2 in ethanol and mixed solvent of water and ethanol (ratio 1:10 in volume) for 10 h, respectively, and there was no evidence of any hydrolysis. These data lead to the conclusion that the partial hydrolytic destruction of ligand H_2L^2 depends, in this case, upon the coordination-induced effect of cadmium(II). It is well-known from the potential coordination modes of dipolar ligand H_2L^2 that complexation to Cd^{II} ion generates coordinatively unsaturated metal sites within complexes, which could further bind different exogenous auxiliary ligands by

Scheme 2. Proposed Mechanism for the Formation of 2
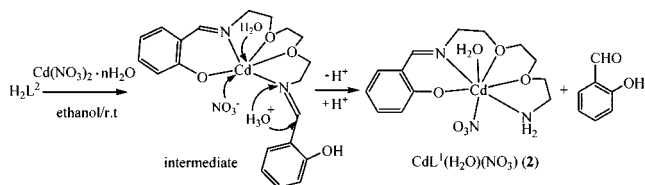
occupying the vacant positions. Once the reaction conditions are appropriate, like Cu^{II} and Zn^{II} reported in the literature, the Cd^{II}-catalyzed partial degradation of imine−phenol ligand takes place as reported here. According to the idea proposed earlier by J. Parr and co-workers,[7c] a proposed mechanism for the formation of **2** was suggested in Scheme 2. Coordination and so deprotonation of one arm of the dipolar ligand H_2L^2 to Cd^{2+} possibly forms small quantities of $H_3O^+NO_3^-$, which catalyzes the hydrolysis of the remaining unbound salicylidene arms back to amine groups more rapidly than the cascade of complexations of the remaining salicylidene units. The amine groups so generated then bind to the metal center in preference to any condensation with free salicylaldehydes present in solution (that is, template destruction). Because there has been no direct evidence of some intermediates, either from ${}^1H$ NMR or from mass spectrometry, the detailed mechanism of this cadmium-driven ligand degradation reaction is currently under investigation.

Tripodal imine−phenol ligand $N[CH_2CH_2N]]CHC_6H_4−OH-2]_3$ (H_3L^1) has a well-explored coordination chemistry.[7] Complexation of larger cations such as lanthanides and Bi^{III} etc. by triply deprotonated ligand L^{3-} gives rise to N_4O_3 donor sets at the metal center. However, small cations, for example, Cu^{2+}, Zn^{2+} etc., with such ligands are usually assembled into five- or four-coordinate complexes containing one unbound arm with the partial hydrolysis of ligands. By comparison, because of the size of Cd(II) ion lying in between, the formed Δ- and Λ-Cd^{II}(trensal)$^-$ species as tridentate bridging SBUs further coordinated to the Cd^{II} ion with the large coordination flexibility compared with Cu^{2+} and Zn^{2+}, resulting in the formation of trinuclear compound **1** with the high thermal and chemical stability. In other words, via the template effect of Cd^{2+}, two different chiral Cd^{II}(trensal)$^-$ units are assembled into compound **1** (namely, template assembly). Obviously, the high stability of compound **1** may be attributed to large chelating effect in the molecule, in which there exist six six-membered, six five-membered and six four-membered chelating rings. Accordingly, unlike Cu^{II} and Zn^{II}, hydrated Cd^{II} salt can not promote the partial hydrolysis of tripodal ligand H_3L^1 at the reaction conditions employed.

From the above analysis and discussion, though the difference of two ligands (L^1 is tripodal and L^2 dipolar), the coordination-induced effect of cadmium(II) plays a very important role in the different assembling process of compounds **1** and **2** under the employed reaction conditions. Cd^{2+} ion (radius, big; CN, high) makes ligand L^1 facilitate the template assembly, and ligand L^2 tend to the template destruction. Our recent findings $[ZnL^4][ClO_4]$ (**3**)[14] and ZnL^2 (**4**),[15] respectively from reactions of H_3L^1 and H_2L^2 with Zn^{2+}(cif files and molecular structures for **3** and **4** are presented in Supporting Information S7−S9), further approve this idea, following which Zn^{2+} (radius, small; CN, low) favors ligand L^1, template destruction, and facilitates L^2, template assembly, which are confirmed by the crystal structures of **3** and **4** (Scheme 3 and Supporting Informatin S8−S9).

Compound **1** exhibits a photoluminescence emission maximum at $\lambda = 437$ nm (upon excitation at $\lambda = 377$ nm), which may be assigned to ligand−metal charge transfer LMCT,[16] whereas the emission maximum of H_3L^1 at 448 nm (upon excitation at $\lambda = 367$ nm) is attributable to the $\pi^* \rightarrow n$ transitions (see Supporting Information S6). The lifetime of **1** is about 12 ns, which is similar to other Cd−organic complexes.[17] The enhancement and blue-shift of the photoluminescence of the coordinated trensal^{3-} ligand

Scheme 3. Different Assembling Strategies Induced by the Coordination Effect in 1 and 2
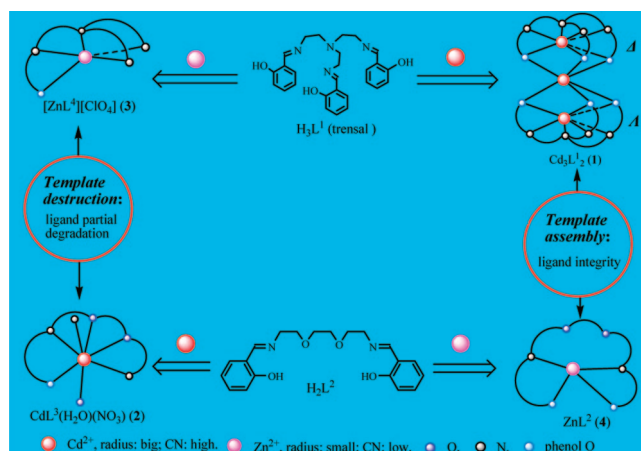
compared to that of the free trensal^{3-} molecule may, therefore, be attributed to the chelating of the trensal^{3-} ligand to the metal ion, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay of the intraligand emission exited state.[18] The strong fluorescence emission of **1** makes it a potentially useful photoactive material in photophysical chemistry for its high thermal and chemical stability.

In conclusion, two novel cadmium(II) complexes have been synthesized and characterized through two different synthetic strategies, template assembly for **1** and template destruction for **2**. To the best of our knowledge, such $Cd_3L^1_2$ (**1**) mesocate with S_6 symmetry represents the first crystallographically characterized example, which enriches the topological geometries of discrete molecular architectures. However, compound **2** is first constructed from in situ Cd^{II}-catalyzed partial degradation of dipolar imine−phenol ligand under the same reaction conditions, which further expands studying models of the hydrolysis of the imine−phenol Schiff base types. Obviously, the coordination-induced effect presented here, yielding a new asymmetric tripodal/dipolar multidentate Schiff base ligand, offers the intriguing possibility of preparing asymmetric tripodal/dipolar imine−phenol Schiff base ligands displaced from the metals. Using this synthetic route, we are currently preparing tripodal/dipolar ligands with nonequivalent legs through further substitution in a variety of ways for the arm of NH_2 groups of H_2L^3/HL^4 formed in reaction systems. Moreover, the intense fluorescence property of the complex **1** at room temperature suggests that it exhibits potential application as photoactive materials.

Supporting Information Available: X-ray crystallographic information; scheme description of the potential enantioselective assembly route for **1**; and some supplementary figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) (a) Preparation of $Cd_3L^1{}_2$ (**1**). An ammount of 231 mg (0.75 mmol) of $Cd(NO_2) \cdot 4H_2O$ and 140 mg (0.50 mmol) of H_3L^1 were added to 15 mL of methanol, and the mixture was stirred for 30 min at room temperature. After filtration, the filtrate was kept at room temperature for several days to give colorless crystals upon slow evaporation of the solvent. The crystals were filtered and dried in air. Yield: 28% (based on Cd). Anal. Calcd for $C_{54}H_{54}Cd_3N_8O_6$: C, 51.89; H, 4.48; N, 8.87. Found: C, 51.91; H, 4.33; N, 8.98. IR (KBr, cm^{-1}): ν 2969– 2846 (m), 1630 (s), 1534 (m), 1465(m), 1446(w), 1411(s), 1325(w), 1261(w), 1220(m), 1099(s), 1003(m), 927(m), 809(s), 733(m), 622(s), 575(s), 469(w). (b) Compound **2** was obtained using the same reaction procedure as described in compound **1** taking H_2L^2 in place of H_3L^1. The colorless crystals of **2** were isolated in about 22% yield (based on Cd). Anal. Calcd for $C_{13}H_{21}CdN_3O_7$: C, 35.16; H, 4.73; N, 9.47. Found: C, 35.11; H, 4.80; N, 9.50. IR (KBr, cm^{-1}): ν 3411(br,s), 2923(w), 1634(m), 1567(s),1470(w), 1411(w), 1385(w), 1343(w), 1110(w), 1020(w), 927(w), 653(m).

(11) (a) Crystal data for **1**: $C_{54}H_{54}N_8O_6Cd_3$, MW = 1248.25, rhombohedral, $R\bar{3}$, $a = 13.15130(10)$ Å, $c = 25.8357(5)$ Å, $V = 3869.80(9)$ Å^3, $Z = 3$, $F(000) = 1878$, GOF = 1.015, R1 = 0.0297, wR2 = 0.0631 [$I > 2\sigma(I)$]. For **2**: $C_{13}H_{21}N_3O_7Cd$, MW = 443.73, monoclinic, $C2/c$, $a = 20.903(4)$ Å, $b = 20.726(3)$ Å, $c = 8.3230(14)$ Å, $\beta = 104.681(8)°$, $V = 3488.1(10)$ Å^3, $Z = 8$, $F(000) = 1792$, GOF = 1.022, R1 = 0.0239, wR2 = 0.0592 [$I > 2\sigma(I)$]. CCDC-653375 (**1**) and 657168 (**2**) contain the supplementary crystallographic data for this paper.

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(14) Crystal data for **3**: $C_{13}H_{21}ClN_4O_5Zn$, MW = 414.16, monoclinic, $P2(1)/c$, $a = 20.7039(19)$ Å, $b = 13.8092(13)$ Å, $c = 14.7831(13)$ Å, $V = 4213.1(7)$ Å^3, $Z = 8$, $F(000) = 1712$, GOF = 1.147, R1 = 0.1047, wR2 = 0.1500 [$I > 2\sigma(I)$].

(15) Crystal data for **4**: $C_{20}H_{22}N_2O_4$, MW = 419.77, triclinic, $P\bar{1}$, $a = 8.4141(2)$ Å, $b = 10.4120(3)$ Å, $c = 12.3978(3)$ Å, $V = 959.66(4)$ Å^3, $Z = 2$, $F(000) = 436$, GOF = 1.059, R1 = 0.0267, wR2 = 0.0683 [$I > 2\sigma(I)$].

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