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Self-Assembly of *N*,*N*′,*N*′′,*N*′′′-Tetra(pyridin-4-yl)-1,4,7,10-tetraazacyclododecane-1,4,7,10-tetracarboxamide with Zn^{2+} or Cd^{2+} Ions

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Keywords: Charge transfer / Luminescence / Metallomacrocycles / Self-assembly / Supramolecular chemistry

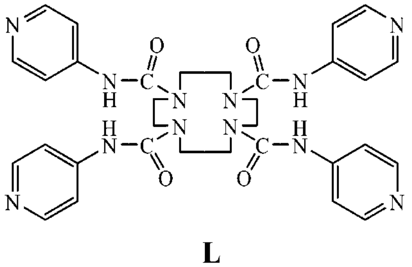
We report the design and synthesis of *N*,*N*′,*N*′′,*N*′′′-tetra(pyridin-4-yl)-1,4,7,10-tetraazacyclododecane-1,4,7,10-tetracarboxamide (**L**), which contains four *N*-(pyridin-4-yl)carboxamide groups as functional appendages, as well as the structural and luminescence properties of its Zn^{2+} and Cd^{2+} complexes. The reaction of $ZnBr_2$ with **L** forms the two-dimensional coordination polymer $[ZnBr_2(\mathbf{L})_{1/2}]_n$ (**1**). In the two-dimensional domain, the 68-membered metallomacrocycles as well as 12-membered 1,4,7,10-tetraazacyclododecane (cyclen) units propagate into two-dimensional extended structures. Interestingly, the metallomacrocycles are stacked to form one-dimensional parallelogram channels in the solid state. In addition, the reaction of CdX_2 (X = Br, I) with **L** forms the isomorphous, three-dimensional coordination networks $[CdX_2(\mathbf{L})]_n$ [X = Br (**2**), I (**3**)], which have tubular channels in the solid state. **L** in **1**–**3** is tetradentate and acts as a versatile connector in the construction of supramolecular coordination networks. The 34-membered metallomacrocycles and 12-membered cyclen macrocycles of **2** and **3** also propagate into three-dimensional extended structures. Unlike those of **1** and **2**, the emission maximum at around 439 nm in the iodo compound **3** can be assigned to a ligand-to-metal charge-transfer (LMCT) transition as the excited state upon photoexcitation.

Introduction

The widespread use of the coordinative-bond approach in the construction of supramolecular coordination compounds by self-assembly is well established.[1] So far, a variety of one-, two-, and three-dimensional infinite solid-state coordination architectures[2] as well as discrete molecular structures have been isolated and structurally characterized.[1] Applications, including chemical sieving, sensing, and catalysis based on the supramolecular coordination compounds have been discovered, and some have shown really exciting and valuable progress.[3] Surprisingly, the ligands used in the assembly of materials are generally didentate, with some tridentate ones;[1,2] tetradentate ligands are relatively scarce.[4] A macrocyclic ligand with a tetraaza macrocycle seems a good candidate in this regard since macrocyclic compounds have long attracted great interest owing to their intriguing structural and spectroscopic properties as well as host–guest chemistry.[5] In addition, tetraaza macrocycles can be easily functionalized by several groups, such as alkynyl,[6] phosphanylmethyl,[7] carboxyl,[8] and pyridyl[9] on their secondary N-sites to produce some novel properties in coordination, electro- and photoluminescent, and catalytic chemistry.

We have previously reported a study of metal-containing cyclic amides based on a didentate *N*-pyridylcarboxamide ligand – *N*,*N*′-bis(4-methylpyridyl)oxalamide – where interesting solid-state frameworks featuring cyclic peptides are constructed from hydrogen bonding/π···π interactions.[10]

Organic amides have proved to be very useful in self-assembly through hydrogen bonding, and the assembled products often have relevance to biological systems. Most remarkably, cyclic oligoamides can give rise to interesting nanotube frameworks through inter-ring NH···O=C hydrogen bonding, as reported by Ghadiri et al.[11] A new *N*-pyridylcarboxamide ligand (**L**) is used here as a tetradentate ligand for a crystal-engineering study. We report the design and synthesis of *N*,*N*′,*N*′′,*N*′′′-tetra(pyridin-4-yl)-1,4,7,10-tetraazacyclododecane-1,4,7,10-tetracarboxamide (**L**), which contains four *N*-(pyridin-4-yl)carboxamide groups as functional appendages, as well as the structural and luminescence properties of its Zn^{2+} and Cd^{2+} complexes.



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Results and Discussion

Hosseini and co-workers[4c] have recently reported an interesting porphyrinic ligand with four *N*-pyridylcarboxamides as appendages for the construction of one- and two-dimensional Cu^{2+}-containing coordination networks as an example of supramolecular isomerism. Another new type of tetraaza macrocycle that contains four *N*-(pyridin-4-yl)-carboxamide groups as functional appendages for the construction of supramolecular coordination frameworks has also been designed and synthesized in this study. Unlike most of the literature studies, the tetradentate ligand (**L**) studied here is a rare example of a tetradentate ligand in a crystal-engineering study. A methanolic solution of $ZnBr_2$ and CdX_2 (X = Br, I) was carefully layered on top of a DMSO solution of **L** to give pale-yellow crystals of **1**·DMSO·4CH$_3$OH or colorless crystals of **2**·4DMSO and **3**·4DMSO, respectively, in good yield (70–80%) within a couple of days. The compounds are all air stable and photoluminescent in the solid state.

Description of the Crystal Structures

Complexes **1**–**3** were isolated and their molecular structures determined by an X-ray diffraction study, which confirmed the formation of coordination polymers in the solid state. The molecular structure of **1** (Figure 1, a) displays a two-dimensional coordination polymer where **L** acts as a tetradentate ligand. The cyclen macrocycle contains four *N*-pyridylcarboxamide appendages, each of which coordinates to tetrahedral Zn^{2+} ions; the Zn^{2+} ions coordinate to two bromides and another *N*-pyridylcarboxamide appendage. In the two-dimensional domain, the 68-membered metallomacrocycles built from four **L** and four $ZnBr_2$ units, as well as the 12-membered macrocycles of the cyclen units, propagate into two-dimensional extended structures. Interestingly, the metallomacrocycles are stacked to form one-dimensional parallelogram channels (as viewed along the *a* axis) in the solid state, as shown in Figure 1 (b); the diagonal distances of these parallelogram channels are 26.59 and 15.73 Å. In addition, doubly hydrogen-bonding interactions [N(3)–H(3A)···O(3): N(3)···O(3) = 3.041(7) Å, N(3)–H(3A)···O(3) = 159.95°; N(5)–H(5A)···O(3): N(5)···O(3) = 2.913(9) Å, N(5)–H(5A)···O(3) 167.09°] between the solvated DMSO molecules and amide groups are observed in the solid state; the channels are also filled with methanol molecules. Although **1** has a high *R* value due to the fast loss of solvated solvents, there is no doubt that the structural framework of **1** can be still corroborated by the X-ray diffraction study.

Both **2** and **3** are essentially isomorphous, therefore the molecular structure and the extended structural framework of **3** are shown in Figure 2, parts a and b, respectively, as a representative example. Unlike the two-dimensional coordination network of **1**, **2** and **3** both form three-dimensional coordination networks with octahedral Cd^{2+} ions coordinating to two anionic (Br, I) and four bridging **L** ligands, as shown in part a of Figure 2. In more detail, the four *N*-pyridylcarboxamide appendages of the cyclen macrocycle each coordinate to octahedral Cd^{2+} ions, which also coordinate to two bromides and another three N-pyridylcarboxamides. The cyclen plane is approximately perpendicular to that of the CdN_4 (pyridyl) unit, with two pyridyl groups (at positions 1 and 7) roughly coplanar with the cyclen plane and the other two (at positions 4 and 10) above and below the plane. This different orientation of **L** results in the formation of interesting three-dimensional coordination networks. Furthermore, the metallomacrocycles with 34-membered rings built from two $CdBr_2$ and two **L** units are packed into columns that form interesting tubular channels (viewed along the *b* axis) in the solid state, as shown in Figure 2 (b). Thus, the metallamacrocycles and cyclen macrocycles also propagate into three-dimensional extended structures. Hydrogen-bonding interactions [N(6)–H(6A)···O(4): N(6)···O(4) = 2.955(7) Å, N(6)–H(6A)···O(4) = 153.31°] between the solvated DMSO molecules and amide groups are observed in the solid state, and the channels are also filled with DMSO molecules. Upon changing the anion from Br^- to I^-, the *trans*-CdN_4X_2 geometry remains unchanged, and thus the structural frameworks also retain a similar structural motif.

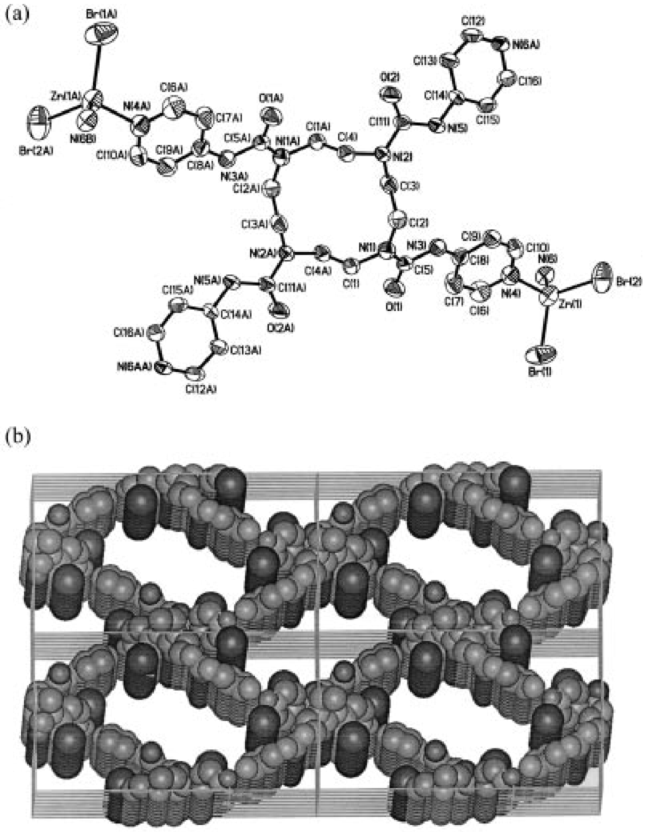

Figure 1. (a) Molecular structure of **1**·DMSO. ORTEP diagram shows 50% probability ellipsoids, and (b) its two-dimensional extended framework showing a 1-D channel structure with solvates omitted (viewing through the a axis) in the solid state.

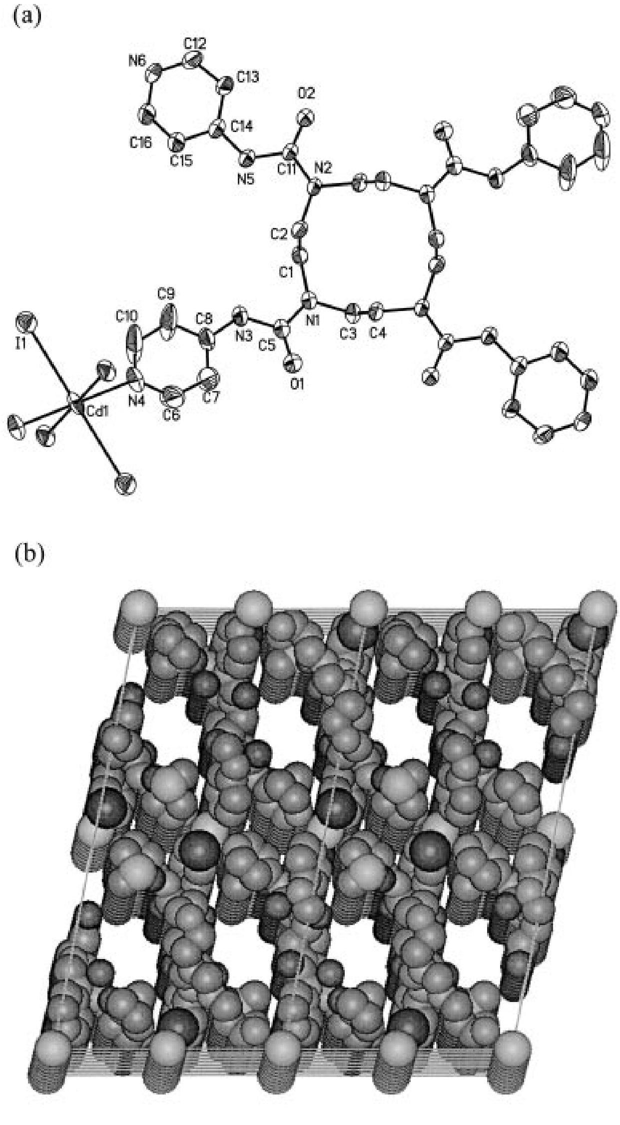

Figure 2. (a) Molecular structure of **3**. ORTEP diagram shows 30% probability ellipsoids, and (b) its three-dimensional extended framework showing a 1-D channel structure with solvates omitted (viewing through the b axis) in the solid state.

Very recently, Cao et al.[4a] reported a cyclam (1,4,8,11-tetraazacyclotetradecane)-based tetradentate ligand containing pyridylmethyl groups as appendages as well as the structural study of its two novel Cd^{2+} polymeric metallomacrocyclic complexes, where the ligand adopts μ_2- or μ_4-coordination modes in the structural framework. Indeed, the different coordination modes that co-exist in the same structure result in the formation of interesting three-dimensional coordination networks. In this study, it is interesting to find that given the same bridging ligands (**L**) and only one coordination mode (μ_4) in the system, the structural motif changes dramatically and the supramolecular complexity increases upon changing the metal ions from tetrahedral (four-coordinate) Zn^{2+} to octahedral (six-coordinate) Cd^{2+} ions. Unlike the structures reported by Cao et al.,[4a] which contain two coordination modes for the ligands in the same framework, the structures of **2** and **3** also form three-dimensional networks with tubular channels only due to the different orientation of the *N*-pyridylcarboxamide appendages of the cyclen moieties. In this context, **L** has been shown to be a tetradentate ligand that acts as a versatile connector in the construction of interesting supramolecular coordination networks. Unfortunately, crystals of **1**–**3** easily lose solvent, which causes the crystal lattices to collapse instantaneously and thus prevents further studies by TGA and powder XRD analysis that might allow us to gain some insight into the channel structures.

Solid-State Emission Spectra

L and **1**–**3** are all luminescent in the solid state, as shown in Figure 3 (a), at room temperature. Upon photoexcitation at 325 nm, **1** shows a broad emission with a maximum at around 412 nm, whereas **L** displays a similar emission at around 403 nm. Given the high similarity between these emissions, they were tentatively assigned to an intraligand (IL) transition. The solid-state emission of **2** (Figure 3, b) at room temperature has an emission maximum at around

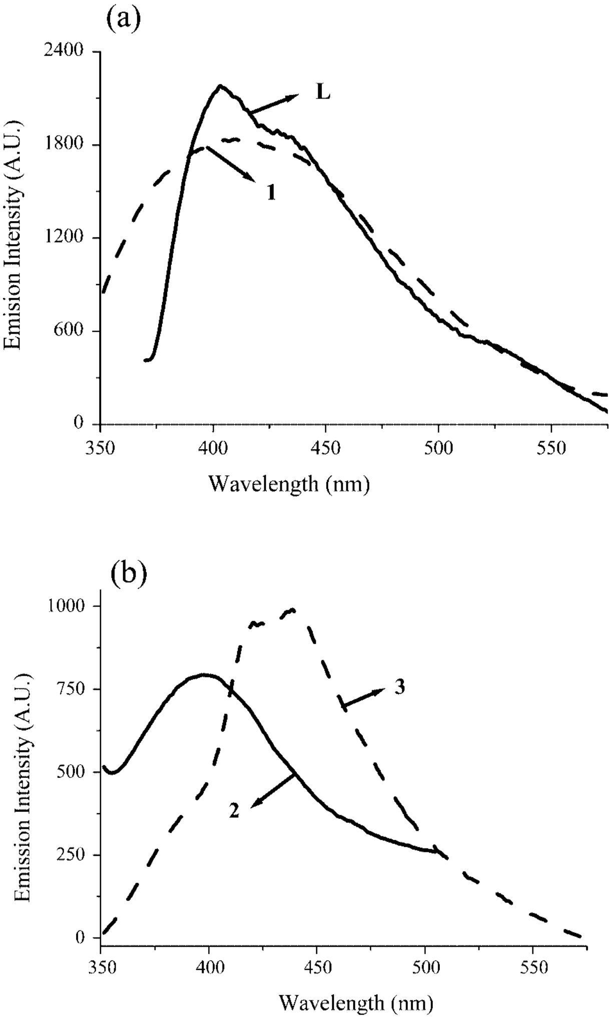

Figure 3. (a) The solid-state emission spectra of **L** and **1**, and (b) the solid-state emission spectra of **2** and **3** measured at room temperature with an excitation wavelength at 325 nm.

398 nm, which is also comparable to those of **L** and **1**. Thus, it seems reasonable that the excited state responsible for the emission for **2** is also an IL transition. Most importantly, **3** shows a solid-state emission with an emission maximum at around 439 nm, which is red-shifted with respect to those of **1** and **2**. In light of previous studies[10,12] and the red-shift in emission energy on going from the bromo to the iodo complex, this emission can tentatively be assigned to a ligand-to-metal charge-transfer (LMCT) transition, although intraligand transition mixing with LMCT cannot be excluded. Intraligand transitions as excited states are not uncommon for Zn^{2+} and Cd^{2+} complexes, but charge-transfer excited states are so far still rare.[13]

Conclusion

A new type of tetraaza macrocycle (**L**) containing four *N*-pyridylcarboxamide groups as functional appendages has been designed and synthesized in this study, which is a rare example of the use of a tetradentate ligand in a crystal-engineering study. Complex **1** can be isolated as a two-dimensional coordination polymer upon reaction of $ZnBr_2$ with **L**. In the two-dimensional domain, the 68-membered metallomacrocycles built from four **L** and four $ZnBr_2$ units, as well as the 12-membered macrocycles of cyclen, propagate into two-dimensional extended structures. Interestingly, the metallomacrocycles are stacked to form one-dimensional parallelogram channels in the solid state. In addition, reaction of CdX_2 (X = Br, I) with **L** leads to the formation of **2** and **3**, respectively, which form isomorphous three-dimensional coordination networks with tubular channels due to the different orientation of the *N*-pyridylcarboxamide appendages of the cyclen moieties. Again, the 34-membered metallomacrocycles built from two CdX_2 and two **L** units, as well as the 12-membered macrocycles of the cyclen units, propagate into three-dimensional extended structures in **2** and **3**. Unlike those of **1** and **2**, the emission maximum of the iodo compound **3** at around 439 nm can be tentatively assigned to a ligand-to-metal charge-transfer transition upon photoexcitation. The channel structure, as well as the luminescence properties, of these tetraazamacrocycle-based materials may be anticipated to hold potential for use as luminescent sensors. Moreover, the cyclen moiety acts as a versatile connector in the construction of supramolecular coordination networks, and is also capable of functioning as a receptor site for recognition events.

Experimental Section

General Information: All solvents for syntheses (analytical grade), which were used without further purification, and metal salts [$ZnBr_2$, CdX_2 (X = Br, I)] are commercially available. *N*,*N′*,*N′′*,*N′′′*-Tetra(pyridin-4-yl)-1,4,7,10-tetraazacyclododecane-1,4,7,10-tetracarboxamide (**L**) was prepared following literature methods.[14] MS: positive-ion FAB mass spectra were recorded with a Finnigan MAT95 mass spectrometer. Steady-state emission spectra were recorded with a SPEX Fluorolog-2 spectrophotometer.

Synthesis of *N*,*N′*,*N′′*,*N′′′*-Tetra(pyridin-4-yl)-1,4,7,10-tetraazacyclododecane-1,4,7,10-tetracarboxamide (L): Isonicotinic acid (2.00 g, 16.24 mmol) was put into a 250-mL, two-necked flask with toluene (100 mL), under an atmosphere of nitrogen, and the mixture was stirred for ten minutes after addition of triethylamine (2.72 mL, 19.49 mmol). After addition of phosphorazidic acid diphenyl ester (3.15 mL, 14.62 nm) the solution was stirred for one hour; it gradually became colorless. The solution was later refluxed for three hours at 90 °C (it became yellow) and was then cooled to room temperature. 1,4,7,10-Tetraazacyclododecane (0.56 g, 3.25 mmol) dissolved in 100 mL of toluene was slowly and carefully transferred into the above two-necked flask to give a pale-yellow precipitate after stirring for two days at room temperature. The toluene was then removed under vacuum and the ligand was recrystallized from 200 mL of methanol to give a pure and white solid (0.64 g, 0.975 mmol) in 30% yield. MS (FAB): *m*/*z* (%) = 654 (35) [M^+]. ^1H NMR (400 MHz, [D6]DMSO, 25 °C): δ = 3.69 (s, 4 H, C*H*2), 7.48 (d, 2 H, NCH2C*H*2], 8.32 (d, 2 H, NC*H*2), 8.88 (s, 1 H, N*H*) ppm. ^{13}C NMR (400 MHz, [D6]DMSO, 25 °C): δ = 47.67,

Table 1. Crystallographic data for **1**·DMSO·4CH_3OH, **2**·4DMSO and **3**·4DMSO.

	1·DMSO·4CH3OH	**2**·4DMSO	**3**·4DMSO
Empirical formula	$C_{22}H_{40}Br_2N_6O_7SZn$	$C_{40}H_{60}Br_2CdN_{12}O_8S_4$	$C_{40}H_{60}CdI_2N_{12}O_8S_4$
Formula mass	757.85	1237.46	1331.46
Crystal system	monoclinic	monoclinic	monoclinic
Space group (No.)	$P2_1/c$	$C2/c$	$C2/c$
a [Å]	10.5783(5)	32.643(2)	33.074(3)
b [Å]	26.5867(12)	9.9817(6)	9.8463(7)
c [Å]	15.7293(7)	16.6382(11)	16.8512(12)
β [°]	108.604(2)	101.032(2)	101.712(2)
V [Å^3], Z	4192.6(3), 4	5321.2(6), 4	5373.5(7), 4
F(000) (e)	1544	2520	2656
μ (Mo-$K\alpha$) [mm^{-1}]	2.577	2.127	1.769
T [K]	295(2)	295(2)	295(2)
Reflections collected	41668	30975	31119
Independent reflections [$F_o \geq 2\sigma(F_o)$]	9627 (R_{int} = 0.070)	6495 (R_{int} = 0.055)	6553 (R_{int} = 0.032)
Refined parameters	367	308	307
Goodness-of-fit on F^2	1.039	1.032	1.072
R[a], R_w[b] [$I \geq 2\sigma(I)$]	0.096, 0.283	0.072, 0.178	0.055, 0.150
R[a], R_w[b] (all data)	0.162, 0.344	0.102, 0.200	0.068, 0.163

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

113.71, 147.46, 150.03, 155.48 ppm. FT-IR (KBr): ν_{NH} = 3358 and $\nu_{C=O}$ = 1654 cm^{-1}. $C_{32}H_{36}N_{12}O_4$ (652.71): calcd. C 58.88, H 5.56, N 25.75; found C 59.05, H 5.78, N 25.67.

Synthesis of $[ZnBr_2(L)_{1/2}]_n$ (1) and $[CdX_2(L)]_n$ [X = Br (2), I (3)]

1: $ZnBr_2$ (30 mg, 0.14 mmol) dissolved in 2 mL CH_3OH was carefully layered onto a DMSO solution of **L** [90 mg (0.14 mmol), dissolved in 2 mL of DMSO]. The pale-yellow crystals were obtained in two days with a ca. 70% yield. FT-IR (KBr): ν_{NH} = 3300 and $\nu_{C=O}$ = 1681 cm^{-1}. $C_{16}H_{18}Br_2N_6O_2Zn$ (551.55): calcd. C 34.84, H 3.29, N 15.24; found C 34.58, H 3.48, N 15.09.

2: $CdBr_2$ [30 mg, 0.11 mmol] dissolved in 2 mL CH_3OH was carefully layered onto a DMSO solution of **L** [70 mg (0.11 mmol), dissolved in 2 mL of DMSO]. The colorless crystals were obtained in three days with a ca. 80% yield. FT-IR (KBr): ν_{NH} = 3313 and $\nu_{C=O}$ = 1669 cm^{-1}. $C_{32}H_{36}Br_2CdN_{12}O_4$ (924.93): calcd. C 41.55, H 3.92, N 17.28; found (%): calcd. C 41.18, H 3.78, N 17.09. **3**: It was prepared in a similar method as **2** except using CdI_2 instead of $CdBr_2$ and the colorless crystals were obtained in a ca. 80% yield. FT-IR (KBr): ν_{NH} = 3300 and $\nu_{C=O}$ = 1681 cm^{-1}. $C_{32}H_{36}CdI_2N_{12}O_4$ (1018.93): calcd. C 37.72, H 3.56, N 16.50; found C 37.35, H 3.78, N 16.69.

X-ray Crystallography: Suitable single crystals of **1**·DMSO·4CH_3OH, **2**·4DMSO, and **3**·4DMSO were mounted on a glass capillary respectively, and data collection was carried out on a Bruker SMART CCD diffractometer with Mo radiation (0.71073 Å) at 295(2) K. A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 15 frames each, each frame corresponding to 0.3° scan in 15 s, followed by spot integration and least-square refinement. Data were measured using an ω scan of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART[15] software and refined with SAINT[16] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[17] The structure was solved by direct methods with the SHELX93[18] program and refined by full-matrix least-squares methods on F^2 with SHEXLTL–PC V 5.03.[18] All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. Detailed data collection and refinement of the four complexes are summarized in Table 1. Selected bond lengths and angles in the structures are summarized in Table 2, and hydrogen bonds are given in Table 3, respectively.

Table 2. Selected bond lengths [Å] and angles [°] for **1**, **2**, and **3**.

1	Zn(1)–N(4)	2.039(6)	Zn(1)–N(6)	2.012(5)
	Zn(1)–Br(1)	2.352(2)	Zn(1)–Br(2)	2.350(2)
	N(6)–Zn(1)–N(4)	107.2(2)	N(6)–Zn(1)–Br(2)	107.6(2)
	N(4)–Zn(1)–Br(2)	107.9(2)	N(6)–Zn(1)–Br(1)	109.8(2)
	N(4)–Zn(1)–Br(1)	108.0(2)	Br(2)–Zn(1)–Br(1)	116.0(1)
2	Cd(1)–N(1)	2.385(5)	Cd(1)–Br(1)	2.890(1)
	N(1)–Cd(1)–Br(1)	92.1(2)	C(1)–N(1)–Cd(1)	119.9(5)
	C(5)–N(1)–Cd(1)	125.8(5)		
3	Cd(1)–N(4)	2.421(4)	Cd(1)–I(1)	3.080(1)
	N(4)–Cd(1)–I(1)	91.9(1)	C(10)–N(4)–Cd(1)	119.8(5)
	C(6)–N(4)–Cd(1)	126.9(5)		

CCDC-282733 to -282735 (for complexes **1**, **2**, and **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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Table 3. Hydrogen bonds in the structures for **1**·DMSO·4CH_3OH, **2**·4DMSO, and **3**·4DMSO.[a]

Complex	D–H···A [Å]	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
1·DMSO·4CH_3OH	N(3)–H(3A)···O(3)	0.860	2.219	3.041(7)	159.95
	N(5)–H(5A)···O(3)	0.860	2.068	2.913(9)	167.09
2·4DMSO	N(6)–H(6A)···O(4)	0.860	2.161	2.955(7)	153.31
3·4DMSO	N(5)–H(5A)···O(3)[a]	0.860	2.136	2.940(7)	155.52

[a] Symmetry positions of atoms: (a) 1 –*x*, *y*, 1/2 – *z*.

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