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Synthesis, Structure, and Stereochemistry of Trinuclear Metal Complexes Formed from the Phosphorus-Based Achiral Tripodal Ligand $\{P(S)[N(Me)N{=}CHC_6H_4\text{-}o\text{-}OH]_3\}$ (LH_3): Luminescent Properties of $L_2Cd_3\cdot 2H_2O$

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Neutral trinuclear metal complexes $L_2Cd_3\cdot 2H_2O$, $L_2Mn_3\cdot MeOH$, and $L_2Zn_3\cdot MeOH$ were isolated in the reaction between the phosphorus-centered achiral tris(hydrazone) $P(S)[N(Me)N{=}CHC_6H_4\text{-}o\text{-}OH]_3$ (LH_3) and the corresponding divalent metal ions. The trinuclear complexes contain two equivalent terminal metal ions (M_t) and a central metal ion (M_c). The ligand encapsulates M_t in a facial N_3O_3 coordination environment. From the coordination sphere of the two terminal metal ions a pair of phenolic oxygen atoms further coordinate to the central metal ion. The coordination requirements of M_c are completed by the solvents of coordination. The achiral trianionic tripodal ligand $(L)^{3-}$ induces chirality in the metal complexes. This results in a Δ (clockwise) or Λ (anticlockwise) configuration for the terminal metal ions. The enantiomeric complexes **2**–**4** (Δ–Δ or Λ–Λ) crystallize as racemic compounds. The supramolecular structures of **2**–**4** reveal chiral recognition in the solid-state; every molecule with the Δ–Δ configuration interacts stereospecifically, through C–H···S=P bonds, with two Λ–Λ molecules to generate a one-dimensional polymeric chain. Photophysical studies of the diamagnetic trinuclear complexes reveal that the tricadmium complex is luminescent in the solid state as well as in solution. In contrast LH_3 and $L_2Zn_3\cdot MeOH$ are nonluminescent.

Introduction

Chirality is a fundamental trait that pervades the living world, and the preference for one enantiomer over the other is a peculiar feature of the biological milieu. However, this phenomenon is not restricted or important only for the living beings. The concept of chirality is of great importance in chemistry, pharmacy, biochemistry, and material science.[1] Since the pioneering demonstration by Alfred Werner that *pure inorganic complexe*s can also possess chirality and optical activity, the importance of this phenomenon in inorganic chemistry and coordination chemistry has been well recognized. Chiral coordination complexes find applications in enantioselective synthesis, in asymmetric catalysis, as nonlinear optical materials, or even as novel magnetic materials.[1−3] Expression of chirality in coordination complexes occurs both at the molecular and supramolecular level.[4] At the molecular level chiral coordination compounds

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may be obtained by any of the following two routes: (1) by enantioselective synthesis using enantiopure ligands;[5] (2) by a spontaneous resolution upon crystallization of a racemic compound.[6,7] Thus, a racemate (a mixture of equal amounts of both the mirror images or the left and right-handed configurations of a compound) can crystallize in three ways;[8] (1) It can crystallize to generate a *racemic compound* where both the enantiomers are present in *every* crystal in an *ordered arrangement*. (2) It can crystallize to generate a *conglomerate*, where the two enantiomers crystallize out separately. This process is in fact spontaneous resolution under crystallization conditions. The classic example of this phenomenon is the one discovered by Louis Pasteur.[9] (3) It can crystallize to generate a *pseudoracemate*, where both the enatiomers are present in *every* crystal in a *disordered arrangement*. Jaques et al. have pointed out that only less than 10% of the racemates form conglomerates.[8] Also, the formation of the latter cannot be predicted a priori; the laws of physics determining these processes are not well understood.[10] In this study, we show the generation of chirality in trinuclear metal complexes $L_2Cd_3{\cdot}2H_2O$ (**2**), $L_2Mn_3{\cdot}MeOH$ (**3**), and $L_2Zn_3{\cdot}MeOH$ (**4**). These complexes are assembled from the phosphorus-based achiral ligand $P(S)[N(Me)N{=}CHC_6H_4\text{-}o\text{-}OH]_3$ (LH_3). Complexes **2**−**4** crystallize as racemic compounds and show chiral recognition in their crystal structures. We also report interesting luminescent properties of the trinuclear cadmium complex **2** in solution and the solid state as well as in a polymer matrix.

Experimental Section

Reagents and General Procedures. Solvents and other general reagents used in this work were purified according to standard procedures.[11] $P(S)Cl_3$ and salicylaldehyde (Fluka, Switzerland) were used as purchased. *N*-Methylhydrazine was obtained as a gift from the Vikram Sarabhai Space Research Centre, Thiruvananthapuram, India, and was used as such. $Cd(NO_3)_2{\cdot}4H_2O$, $Mn(OAc)_2{\cdot}4H_2O$, and $Zn(OAc)_2{\cdot}2H_2O$ were obtained from S.D. Fine Chemicals, Mumbai, India.

Instrumentation. Electronic spectra were recorded on a Perkin-Elmer-Lambda 20 UV−vis spectrometer using dichloromethane as the solvent. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating from 400 to 4000 cm^{-1}. Elemental analyses of the compounds were obtained from Thermoquest CE instruments CHNS-O, EA/110 model. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV, and the spectra were recorded at room temperature. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded in $CDCl_3$ solutions on a JEOL JNM LAMBDA 400 model spectrometer operating at 400.0, 135.0, and 100.4 MHz, respectively. Chemical shifts are reported in ppm with respect to internal tetramethylsilane (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Solution state emission spectra were recorded in a Perkin-Elmer LS 50B luminescence spectrofluorometer interfaced to the computer, and solid-state emission spectra were recorded in a computer-interfaced optical fiber spectrum analyzer with a He−Cd laser source (325 nm).

X-ray Crystallography. The crystal data and the refinement parameters for **2**−**4** are given in Table 1. Single crystals suitable for X-ray crystallographic analyses for **2** ($L_2Cd_3{\cdot}2H_2O$) were obtained by vapor diffusing *n*-hexane into its chloroform solution while those of **3** ($L_2Mn_3{\cdot}CH_3OH$) and **4** ($L_2Zn_3{\cdot}CH_3OH$) were obtained by vapor diffusing methanol into their chloroform solutions. All the crystals (**2**−**4**) lose their solvents of crystallization rapidly when taken out of the mother liquor at room temperature.

The crystal data for the compound **2** were collected on a Stoe IPDS machine, and data for **3** and **4**, on a Bruker AXS Smart Apex diffractometer. All structures were solved by direct methods using the programs SHELXS-97 and refined by full-matrix least-squares methods against F^2 with SHELXL-97.[12] Hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Preparation of Doped Polymer Films. Doped polymer thin films were prepared from a solution of 90% polystyrene (M_w = 35 000) and 10% L_2Cd_3 complex in dichloromethane. This solution was then spin coated on a quartz slide to ensure uniform distribution. Doped polymer thin films were obtained by drying the quartz slides in a vacuum oven at 60 °C.

Synthesis. The compounds $(S)P[N(Me)N{=}CHC_6H_4\text{-}o\text{-}OH]_3$-($LH_3$), $\{(S)P[N(Me)N{=}CHC_6H_4\text{-}o\text{-}O]_3\}_2Mn_3$ (L_2Mn_3), and $\{(S)P\text{-}[N(Me)N{=}CHC_6H_4\text{-}o\text{-}O]_3\}_2Zn_3$ (L_2Zn_3) were synthesized as reported previously.[13]

Synthesis of $\{(S)P[N(Me)N{=}CHC_6H_4\text{-}o\text{-}O]_3\}_2Cd_3$ (2). To a solution of the ligand LH_3 (0.6 mmol) and triethylamine (6 mmol) in chloroform (30 mL) was added dropwise a solution of the $Cd(NO)_3{\cdot}4H_2O$ (0.9 mmol) in methanol (30 mL) at room temperature, and the new solution was stirred for 6 h. The metal complex precipitated out of the reaction mixture and was filtered. This was dissolved in a minimum amount of dichloromethane (5 mL), and *n*-hexane was added to it until a slight turbidity appeared. This

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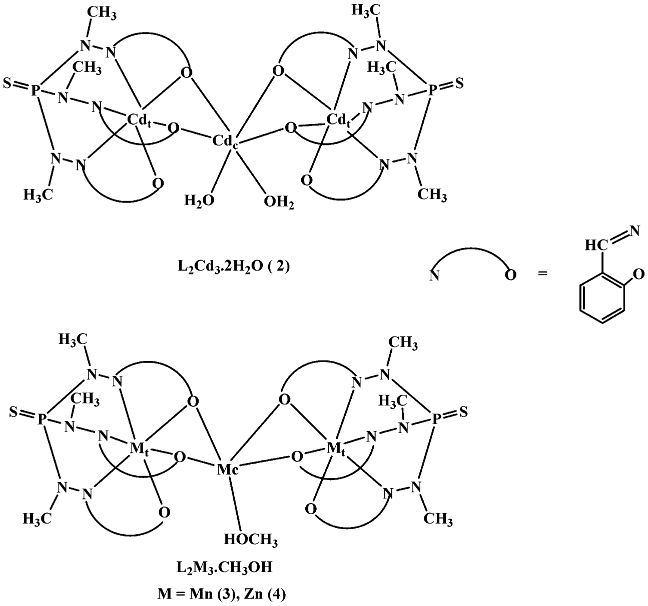
Table 1. Crystal and Structure Refinement Parameters for Compounds **2**−**4**

params	$L_2Cd_3{\cdot}2H_2O$ (**2**)	$L_2Mn_3{\cdot}CH_3OH$ (**3**)	$L_2Zn_3{\cdot}CH_3OH$ (**4**)
empirical formula	$C_{50}H_{52}Cd_3Cl_6N_{12}O_8P_2S_2$	$C_{51}H_{54}Cl_6Mn_3N_{12}O_7P_2S_2$	$C_{51}H_{54}Cl_6Zn_3N_{12}O_7P_2S_2$
fw	1625.00	1450.64	1481.93
temp (K)	200(2)	150(2)	150(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst system	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
unit cell dimens (Å, deg)	$a = 21.163(4)$, $\alpha = 90$ $b = 14.845(3)$, $\beta = 110.38(3)$ $c = 21.462(4)$, $\gamma = 90$	$a = 21.0597(10)$, $\alpha = 90$ $b = 14.8212(7)$, $\beta = 113.1320(10)$ $c = 21.1365(10)$, $\gamma = 90$	$a = 20.9480(13)$, $\alpha = 90$ $b = 14.9060(9)$, $\beta = 113.3(10)$ $c = 20.6966(13)$, $\gamma = 90$
V (Å^3, Z)	6321(2), 4	6066.9(5), 4	5935.5(6), 4
d(calcd) (Mg/m^3)	1.708	1.568	1.658
abs coeff (mm^{-1})	1.430	1.061	1.659
F(000)	3232	2956	3016
cryst size (mm^3)	0.2 × 0.3 × 0.2	0.5 × 0.4 × 0.3	0.4 × 0.3 × 0.16
θ range for data collcn (deg)	2.16−24.43	1.73−25.03	1.73−25.03
limiting indices	$-24 \leq h \leq 24$, $-17 \leq k \leq 16$, $-24 \leq l \leq 24$	$-24 \leq h \leq 25$, $-17 \leq k \leq 9$, $-24 \leq l \leq 25$	$-24 \leq h \leq 24$, $-13 \leq k \leq 17$, $-22 \leq l \leq 24$
reflcns collcd	20 352	15 664	15 355
indepndt reflcns	4768 ($R_{int} = 0.1029$)	5368 ($R_{int} = 0.0183$)	5240 ($R_{int} = 0.0468$)
completeness to θ (%)	91.4	99.9	99.8
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
data/restraints/params	4768/30/375	5368/34/388	5240/0/383
goodness-of-fit on F^2	1.099	1.033	0.998
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0580, wR2 = 0.1472	R1 = 0.0596, wR2 = 0.1642	R1 = 0.0505, wR2 = 0.1444
R indices (all data)	R1 = 0.0628, wR2 = 0.1553	R1 = 0.0637, wR2 = 0.1680	R1 = 0.0625, wR2 = 0.1513
largest diff peak and hole (e·Å^{-3})	1.478 and −0.932	2.127 and −1.542	2.318 and −0.946

was kept at 5 °C to obtain the title compound as a crystalline product. Yield: 0.32 g, 79.0%. Mp: >280 °C. UV−vis (CH_2Cl_2) [λ_{max}/nm (ϵ/L mol^{-1} cm^{-1})]: 355 (31 873), 282 (44 567). FT-IR ($\nu_{C=N}$/cm^{-1}): 1595 cm^{-1}. ^{1}H NMR: 3.38 (d, 9H, −N(C*H*$_3$); ^3J(^{1}H−^{31}P) =10.8 Hz), 6.33−6.37 (m, 3H, aromatic), 6.68−6.77 (m, 6H, aromatic), 6.88−6.90 (m, 3H, aromatic), 8.05 (s, 3H, imino). ^{13}C NMR: 37.55 (N−*C*H$_3$), 114.94, 117.60, 123.22, 133.33, 135.17, 161.41 (aromatic carbons), 168.14 (N═*C*H). ^{31}P NMR: 67.39 (s). FAB-MS: *m*/*z* 1352 (M$^+$). Anal. Calcd for $C_{48}H_{48}N_{12}O_6P_2S_2Cd_3$: C, 42.63; H, 3.58; N, 12.43. Found: C, 42.40; H, 3.24; N, 12.18.

Results and Discussion

Chart 1. Molecular Structures of $L_2Cd_3{\cdot}2H_2O$ (**2**) and $L_2M_3{\cdot}CH_3OH$ [M = Mn (**3**) and Zn (**4**)]



Acyclic phosphorus hydrazides have been very well studied by Majoral and co-workers for the formation of macrocycles and cryptands.[15] Katti and co-workers have shown that certain acyclic phosphorus hydrazides have excellent binding properties toward transition metal ions.[16] We have recently demonstrated that the phosphorus-centered tripodal hexadendate tris(hydrazone) P(S)[N(Me)N═CHC$_6$H$_4$-*o*-OH]$_3$ (LH$_3$) (**1**) is an effective ligand for the construction of neutral trinuclear metal arrays involving divalent metal ions.[13,14] The trinuclear cadmium complex (**2**) has been synthesized by reacting LH$_3$ with $Cd(NO_3)_2{\cdot}4H_2O$ in a 2:3 stoichiometric ratio. The ^{31}P{^{1}H} NMR chemical shift of this diamagnetic complex appears at 67.4 ppm (cf. δ(^{31}P{^{1}H}) of LH$_3$: 71.7). The complexes **3** and **4** have been synthesized as reported by us earlier by the reaction of the corresponding metal acetates with LH$_3$.[13] To understand the stereochemical implications of coordination by solvents, we carried out the X-ray crystal structures of $L_2Mn_3{\cdot}MeOH$ (**3**) and $L_2Zn_3{\cdot}MeOH$ (**4**). The molecular structures of **2**−**4** are depicted in Chart 1. As will be shown, vide infra, the coordinated solvent molecules have a significant influence on their crystal structures. In each of these trinuclear complexes the metal

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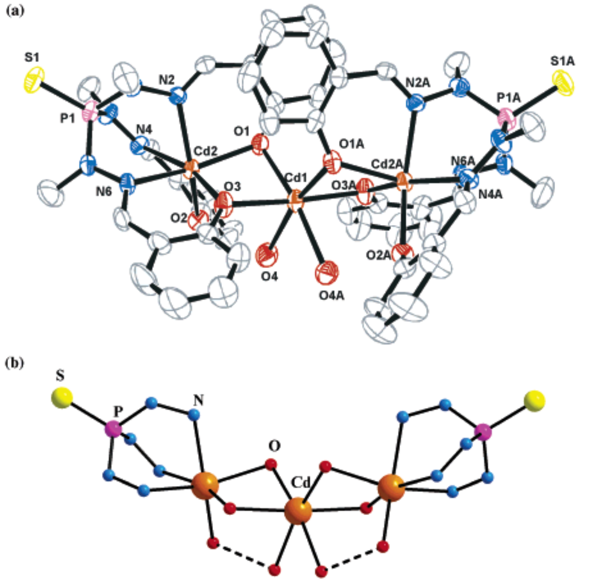

Figure 1. (a) ORTEP diagram of $L_2Cd_3{\cdot}2H_2O$ (**2**). Hydrogen atoms have been omitted for clarity. (b) Side view of the core of $L_2Cd_3{\cdot}2H_2O$.

ions are present in an oxidation state of +2. Two molecules of the tris(hydrazone) ligand (LH_3) are involved in the coordination to the three metal ions. Thus, each tris(hydrazone) molecule (LH_3) behaves as a tris-chelating, trianionic hexadentate ligand $(L)^{3-}$, supplying three imino nitrogen atoms and three phenolate oxygen atoms for coordination to the terminal metal ion (M_t).

X-ray Crystal Structures of 2−4. X-ray Crystal Structure of 2. The ORTEP diagram of the trinuclear cadmium(II) complex is shown in Figure 1a. Selected bond parameters for **2** are summarized in Table 2. The terminal (Cd_t) and central cadmium (Cd_c) ions are six-coordinate. The terminal cadmium ions are encapsulated in a facial N_3O_3 coordination environment (three imino nitrogens, three phenolate oxygens) and possess a distorted octahedral geometry. The central cadmium ion is also six-coordinate (6O), but the ligand environment is provided by four phenolate oxygen atoms and two water molecules. The four phenolate oxygen through their residual basicity serve to bridge the two terminal Cd_t's with the central Cd_c. In this regard the structure of **2** (and also **3** and **4**; vide infra) is different from other trinuclear complexes prepared from LH_3. In the latter the central metal ion is six-coordinate (6O), but all the six ligating oxygen atoms are derived from the phenolate ligands.

The coordinated water molecules on the central cadmium ion in **2** are present in a cis orientation [O(4)−Cd(1)−O(4A) = 72.1(3)°]. Two types of Cd_t−N [2.431(6) Å and 2.314(6) and 2.303(6) Å] and Cd_t−O [2.260(5) Å and 2.220(5) and 2.204(5) Å] bond distances are observed around the terminal cadmium centers. The longer distances are associated with the *axial* (Cd−N and Cd−O) bonds that are perpendicular to the N_2O_2Cd plane. The two water molecules attached to the central cadmium atom are intramolecularly hydrogen bonded to phenolate oxygen atoms (O2 and O2A) (Figure 1b). The inter-Cd−Cd distance is 3.4150(10) Å. The Cd−Cd−Cd angle is 153.71(3)°. The molecular structure of **2** reveals interesting intramolecular $\pi-\pi$ interaction of two aryl rings (Figure 1a). Such an interaction is also seen for **3** and **4** (Figure 2a).[17]

X-ray Crystal Structures of 3 and 4. ORTEP diagram for the complex **3** is shown in the Figure 2a. The structure of **4** is similar to that of **3**, and it is given in the Supporting Information. Selected bond parameters for **3** are summarized in Table 3. Previously we had determined the crystal structures of L_2Mn_3 and L_2Zn_3, where coordinated solvent was absent.[13] As will be shown, vide infra, the effect of the coordinated solvent is to alter the stereochemical arrangement of the ligands around the terminal metal ions in **3**. Another effect is the change of coordination environment around the central metal ion in **3** and **4**. Third, the coordinated solvent also influences the bond parameters including the M−M distances and M−M−M angles in both **3** and **4**.

As in the case of **2**, the terminal metal ions in **3** and **4** are six-coordinate and contain a facial N_3O_3 coordination environment. The central metal in **3** and **4** is five-coordinate. The coordination environment comprises of four phenolate oxygens and one coordinated methanol molecule. The latter is positionally disordered and is present in 50% occupancy. The effect of the coordinated methanol molecule is to relieve two of the phenolate oxygens from influencing their residual basicity-based coordination to the central metal ion. The average Mn_t−N distance is 2.257(4) Å while the average Zn_t−N distance is 2.186(3) Å. These values are comparable with that found for L_2Mn_3 and L_2Zn_3.[13] The average Mn_t−O [2.113(3) Å], Mn_c−O [2.122(3) Å], Zn_t−O [2.059(3) Å], and Zn_c−O [2.048(3) Å] are in accordance with that observed for literature precedents.[13] The distance between the two adjacent manganese centers in **3** is 3.1777(7) Å [cf. in L_2Mn_3, this value is 2.949(2) Å], while the inter-zinc distance in **4** is 3.1084(7) [cf. the average distance in L_2Zn_3 is 2.8734(15) Å].[13]

Stereochemistry of the Trinuclear Complexes. The stereochemical aspects of the tripodal ligand LH_3 are quite interesting. The ligand is achiral and possesses a C_3 symmetry; the molecular C_3 axis passes through the S=P unit. Upon coordination with metal ions the ligand induces chirality; Δ (clockwise) and Λ (anticlockwise) configurations are formed due to the screw coordination arrangement of the ligand (Chart 2). These possibilities are similar to those delineated by Wieghardt and co-workers in their work on triarmed triazacyclononane ligands.[18]

The stereochemistry of the trinuclear complexes studied by us can be summarized as follows:

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(17) (a) Janiak, C. J. *Chem. Soc., Dalton Trans.* **2000**, 3885. (b) Childs, L. J.; Alcock, N. W.; Hannon, M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1079. (c) Thallapally, P. K.; Katz, A. K.; Carrell, H. L.; Desiraju, G. R. *CrystEngComm* **2003**, *5*, 87. (d) For **2**, the centroid−centroid distance is 3.728(43) Å. For **3**, the centroid−centroid distance is 3.790(2) Å. For **4**, the centroid−centroid distance is 3.922(2) Å.

(18) (a) Beissel, T.; Birkelbach, F.; Bill, E.; Glaser, T.; Kesting, F.; Krebs, C.; Weyhermûller, T.; Wieghardt, K.; Butzlaff, C.; Trautwein, A. X. *J. Am. Chem. Soc.* **1996**, *118*, 12376. (b) Albela, B.; Bothe, E.; Brosch, O.; Mochizuki, K.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **1999**, *38*, 5131. (c) Glaser, T., Beissel, T.; Weyhermuller, T.; Schunemann, V.; Meyer-Klaucke, W.; Trautwein, A. X., Wieghardt, K. *J. Am. Chem. Soc.* **1999**, *121*, 2193. (d) Glaser, T.; Bill, E.; Weyhermuller, T.; Meyer-Klaucke, W.; Wieghardt, K. *Inorg. Chem.* **1999**, *38*, 2632.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $L_2Cd_3{\cdot}2H_2O$ (**2**)

		Bond Lengths			
Cd(2)−N(2)	2.314(6)	Cd(1)−O(1)	2.305(5)	N(1)−N(2)	1.440(8)
Cd(2)−N(6)	2.303(6)	Cd(1)−O(3)	2.249(5)	N(5)−N(6)	1.413(9)
Cd(2)−N(4)	2.431(6)	Cd(1)−O(4)	2.376(6)	N(3)−N(4)	1.398(9)
Cd(2)−O(1)	2.220(5)	Cd(1)−Cd(2)	3.4150(10)	C−N(im)$_{avg}$	1.28(10)
Cd(2)−O(3)	2.260(5)	S(1)−P(1)	1.927(3)	P−Navg	1.670(7)
Cd(2)−O(2)	2.204(5)				
		Bond Angles			
O(2)−Cd(2)−N(2)	152.45(19)	O(2)−Cd(2)−N(6)	109.2(2)	O(3)−Cd(1)−O(1A)	100.49(19)
O(1)−Cd(2)−N(2)	81.4(2)	O(1)−Cd(2)−N(6)	147.9(2)	O(3)−Cd(1)−O(4A)	102.7(2)
O(3)−Cd(2)−N(2)	107.0(2)	O(3)−Cd(2)−N(6)	79.6(2)	O(1)−Cd(1)−O(4A)	165.1(2)
N(6)−Cd(2)−N(2)	83.5(2)	O(2)−Cd(2)−O(1)	97.05(19)	O(3)−Cd(1)−O(4)	81.1(2)
N(2)−Cd(2)−N(4)	77.6(2)	O(2)−Cd(2)−O(3)	99.4(2)	O(3A)−Cd(1)−O(4))	102.7(2
O(2)−Cd(2)−N(4)	79.24(19)	O(1)−Cd(2)−O(3)	77.99(18)	O(1)−Cd(1)−O(4)	93.2(2)
O(1)−Cd(2)−N(4)	118.89(19)	O(3)−Cd(1)−O(3A)	175.4(3)	O(1A)−Cd(1)−O(4)	165.1(2)
O(3)−Cd(2)−N(4)	163.1(2)	O(3)−Cd(1)−O(1)	76.50(18)	O(4A)−Cd(1)−O(4)	72.1(3)
N(6)−Cd(2)−N(4)	84.9(2)	O(3A)−Cd(1)−O(1)	100.49(19)	O(1)−Cd(1)−O(1A)	101.5(3)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $L_2Mn_3{\cdot}CH_3OH$ (**3**)

		Bond Lengths			
Mn(1)−N(2)	2.267(4)	Mn(1)−O(3)	2.153(3)	N(1)−N(2)	1.402(5)
Mn(1)−N(4)	2.306(4)	Mn(2)−O(1)	2.142(3)	N(3)−N(4)	1.400(5)
Mn(1)−N(6)	2.198(4)	Mn(2)−O(3)	2.101(3)	N(5)−N(6)	1.442(5)
Mn(1)−O(1)	2.122(3)	Mn(1)−Mn(2)	3.1777(7)	C−N(im)$_{avg}$	1.286(6)
Mn(1)−O(2)	2.063(3)	S(1)−P(1)	1.9279(16)	P−N$_{avg}$	1.676(4)
		Bond Angles			
N(2)−Mn(1)−O(1)	82.43(13)	N(6)−Mn(1)−O(2)	158.43(13)	O(1)−Mn(1)−O(3)	79.80(12)
N(2)−Mn(1)−O(2)	104.94(14)	N(6)−Mn(1)−O(3)	81.60(13)	O(2)−Mn(1)−O(3)	93.87(13)
N(2)−Mn(1)−O(3)	154.65(14)	N(2)−Mn(1)−N(4)	84.60(14)	O(1)−Mn(2)−O(3A)	80.50(12)
N(4)−Mn(1)−O(1)	164.82(13)	N(2)−Mn(1)−N(6)	86.52(14)	O(3)−Mn(2)−O(3A)	108.34(19)
N(4)−Mn(1)−O(2)	83.00(13)	N(4)−Mn(1)−N(6)	79.93(16)	O(3)−Mn(2)−O(1)	102.90(12)
N(4)−Mn(1)−O(3)	114.94(13)	O(1)−Mn(1)−O(2)	92.76(13)	O(1)−Mn(2)−O(1A)	174.31(12)
N(6)−Mn(1)−O(1)	107.02(13)				

(1) The tripodal ligand LH_3 forms three chelate rings upon complexation with the terminal metal ion $P-[N-N-C-C-C-O-M]_3$.

(2) The conformation of these three chelate rings can be $\lambda\lambda\lambda$ (all the rings oriented in the same direction, clockwise, with respect to the inter-metal axis) or $\delta\delta\delta$ (all the rings oriented in the same direction, anticlockwise, with respect to the inter-metal axis). In all the cases we have *always* observed the same conformation for all the three rings. In no case we have observed a conformational mix such as $\lambda\lambda\delta$, $\lambda\delta\lambda$, etc. Chirality of the terminal metal atoms can be described either as $\Delta(\delta\delta\delta)$ or $\Lambda(\lambda\lambda\lambda)$ (Chart 2).

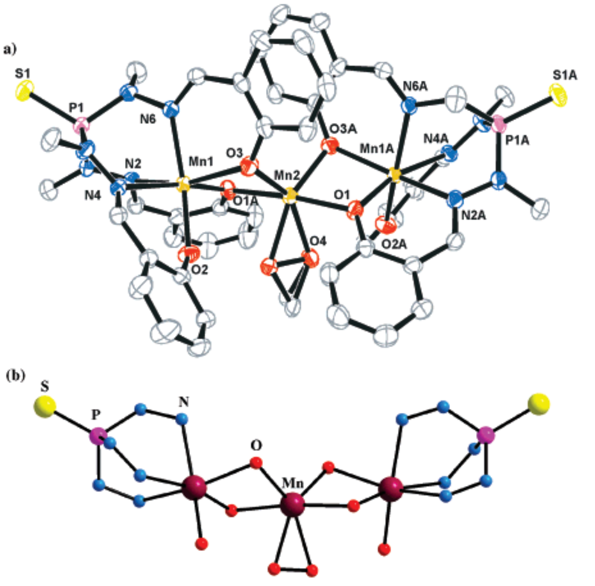
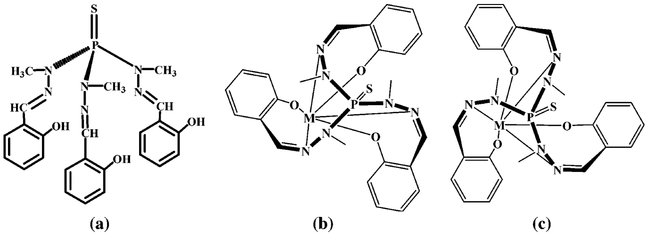


Figure 2. (a) ORTEP diagram of $L_2Mn_3{\cdot}CH_3OH$ (**3**). The coordinated methanol on the central Mn is positionally disordered. Hydrogen atoms have been omitted for clarity. (b) Side view of the core of $L_2Mn_3{\cdot}CH_3OH$.

Chart 2. (a) Molecular Structure of Phosphorus-Based Tripodal Ligand LH_3 Possessing C_3 Symmetry, (b) $\Delta(\lambda\lambda\lambda)$ (Clockwise) Form of the Configuration Formed by the Ligand LH_3 after Coordination with the Terminal Metal Atom, and (c) $\Lambda(\delta\delta\delta)$ (Anticlockwise) Form of the Configuration Formed by the Ligand LH_3 after Coordination with the Terminal Metal Atom



(3) If the orientation of the three chelating rings of the front side of the trinuclear complex is the same as that of the backside (for example $\lambda\lambda\lambda$ and $\lambda\lambda\lambda$), a pure enantiomer is the result. On the other hand if the orientations of the two sides are opposite with respect to each other ($\lambda\lambda\lambda$ and $\delta\delta\delta$), a meso formation is the result. In the present instance, compounds **2**−**4** exist as pure enantiomers in their molecular structures and as racemic compounds in their crystal structures.

Table 4 summarizes the stereochemistry of all the trinuclear derivative obtained from LH_3. Only L_2Mn_3 and L_2Mg_3 are achiral (meso) (entries 4 and 8). The remaining

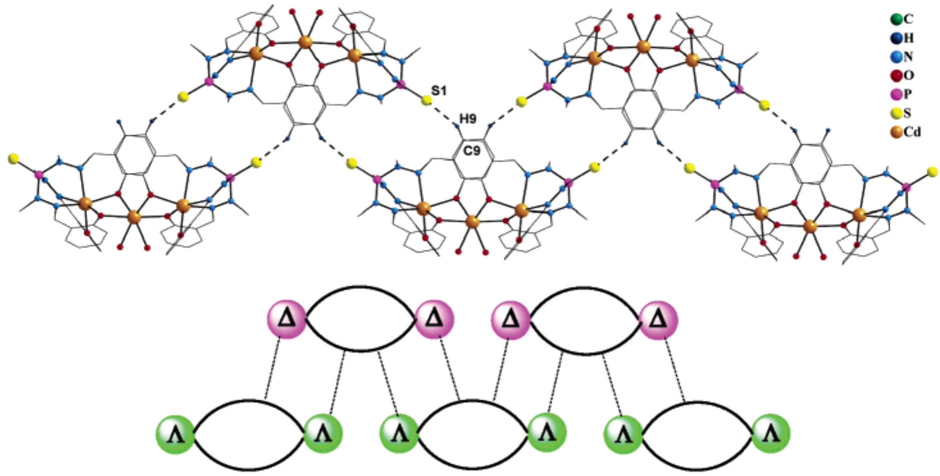


Figure 3. Intermolecular C−H⋯S═P interactions in $L_2Cd_3{\cdot}2H_2O$ (**2**). All the hydrogen atoms which are not involved in the hydrogen bonding have been omitted for clarity. The bond parameters for the C(9)−H(9)⋯S(1) contact are C−H 0.950(11) Å, H⋯S 3.00(4) Å, C⋯S 3.704(35) Å, and C−H⋯S 132.01(62)°. The symmetry is x, $1 - y$, $0.5 + z$.

Table 4. Inter-Metal Bond Parameters and Stereochemical Configurations of the Trinuclear Complexes Formed from LH_3

entry	compd	confign	$M_t{-}M_c{-}M_t$ (deg)	$M_t{-}M_t$ (Å)	$M_t{-}M_c$ (Å)	ref
1	$L_2Cd_3{\cdot}2H_2O$ (**2**)	$\Delta(\lambda\lambda\lambda)\cdots\Delta(\lambda\lambda\lambda)$ $\Lambda(\delta\delta\delta)\cdots\Lambda(\delta\delta\delta)$	153.71(3)	6.651	3.4150(10)	this work
2	$L_2Mn_3{\cdot}CH_3OH$ (**3**)	$\Delta(\lambda\lambda\lambda)\cdots\Delta(\lambda\lambda\lambda)$ $\Lambda(\delta\delta\delta)\cdots\Lambda(\delta\delta\delta)$	161.51(4)	6.273	3.1777(7)	this work
3	$L_2Zn_3{\cdot}CH_3OH$ (**4**)	$\Delta(\lambda\lambda\lambda)\cdots\Delta(\lambda\lambda\lambda)$ $\Lambda(\delta\delta\delta)\cdots\Lambda(\delta\delta\delta)$	161.87(3)	6.139	3.1084(7)	this work
4	L_2Mn_3	$\Delta(\lambda\lambda\lambda)\cdots\Lambda(\delta\delta\delta)$	180(7)	5.897	2.949(2)	13
5	L_2Co_3	$\Delta(\lambda\lambda\lambda)\cdots\Delta(\lambda\lambda\lambda)$ $\Lambda(\delta\delta\delta)\cdots\Lambda(\delta\delta\delta)$	176.67(3)	5.755	2.8755(8) 2.8817(8)	13
6	L_2Ni_3	$\Delta(\lambda\lambda\lambda)\cdots\Delta(\lambda\lambda\lambda)$ $\Lambda(\delta\delta\delta)\cdots\Lambda(\delta\delta\delta)$	174.71(3)	5.588	2.7968(7)	13
7	L_2Zn_3	$\Delta(\lambda\lambda\lambda)\cdots\Delta(\lambda\lambda\lambda)$ $\Lambda(\delta\delta\delta)\cdots\Lambda(\delta\delta\delta)$	174.30(3)	5.740	2.8653(15) 2.8815(14)	13
8	L_2Mg_3	$\Delta(\lambda\lambda\lambda)\cdots\Lambda(\delta\delta\delta)$	180	5.566	2.7828(13)	14

trinuclear derivatives exist as enantiomers in the solid state either in the $\Delta(\lambda\lambda\lambda)\cdots\Delta(\lambda\lambda\lambda)$ or $\Lambda(\delta\delta\delta)\cdots\Lambda(\delta\delta\delta)$ forms. Interestingly, in the two cases where the meso forms are found the $M_t{-}M_c{-}M_t$ angles are perfectly linear. In all other cases this angle is less than 180°. The effect of the $M_t{-}M_c{-}M_t$ angle on the formation of the enantiomer is further gauged by the fact that in $L_2Mn_3{\cdot}MeOH$ (**3**) (entry 2) the angle is reduced to 161.51(4)°. This is accompanied by the change from meso to a pure enantiomer in the solid state. Interestingly, the trinuclear cadmium complex **2** has the smallest $M_t{-}M_c{-}M_t$ angle [153.71(3)°] (entry 1).

The $M_t{-}M_c$ distances and the $M_t{-}M_t$ distances within the trinuclear complexes are summarized in Table 4. The longest $M_t{-}M_t$ distance is found for the tricadmium derivative **2** (6.651 Å), while the shortest distance is found for the magnesium derivative **8** (5.566 Å).[14] There is a marked elongation of the $M_t{-}M_t$ bond distances upon the central metal being coordinated with methanol (see entries 2, 4 and 3, 7).

The crystal structures of **2**−**4** show the presence of persistent C−H⋯S═P-mediated intermolecular interactions[13,14,19] leading to the formation of a zigzag one-dimensional double bridged polymeric chain. Interestingly, there is a strong stereochemical preference among the interacting molecules. The supramolecular one-dimensional polymer of $L_2Cd_3{\cdot}2H_2O$ is shown in Figure 3. Molecules with a Λ−Λ configuration interact stereospecifically with those that have the opposite Δ−Δ configuration. This corresponds to an example of chiral recognition among molecules.[20] The supramolecular formation occurs as a result of each molecule interacting through the terminal P═S units with the aromatic hydrogens of two neighboring molecules. Thus, from every molecule the terminal sulfur atoms function as proton acceptors. Also, from every molecule two aromatic ring C−H's (para to the phenolate oxygen) function as proton donors (Figure 3). Supramolecular chiral recognition is an area of contemporary interest, although this aspect has been much less studied in inorganic coordination compounds. Recently, Amouri and co-workers have reported that the crystal structure of *rac*-$[Ru(2,2'\text{-bipyridine})_2(4,4'\text{-dicarboxy-}2,2'\text{-bipyridine})][PF_6]_2$ shows a one-dimensional supramolecular sheetlike structure containing strong hydrogen bond-

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[19] (a) Potrzebowski, M. J.; Michalska, M.; Koziol, A. E.; Kazmierski, S.; Lis, T.; Pluskowski, J.; Ciesielski, W. *J. Org. Chem.* **1998**, *63*, 4209. (b) Muralidharan, K.; Venugopalan, P.; Elias, A. J. *Inorg. Chem.* **2003**, *42*, 3176.

[20] (a) Caspar, R.; Musatkina, L.; Tatosyan, A.; Amouri, H.; Gruselle, M.; Guyard-Duhayon, C.; Duval, R.; Cordier, C. *Inorg. Chem.* **2004**, *43*, 7986. (b) Kobayashi, Y.; Morisawa, F.; Saigo, K. *Org. Lett.* **2004**, *6*, 4227. (c) Kobayashi, Y.; Kodama, K.; Saigo, K. *Org. Lett.* **2004**, *6*, 2941. (d) Moriuchi, T.; Yoshida, K.; Hirao, T. *Org. Lett.* **2003**, *5*, 4285. (e) Kim, S.-G.; Kim, K.-H.; Kim, Y. K.; Shin, S. K.; Ahn, K. H. *J. Am. Chem. Soc.* **2003**, *125*, 13819.

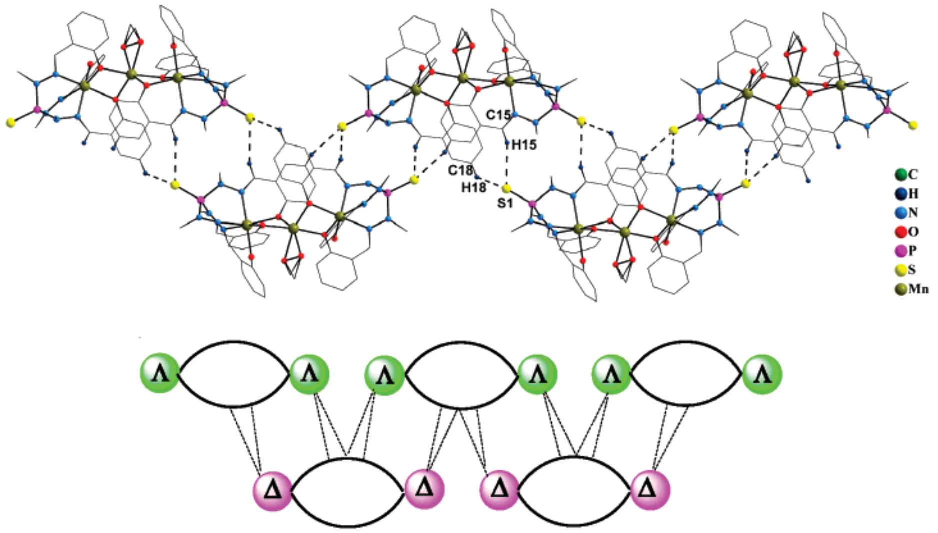

Figure 4. Intermolecular C−H···S═P interactions in $L_2Mn_3{\cdot}CH_3OH$ (**3**). All the hydrogen atoms which are not involved in the hydrogen bonding have been omitted for clarity. The bond parameters and the symmetry for these supramolecular contacts is as follows: (1) C(18)−H(18)···S(1) contact, C−H 0.950(6) Å, H···S 2.872(2) Å, C···S 3.511(6) Å, and C−H···S 125.67(36)°, symmetry x, $1 - y$, $-0.5 + z$; (2) C(15)−H(15)···S(1) contact, C−H 0.950 (5) Å, H···S 2.947(1) Å, C···S 3.848(5) Å, and C−H···S 158.73(27)°, symmetry $-x$, $1 - y$, $1 - z$.

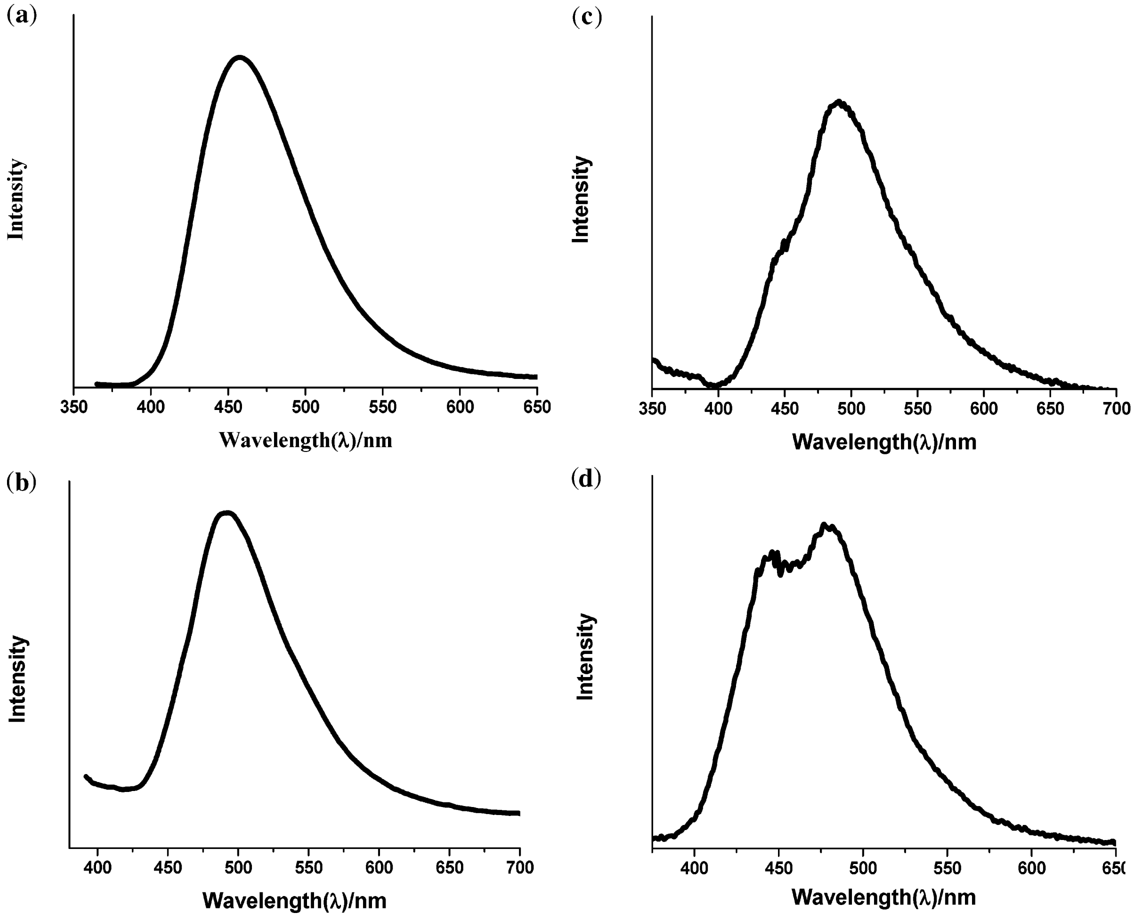

Figure 5. Emission spectra of the L_2Cd_3 complex (a) in solution state, (b) in solid state, (c) in thin film, and (d) in doped polymer.

ing (O−H···O) between carboxylic acid groups of the two enantiomers (Δ and Λ).[20a] This is in contrast to the present instance where chiral recognition occurs through C−H···S═P contacts. Chiral recognition through noncovalent interactions among organic compounds is attracting interest particularly from the point of view of enantioseparation.[20b−e] For example, recently an enantiopure *O*-alkyl phosphonothioic acid has been used in the enantioseparation of racemic (1-phenylethyl)amine derivatives.[20b] This is accomplished by hydrogen bond-mediated diastereomeric salt formation.

The crystal structures of **3** and **4** also show intermolecular chiral recognition similar to that for **2**. The details of the supramolecular interaction are, however, slightly different. Thus, the terminal P═S moieties of every molecule are involved in a bifurcated hydrogen bonding with two protons derived from an aromatic ring and the CH═N group. This leads to the formation a zigzag one-dimensional polymeric chain in the solid state (Figure 4).

Luminescent Properties of 2. The diamagnetic trinuclear metal complexes **2** and **4** were investigated for photoluminescence, in view of the demonstration of such a behavior by L_2Mg_3.[14] The ligand LH_3 does not show fluorescence. The trinuclear zinc derivative also does not exhibit fluorescence. However, the optical behavior of the cadmium complex is quite interesting in that it shows emission both in solution as well as in the solid state. The emission spectra of the cadmium complex in solution (CH_2Cl_2; $\lambda_{ex} = 355$ nm) and in the solid state (powder in a quartz tube; $\lambda_{ex} = 325$ nm) are shown in Figure 5a,b. In dichloromethane solution an intense emission with a peak maximum at 458 nm is observed. In comparison, the solid-state emission peak occurs at 493 nm. The excited-state emission spectrum of the trinuclear cadmium complex **2** obtained at different excitation wavelengths in dichloromethane is similar to its UV−vis absorption spectrum with intense peaks around 282 and 355 nm, indicating that the emission is from the vertically excited state and that the molecular structure of the complex remains invariant in the excited state (see Supporting Information).[14,21] The luminescent properties of the trinuclear cadmium complex **2** were also investigated in its thin film as well as in a polymer matrix. Thus, a spin-coated thin-film sample of the cadmium complex was prepared from its dichloromethane solution and its emission spectrum studied (Figure 5c). We also prepared a doped polymer thin film from a solution of 90% polystyrene and 10% cadmium complex in dichloromethane. The emission spectrum of such a polymer film is shown in Figure 5d. The emission peaks of both the solid thin films as well as polymer-doped thin films are closely similar to that observed in the solid state. In this regard the photophysical behavior of **2** parallels that of the trinuclear magnesium complex (L_2Mg_3) although the quantum yields of the former ($\Phi = 0.004$) are much lower than that found in the latter ($\Phi = 0.03$).[22]

Conclusion

In conclusion we observe that the phosphorus-based tris(hydrazone) LH_3 is an excellent ligand for the formation of linear trinuclear divalent metal complexes. We have observed that the achiral ligand induces chirality in the complexes, which crystallize as racemic compounds. Further, the supramolecular structures of **2**−**4** reveal the presence of intermolecular chiral recognition among the interacting molecules. The trinuclear cadmium complex **2** shows emission in solution as well as in the solid state. The luminescence of **2** also persists in doped polymer film. Such a feature indicates the potential of **2** in LED applications.

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Supporting Information Available: Figures S1−S4, showing an ORTEP diagram of **4**, intermolecular interactions in **4**, a UV−vis spectrum of **2**, and excited-state emission spectra of **2**, Table S1, containing selected bond lengths and bond angles for **4**, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Jayanty, S.; Radhakrishnan, T. P. *Chem.*—Eur. J. **2004**, *10*, 791.

(22) Quantum yield for the complexes were found at room temperature in dichloromethane solvent using quinine sulfate as reference standard.