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A Series of Single, Double, and Triple Me$_2$biim-Bridged Dinuclear, Trinuclear, and Polymeric Complexes: Syntheses, Crystal Structures, and Luminescent Properties

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Reaction of $ZnCl_2$ and Me$_2$biim (Me$_2$biim = *N,N′*-dimethyl-2,2-′-biimidazole) in acidic or neutral aqueous solutions gave the noncoordinated $ZnCl_4 \cdot H_2Me_2$biim (**1**) or the double Me$_2$biim bridged [Zn_2Cl_4(μ-Me$_2$biim)$_2$] (**2**). Use of CdX_2 (X = Cl, Br, I) instead of $ZnCl_2$ yielded the single Me$_2$biim bridged one-dimensional coordination polymer [CdX_2(μ-Me$_2$biim)]$_n$ (X = Cl, **3**; Br, **4**; I, **5**). The stacking of the infinite chains are dominated by C–H···X interactions in **3** and **4** but by I···I interactions in **5**, responsible for their different crystal structures. Use of $Zn(NO_3)_2$ instead of $ZnCl_2$ produced the novel triple Me$_2$biim-bridged [Zn_2(μ-Me$_2$biim)$_3$(H_2O)$_2$](NO_3)$_4 \cdot H_2O$ (**6**). The unprecedented hexa-Me$_2$bim bridged trinuclear [Cd_3(μ-Me$_2$biim)$_8$]$_2$(ClO_4)$_{12}$(H_2O)$_6$ (**7**) was obtained by using $Cd(CH_3CO_2)_2$ in the presence of $NaClO_4$. Compounds **1**–**7** were characterized by X-ray crystallography and IR. Examination of photophysical properties of **1**–**7** indicates that the fluorescence emission of Me$_2$biim has been effectively enhanced, quenched, or shifted in its metal complexes **1**–**7**.

Introduction

Biimidazole has been widely used as biomimetic ligands in bioinorganic chemistry,[1] bridging ligands in oligometallic chemistry for catalysis,[2] antitumor drugs,[3] and building blocks of supermolecular framework.[4] Its properties are influenced by both electronic and steric factors. Interaction of two covalently bound π-systems is favored by a plananr conformation, which provides the optimum environment for a resonance delocalization. Thus, H$_2$biim usually behaves as a chelating bidentate ligand[1−4] with the two imidazole rings approximately coplanar although singly bridged dinuclear and polymeric structures are known in Zn[1a] and Ag complexes.[1m] Larger substituents often interact with one another, forcing the two rings out of coplanarity. This effect is particularly appararent for 2,2′-biimidazole as it has lower

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(1) (a) Kirchner C.; Krebs, B. *Inorg. Chem.* **1987**, *26*, 3569−3576. (b) Hester, C. A.; Collier, H. L.; Baughman, R. G. *Polyhedron* **1996**, *15*, 4255−4258. (c) Abushamleh, A. S.; Goodwin, H. A. *Aust. J. Chem.* **1979**, *32*, 513−518. (d) Sakaguchi, U.; Addison, A. K. *J. Chem. Soc., Dalton Trans.* **1979**, 600−608. (e) Bendini, A.; Mani, F. *Inorg. Chim. Acta* **1988**, *154*, 215−219. (f) Fortin S.; Beauchamp, A. L. *Inorg. Chem.* **2000**, *39*, 4886−4893. (g) Lorente, M. A. M.; Dahan, F.; Sanakis, Y.; Petrouleas, V.; Boussedsou, A.; Tuchagues, J.-P. *Inorg. Chem.* **1995**, *34*, 5346−5357. (h) Dance, I. G.; Abushamleh, A. S.; Goodwin, H. A. *Inorg. Chim. Acta* **1980**, *43*, 217−221. (i) Mighell, A. D.; Reimann, C. W.; Maucer, F. A. *Acta Crysyallogr. Sect. B* **1969**, *25*, 60−66. (j) Cancela, J.; Gonzalez Garmendia, M. J.; Qurios, M. *Inorg. Chim. Acta* **2001**, *313*, 156−159. (k) Sang, R.; Zhu, M.; Yang, P. *Acta Crystallogr.* **2002**, *E58*, m172−175. (l) Hester, C. A.; Collier, H. L.; Baughman, R. G. *Polyhedron* **1996**, *15*, 4255−4258; (m) Kirchner, C.; Krebs, B. *Inorg. Chem.* **1987**, *26*, 3569−3576. (n) Ye, B.-H.; Xue, F.; Xue, G.-Q.; Ji, L.-N.; Mak, T. C. W. *Polyhedron* **1999**, *18*, 1785−1790. (o) Hester, C. A.; Baughman, R. G.; Collier, H. L. *Polyhedron* **1997**, *16*, 2893−2895.

(2) (a) Kaiser, S. W.; Saillant, R. B.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* **1976**, *15*, 2681−2687. (b) Kaiser; S. W.; Saillant, R. B.; Rasmussen, P. G. *J. Am. Chem. Soc.* **1975**, *97*, 425−426. (c) Kaiser, S. W.; Saillant, R. B.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* **1976**, *15*, 2688−2694. (d) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 2622−2630. (e) Usón, R.; Gimeno, J.; Forniés, J.; Martínez, F. *Inorg. Chim. Acta* **1981**, *50*, 173−177. (f) Maiboroda, A.; Rheinwald, G.; Lang, H. *Inorg. Chem. Commun.* **2001**, *4*, 381−383. (g) Majumdar, P.; Peng, S.-M.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **1998**, 1569−1574. (h) Garcia, M. P.; López, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *Chem. Commun.* **1988**, 793−795. (i) Usón, R.; Oro, L. A.; Gimeno, J.; Ciriano, M. A.; Cabeza, J. A. *J. Chem. Soc., Dalton. Trans.* **1983**, 233−230.

(3) (a) Casas, J.-S.; Castineiras, A.; Parajo, Y.; Perez-Paralle, M.-L.; Sanchez, A.; Sanchez-Gonzalez, A.; Sordo, J. *Polyhedron* **2003**, *22*, 1113−1121. (b) Sanchez-Gonzalez, A.; Casas, J. S.; Sordo, J.; Russo, U.; Lareo, M. I.; Regueiro, B. J. *J. Inorg. Biochem.* **1990**, *39*, 227−235. (c) Lopez, C.; Sanchez-Gonzalez, G.; Garcia, M. E.; Casas, J. S.; Sordo, J.; Graziani, R.; Casellato, U. *J. Organomet. Chem.* **1992**, *434*, 261−268. (d) Holliday, B. J.; Mirkin, Ch. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2023−2043. (e) Watson, J. D.; Crick, F. H. C. *Nature* **1953**, *171*, 737−738. (f) Zoo, P. A.; Casas, J. S.; Couse, M. D.; Freijanes, E.; Furlani, A.; Scarcial, V.; Sordo, J.; Russo U.; Varela, M. *Appl. Organomet. Chem.* **1997**, *11*, 963−968.

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barriers for conformational inversion than other biaryl molecules.[5a] The study of *N*,*N*′-bridged derivative of 2,2′-biimidazole has shown that the bite angle is too unfavorable to allow bidentate coordination.[5b] This accounts for few reported chelating complexes of the dimethylated derivative, *N*,*N*′-dimethyl-2,2′-biimidazole (Me_2biim).[5c] Although Me_2biim exhibits different proterties, it has been received much less attention. To our knowledge, only several Pt[5c,5d] and Re[1f] complexes have been reported. To conduct a systematic study of this ligand, this paper will describe a series of single, double, and triple Me_2biim bridged dinuclear, trinuclear, and polymeric complexes. Several unprecedented triple Me_2biim-bridged dinuclear and trinuclear complexes have been synthesized and structurally characterized. It also deals with the first investigation into the luminescent properties of biimidazole complexes that exhibit enhanced, shifted, and quenched fluorescence emission via metal coordination.

Experimental Section

General Remarks. Me_2biim was synthesized in accordance with a published procedure.[10] All other chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. Fluorescent spectra were measured with an Edinburgh FLS920 analytical instrument. IR spectra were recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the 4000−400 cm^{-1}.

CAUTION: Perchlorate salts are potentially explosive and should be handled with care and in small amounts.

$[ZnCl_4][H_2Me_2biim]$ (1). Me_2biim (0.081 g, 0.5 mmol) in water (5 mL) was slowly added to an aqueous solution (5 mL) of $ZnCl_2$ (0.034 g, 0.25 mmol) to produce precipitation immediately. The excessive hydrochloric acid was added to the mixture until the precipitation was dissolved. The resulting solution was filtered off. The filtrate was left in air to evaporate. Colorless crystals were obtained after a few days. The product was collected by filtration, washed with ethanol, and dried in air. Yield: 56% (based $ZnCl_2$). Anal. Calcd for $C_8H_{12}Cl_4N_4Zn$ (371.39): C 25.87, H 3.26, N 15.09. Found: C 25.88, H 3.39, N 14.96%. IR (KBr; cm^{-1}): 3199.0m, 3133.5m, 1682.8w, 1571.5s, 1532.8w, 1497.4m, 1448.2w, 1424.7w, 1373.9w, 1287.9s, 1254.0s, 1115.8s, 1101.1w, 920.9w, 808.1m, 791.4m, 718.1s, 617.4w.

$[Zn_2Cl_4(Me_2biim_2)]$ (2). An ethanol solution of Me_2biim (0.5 mmol, 0.081 g, 3 mL) was slowly diffused into a aqueous solution of $ZnCl_2$ (0.25 mmol, 0.034 g, 3 mL) through a layer of an ethanol/water (1:1) mixture (5 mL). After 1 week, colorless crystals of **2** were slowly formed. The crystals were collected, washed with water and ethanol successively, and dried in air. **2** is not soluble in water or common organic solvents. Yield: 85% (based $ZnCl_2$). Anal. Calcd for $C_{16}H_{20}Cl_4N_8Zn_2$ (596.94): C 32.19, H 3.38, N 18.77. Found: C 32.21, H 3.44, N 18.68%. IR (cm^{-1}): 3421.8w, 3134.9m, 3111.7m, 2952.6w, 1674.7w, 1529.7m, 1474.9s, 1416.8s, 1384.4w, 1365.8w, 1346.4m, 1287.2s, 1223.0w, 1154.4s, 1081.2m, 963.4w, 953.4w, 816.5w, 797.1s, 780.5s, 680.9w.

$[CdX_2(\mu\text{-}Me_2biim)]_n$ (X = Cl, 3; Br, 4; I, 5). An ethanol solution of Me_2biim (0.5 mmol, 0.081 g, 3 mL) was slowly diffused into a aqueous solution of $CdCl_2 \cdot 2.5H_2O$ (0.25 mmol, 0.057 g, 3 mL) through a layer of an ethanol/water (1:1) mixture (5 mL) to yield colorless crystals of **3** after 1 week. The crystals were collected, washed with water and ethanol successively, and dried in air. **3** is not soluble in water or common organic solvents. Yield: 75%. Anal. Calcd for $C_8H_{10}N_4CdCl_2$: C, 27.80; H, 2.92; N, 16.21%. Found: C, 27.75; H, 2.99; N, 16.19%. $\tilde{\nu}_{max}$ (cm^{-1}) (KBr): 3435m, 3118m, 1653m, 1470s, 1398s, 1343w, 1278s, 1218w, 1147s, 1074w, 954m, 943m, 871w, 776s, 734s, 681w, 671w, 630w. **4** was synthesized similarly by using $CdBr_24H_2O$ instead of $CdCl_2$. Yield: 83%. Anal. Calcd for $C_8H_{10}N_4CdBr_2$: C, 22.12; H, 2.32; N, 12.90%. Found: C, 22.07; H, 2.40; N, 12.84%. $\tilde{\nu}_{max}$ (cm^{-1}) (KBr): 3436m, 3146w, 3127m, 1633m, 1521w, 1489m, 1471s, 1397s, 1342w, 1279s, 1152s, 1073w, 953w, 942m, 874w, 763s, 733s. **5** was obtained similarly from CdI_2. Yield: 79%. Anal. Calcd for $C_8H_{10}N_4CdI_2$: C, 18.18; H, 1.91; N, 10.61%. Found: C, 18.14; H, 1.98; N, 10.64%. $\tilde{\nu}_{max}$ (cm^{-1}) (KBr): 3435m, 3120m, 1631w, 1493m, 1473s, 1397s, 1339w, 1279s, 1149s, 1073w, 953m, 942m, 764s, 730s.

$[Zn_2(\mu\text{-}Me_2biim)_3(H_2O)_2](NO_3)_4 \cdot H_2O$ (6). $ZnNO_3 \cdot 6H_2O$ (0.149 g, 1 mmol) in 10 mL of water was added to a aqueous solution (5 mL) of Me_2biim (0.162 g, 1 mmol). The mixture was stirred at room temperature for 30 min. The resulting solution was filtered off. The filtrate was left in air to evaporate to form crystals of **6** after a few days. The crystals were collected by filtration, washed with ethanol, and dried in air. Yield: 74%. Anal. Calcd for $C_{24}H_{34}N_{16}O_{14}Zn_2$: C, 31.35; H, 3.95; N, 24.38%. Found: C 31.29, H 4.03, N 24.32%. IR (cm^{-1}): 3481.1m, 3152.5m, 3129.6m, 2955.2m, 1647.2w, 1534.7m, 1498.2s, 1475.2s, 1384.4vs, 1314.3s, 1282.9s, 1221.1w, 1165.9m, 1150.1s, 1041.1w, 968.8w, 955.3w, 826.6w, 778.5m, 737.2s.

$[Cd_3(Me_2biim)_8]_2(ClO_4)_{12}(H_2O)_6$ (7). Me_2biim(0.081 g, 0.5 mmol) in water (5 mL) was slowly added to aqueous solution (15 mL) of $Cd(CH_3COO)_2 \cdot H_2O$ (0.067 g, 0.25 mmol) and $NaClO_4 \cdot H_2O$ (0.70 g 0.5 mmol). The solution was stirred at room temperature for 30 min. The resulting solution was filtered off. The filtrate was left in air to evaporate. Crystals of **7** were obtained after a few days. The product was collected by filtration, washed with ethanol, and dried in a vacuum. Yield: 75%. Anal. Calcd for $C_{64}H_{86}N_{32}O_{27}Cl_6Cd_3$: C, 33.67; H, 3.79; N, 19.62%. Found: C, 33.78; H, 19.75; N, 3.84%. IR (cm^{-1}): 3460.2m, 3138.6m, 2960.1w, 1633.9w, 1562.5m, 1486.0s, 1461.0s, 1411.4m, 1341.4w, 1282.2s, 1092.0vs, 947.5w, 934.6w, 769.1m, 735.9s, 686.8w, 624.7s

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(4) (a) Tadokoro, M.; Isober, K.; Uekusa, H.; Ohashi, Y.; Toyoda, J.; Tashiro, K.; Nakasuji, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 95−98. (b) Tadocoro, M.; Kanno, H.; Kitajima, T.; Shimada-Umemoto, H.; Nakanishi, N.; Isobe, K.; Nakasuji, K. *Proc. Natl Acad Sci U.S.A.* **2002**, *99*, 4950−4955. (c) Tadocomo, M.; Shiomi, T.; Isobe, K.; Nakasuji, K. *Inorg. Chem.* **2001**, *40*, 5476−5478. (d) Tadomoro, M.; Nakasuji, K. *Coord. Chem. Rev.* **2000**, *198*, 205−218. (e) Atencio, R.; Chacon, M.; Gonzalez, T.; Briceno, A.; Agrifoglio, G.; Sierraalta, A. *J. Chem. Soc., Dalton Trans.* **2004**, 505−513. (f) Allen, W. E.; Fowler, C. J.; Lynch, V. M.; Sessler, J. L. *Chem. Eur. J.* **2001**, *7*, 721−729. (g) Ohrstrom, L.; Larsson, K.; Borg, S.; Norberg, S. T. *Chem. Eur. J.* **2001**, *7*, 4805−4810.

(5) (a) Thummel, R. P.; Goulle, V.; Chen, B. *J. Org. Chem.* **1989**, *54*, 3057−3061. (b) Goulle, V.; Thummel R. P. *Inorg. Chem.* **1990**, *29*, 1767−1772. (c) Casas, J.-S. *Acta Crystallogr.* **1998**, *C54*, 1777−1779. (d) Casas, J. S.; Castineiras, Y.; Perez-Paralle, M. L.; Sanchez, A.; Sanchez-Gonzalez, A.; Sordo, J. *Polyhedron* **2003**, *22*, 1113−1121.

(6) Mighell, A. D.; Santoro, A. *Acta Crystallogr.* **1971**, *B27*, 2089−2097.

(7) Strasdeit, H.; Saak, W.; Pohl, S.; Driessen W. L.; Reedijk, J. *Inorg. Chem.* **1988**, *27*, 1557−1563.

(8) (a) Kiriyama, H.; Mizuhashi, Y.; Ootani, J. *J. Bull. Chem. Soc. Jpn.* **1986**, *59*, 381−386. (b) Abriel, W.; Du Bois, A. Z. *Z. Naturforsch, B: Chem. Sci.* **1989**, *44*, 1187−1191. (c) Srivastava, P. C.; Schmidt, H. G.; Roesky, H. W. *Z. Naturforsch, B: Chem. Sci.* **1995**, *50*, 695−696.

(9) (a)Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063−5070. (b) Aakeroy, C. B.; Evans, T. A.; Seddon, K. B.; Palinko, I. *New J. Chem.* **1999**, 145−152.

(10) Piero, M.; Emanuele, D.; Willy, L., Carneri, Ivo de.; Franca, T. *J. Med. Chem.* **1972**, *15*, 927−930.

Table 1. Crystallographic Data for Compounds **1**−**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_8H_{12}Cl_4N_4Zn$	$C_{16}H_{20}Cl_4N_8Zn_2$	$C_8H_{10}CdCl_2N_4$	$C_8H_{10}Br_2CdN_4$	$C_8H_{10}CdI_2N_4$	$C_{24}H_{36}N_{16}O_{15}Zn_2$	$C_{64}H_{86}Cd_3Cl_6N_{32}O_{27}$
M	371.39	596.94	345.50	434.42	528.40	919.43	2285.55
crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic	Monoclinic	triclinic	triclinic
space group	*C*2/*c*	*Pbcn*	*Pn*	*Fdd*2	*Cc*	$P\bar{1}$	$P\bar{1}$
a (Å)	15.816(3)	11.747(3)	8.5217(12)	30.503(5)	5.3546(12)	9.85700(10)	13.681(3)
b (Å)	8.9899(17)	13.566(4)	5.1528(8)	4.8598(9)	15.7642(8)	12.1339(3)	15.381(4)
c (Å)	11.474(2)	14.367(4)	13.719(2)	16.322(3)	15.773(2)	16.9110(4)	21.740(5)
α (°)	90	90	90	90	90	82.5350(10)	77.647(5)
β (°)	117.899(3)	90	97.240(3)	90	96.989(3)	86.4190(10)	79.185(5)
γ (°)	90	90	90	90	90	68.4430(10)	86.666(7)
vol ($Å^3$)	1441.8(5)	2289.5(11)	597.6(19)	2419.6(7)	1321.5(3)	1864.96(7)	4388.3(19)
Z	4	4	4	4	4	2	2
d_{calc} (g/cm_3)	1.711	1.732	1.920	2.385	2.656	1.637	1.730
μ (cm^{-1})	2.428	2.583	2.247	8.384	6.301	1.375	0.998
F(000)	744	1200	336	1632	960	944	2312
crystal size	0.26 × 0.20 × 0.14	0.20 × 0.20 × 0.20	0.30 × 0.26 × 0.12	0.30 × 0.16 × 0.12	0.34 × 0.06 × 0.04	0.40 × 0.20 × 0.16	0.25 × 0.20 × 0.10
data/restraint/ parameters	1268/0/78	2628/0/136	1285/2/136	962/1/70	1294/2/136	6455/0/509	19394/0/1237
reflns collected	2179	16589	1769	2879	1966	9615	33173
unique reflns	1268	2628	1285	962	1294	6455	19394
goodness of fit	1.633	1.137	1.135	1.512	1.813	2.200	1.230
$R_1[I > 2\sigma(I)]$	0.0613	0.0414	0.0442	0.0861	0.0790	0.1022	0.0633
$\omega R_2[I > 2\sigma(I)]$	0.1299	0.1409	0.1242	0.2436	0.1394	0.1701	0.1599
R_1 (all data)	0.0813	0.0453	0.0512	0.0978	0.1072	0.1395	0.0799
wR_2 (all data)	0.1384	0.1452	0.1357	0.2717	0.1528	0.1824	0.1725
residuals ($e \cdot Å^{-3}$)	0.458, −0.569	0.899, −0.517	0.888, −0.891	2.614, −1.329	0.704, −0.647	0.684, −0.698	1.891, −1.738

Table 2. Selected Bond Lengths (Å) and Angles (°) for Compounds **1**, **2,** and **6**[a]

Complex **1**							
Zn1−Cl2 #1	2.2597(16)	Zn1−Cl2	2.2597(16)	Zn1−Cl1 #1	2.2881(15)	Zn1−Cl1	2.2881(15)
Cl2#1-Zn1−Cl2	111.35(9)	Cl2#1-Zn1−Cl1#1	109.81(6)	Cl2−Zn1−Cl1 #1	107.24(6)	Cl2#1-Zn1−Cl1	107.24(6)
Cl2−Zn1−Cl1	109.81(6)	Cl1#1-Zn1−Cl1	111.43(8)				
Complex **2**							
Zn−N1	2.024(2)	Zn−N3	2.025(3)	Zn−Cl1	2.2344(9)	Zn−Cl2	2.2463(9)
N1−Zn−N3	112.02(10)	N1−Zn−Cl1	109.27(8)	N3−Zn−Cl1	102.85(8)	N1−Zn−Cl2	104.81(7)
N3−Zn−Cl2	109.90(8)	Cl1−Zn−Cl2	118.17(4)				
Complex **6**							
Zn1−O1	1.951(5)	Zn1−N11	1.995(6)	Zn1−N21	2.020(5)	Zn1−N31	2.005(6)
Zn2−O2	1.953(4)	Zn2−N13	2.034(6)	Zn2−N23	1.991(5)	Zn2−N33	2.015(5)
O1−Zn1−N11	115.9(2)	O1−Zn1−N31	107.7(2)	N11−Zn1−N31	109.42	O1−Zn1−N21	105.0(2)
N11−Zn1−N21	111.8(2)	N31−Zn1−N21	106.6(2)	O2−Zn2−N23	118.9(2)	O2−Zn2−N33	105.2(2)
N23−Zn2−N33	108.4(2)	O2−Zn2−N13	102.2(2)	N23−Zn2−N13	111.5(2)	N33−Zn2−N13	110.3(2)

[a] Symmetry code: #1: $-x, y, -z + 1/2$.

X-ray Crystallographic Study. Suitable single crystals of complexes **1**−**7** were mounted on a Siemens Smart CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298 K. All absorption corrections were performed using the SADABS program. All structures were solved by the direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXTL-97.[11] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located at geometrically calculated positions and treated by a mixture of independent and constrained refinement. Crystallographic data and structural refinements for compounds **1**−**7** are summarized in Table 1. The selected bond lengths parameters are summarized in Tables 2 and 3.

Results and Discussion

Synthesis. Syntheses of compounds **1**−**7** were schematically shown in Scheme 1. Reaction of Me_2biim with $ZnCl_2$ in aqueous solution produced the insoluble, neutral dimer **2**. **2** was redissolved in aqueous solution upon addition of acid to produce the soluble **1** with noncoordinated, protonated Me_2biim. Single crystals of **2** were obtained from careful defusion of ethanol solution of Me_2biim into the aqueous solution of $ZnCl_2$ through the water/ethanol layer. Similar method to obtain the crystalline bromide and iodide derivatives of **2** was unsuccessful. Further replacement of Cl in **2** by using excess Me_2biim to prepare proposed $[Zn_2Cl_2(\mu\text{-}Me_2biim)_3]^{4+}$ was failed. However, use of $Zn(NO_3)_2$ instead of $ZnCl_2$ produced the unprecedented triple Me_2biim-bridged dimer **6** exclusively. Employing CdX_2 (X = Cl, Br, I) instead of $ZnCl_2$ yielded the sigle Me_2biim-bridged polymers **3**−**5** rather than the cadmium analogues of **2**. The reaction of $Cd(CH_3CO_2)_2$ with Me_2biim in the presence of sodium perchlorate leaded to the formation of the unprecedented triple Me_2bim-bridged trimer **7**.

Crystal Structures. (A) $[ZnCl_4][H_2Me_2biim]$ (1). The structure of **1** was shown in Figure 1. It consists of the protonated Me_2biim, $[H_2Me_2biim]^{2+}$, and the counteranion $[ZnCl_4]^{2-}$. The structure has crystallographically imposed C_2

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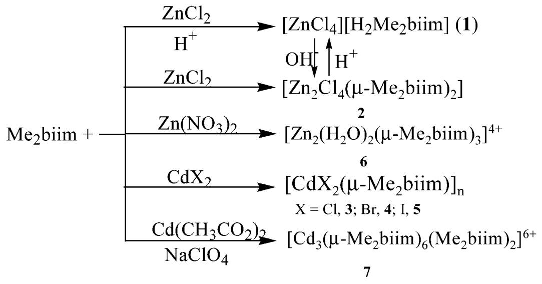
[11] Shelderic, G. M. *SHELXL-97*; University of Gottingen: Gottingen, Germany, 1997.

Table 3. Selected Bond Lengths (Å) and Angles (°) for Compounds **3**−**5** and **7**[a]

			Complex **3**				
Cd−N1	2.240(9)	Cd−N3	2.398(4)	Cd−Cl1	2.398(4)	Cd−Cl2	2.400(4)
N1−Cd−N3	101.1(3)	N1−Cd−Cl1	101.4(3)	N3−Cd−Cl1	113.1(2)	N1−Cd−Cl2	115.2(2)
N3−Cd−Cl2	101.3(3)	Cl1−Cd−Cl2	123.01(17)				
			Complex **4**				
Cd−N1	2.244(15)	Cd−Br	2.532(2)	N1#1-Cd−N1	95.3(10)	N1−Cd−Br	104.1(5)
N1−Cd−Br#1	112.9(4)	Br#1-Cd−Br	123.92(13)				
			Complex **5**				
Cd−N3	2.26(4)	Cd−N1	2.43(6)	Cd−I2	2.702(7)	Cd−I1	2.730(7)
N3−Cd−N1	103.0(9)	N3−Cd−I2	113.3(9)	N1−Cd−I2	108.0(11)	N3−Cd−I1	101.5(9)
N1−Cd−I1	105.3(11)	I2−Cd−I1	123.67(8)				
			Complex **7**				
Cd1−N11	2.360(3)	Cd2−N1	2.290(4)	Cd3−N25	2.278(4)	Cd3−N19	2.456(4)
Cd1−N15	2.395(4)	Cd2−N9	2.329(4)	Cd3−N29	2.279(4)	Cd4−N23	2.365(4)
Cd1−N7	2.418(4)	Cd2−N3	2.476(5)	Cd3−N21	2.290(4)	Cd4−N27	2.394(4)
Cd2−N5#2	2.242(4)	Cd2−O11	2.622(5)	Cd3−N17	2.413(4)	Cd4−N31	2.402(4)
Cd2−N13	2.283(5)	Cd3−O1	2.476(5)	N3−Cd2−O11	90.52(17)	N25−Cd3−O1	83.95(15)
N11#2-Cd1−N15	90.03(13)	N5#2-Cd2−N13	105.71(17)	N17−Cd3−N19	72.96(14)	N29−Cd3−O1	89.83(16)
N11−Cd1−N15	89.97(13)	N5#2-Cd2−N9	104.11(16)	N21−Cd3−N17	82.73(16)	N21−Cd3−O1	162.98(16)
N11#2-Cd1−N7	89.17(13)	N5#2-Cd2−N3	95.90(17)	N21−Cd3−N19	92.84(15)	N17−Cd3−O1	81.04(18)
N11−Cd1−N7	90.83(13)	N9−Cd2−N3	157.34(15)	N25−Cd3−N17	96.67(14)	N9−Cd3−O1	77.56(16)
N15−Cd1−N7	87.59(13)	N13−Cd2−N3	86.42(17)	N25−Cd3−N19	159.93(15)	N23#3-Cd4−N27	89.04(12)
N15#2-Cd1−N7	92.41(13)	N13−Cd2−N9	98.07(15)	N25−Cd3−N21	103.03(15)	N23−Cd4−N27	90.96(13)
N1−Cd2−N3	72.00(16)	N5#2-Cd2−O11	80.15(18)	N25−Cd3−N29	101.84(14)	N23−Cd4−N31#3	89.34(13)
N1−Cd2−N9	85.46(15)	N13−Cd2−O11	173.63(15)	N29−Cd3−N19	85.99(14)	N23−Cd4−N31	90.66(13)
N5#2-Cd2−N1	155.65(18)	N1−Cd2−O11	78.94(18)	N29−Cd3−N17	158.38(14)	N27−Cd4−N31#3	89.24(13)
N13−Cd2−N1	94.79(17)	N9−Cd2−O11	82.66(15)	N29−Cd3−N21	103.63(14)	N27−Cd4−N31	90.76(13)

[a] Symmetry code: #1: −*x* + 1, −*y*, *z*; #2: −*x* + 1, −*y* + 2, −*z*; #3: −*x* + 2, −*y* + 1, −*z* + 1.

Scheme 1. Syntheses of Complexes **1**−**7**



symmetry. Noncoordination of Me_2biim to Zn^{2+} is obviously due to the protonation of the unmethylated N atoms (N1). The N1···Cl distance of 3.199 Å is comparable to the reported N−H···Cl contact (3.112(5) Å),[1f] indicative of the substantial $N···H^+···Cl$ hydrogen bonds. The two imidazole rings of Me_2biim are not coplanar with the dihedral angle of 65.0° caused by the repulsion between the two methyl groups, which is greater than the calculated value for *N*,*N*′-tetramethylene-bridged derivative of 2,2′-biimidazole (41°)[5a] and its Ru(II) derivarive (53°).[5b]

(B) $[Zn_2Cl_4(\mu\text{-}Me_2biim_2)]$ (2). The structure and selected bond lengths and angles of **2** are given in Figure 2 and Table 2, respectively. The parameters of the $[ZnCl_2N_2]$ tetrahedron are similar to those of $[ZnCl_4]^{2-}$. The Zn−Cl bonds in **2** (2.2344(9) and 2.2463(9) Å) are close to those in **1** (2.2597(16), 2.8881(15) Å). The N1−Zn−N3 angle (112.02(10)°) is similar to the corresponding Cl1−Zn−Cl1′ (111.43(8)°), but the Cl1−Zn−Cl2 angle (118.17(4)°) in **2** is wider than in **1** (111.35(9)°). The Zn−N distances (average 2.025(3) Å) are identical to the basal Zn−N bonds but significantly shorter than the apical Zn−N distances in the pentacoordinate $[Zn_2(H_2biim)_5]^{4+}$ and $[Zn(H_2biim)_2(HCO_2)]^+$.[1a] The two imidazole rings of the bridging Me_2biim are almost perpendicular to each other (the dihedral angle is 85°). Consequently, the C1−C1′ (1.478(5) Å) and C5−C5′ (1.471(5) Å) bonds are longer than in $PtI_2(Me_2biim)$ (1.413(13) Å).[5c] The centroid−centroid distance of 3.89 Å

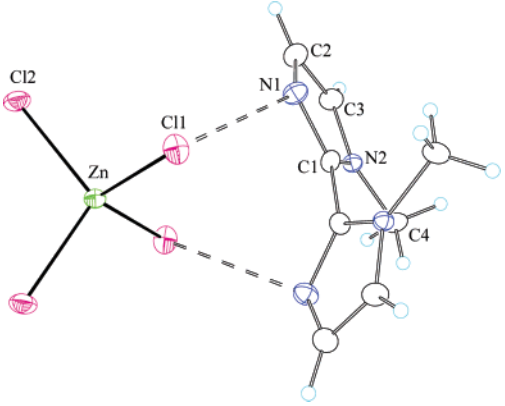


Figure 1. Structure of **1** with 30% thermal ellipsoids.

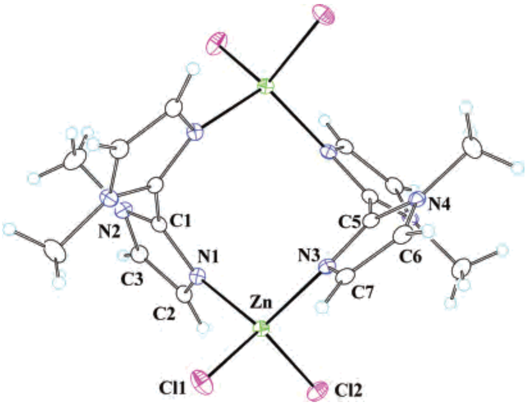


Figure 2. Structure of **2** with 30% thermal ellipsoids.

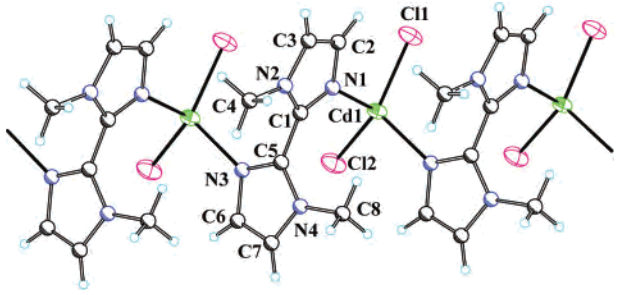


Figure 3. Infinite chain of **3** with 30% thermal ellipsoids.

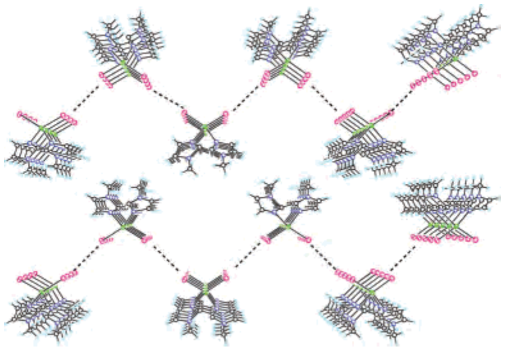


Figure 4. Head-to-head stacking of chains of **5**.

and dihedral angles of 38° between the imidazole rings suggest their weak π interactions.

(C) $[CdX_2(\mu\text{-}Me_2biim)]_n$ (X = Cl, 3; Br, 4; I, 5). Compounds **3**−**5** have similar one-dimensional molecular structures as illustrated in Figure 3 (X = Cl). Their selected bond lengths and angles are given in Table 3. The single Me_2biim links two neighboring CdX_2 into an infinite chain. The Cd atom has distorted $[CdCl_2N_2]$ tetrahedral coordination geometry. The N−Cd−N angle (101.1(3)°) is considerably narrower than in **2** (112.02(10)°) while the Cl−Cd−Cl angle (123.01(17)°) is correspondingly wider. The Cd−N distances (2.274(9) Å) are slightly shorter than those reported in the hexacooridnate $[CdBr_2(H_2biim)]$ (2.337(8) Å)[1b] and $[Cd(imidazole)_6]^{2+}$ (2.361(3) Å).[6] The "standard" Cd-aliphatic amine distances were reported as 2.33 ± 0.05 Å.[7] The Cd−Cl (2.400(9) Å) is shorter than the Cd−Br (2.532(2) Å) and Cd−I (2.717(8) Å), in accordance with their difference in covalent radii. Note that the Cd−Br bond is considerably shorter than in the hexacoordinate $[CdBr_2(H_2biim)]$ [2.702 Å (equatorial) and 2.892(1) Å (axial)].[1b] As in the case of **2**, steric requirements force the two imidazole rings to form the dihedral angle of 88.9(4)°. It is interesting that compounds **3**−**5** are not isomorphous because of the fact that packing of the infinite chains is directed by the C−H···Cl and C−H···Br hydrogen bonds in **4** and **5**, respectively, but by the I···I interactions in **3**. Figure 4 shows the "head-to-head" stacking of the $[CdI_2Me_2biim]_n$ chains with the Cd−I bonds from the different chains pointed to each other. The shortest I···I distance of 5.598 Å is suggestive of weak I···I interactions.[8] "Head-to-tail" stacking of the $[CdBr_2Me_2biim]_n$ chain is observed for **4** (Figure 5), allowing for the interchain C−H···Br interactions. The H···Br distances of 3.02 Å (∠C−H···Br = 147°) are slightly shorter than the sum of the corresponding van der Waals radii (3.05 Å). **3** has similar

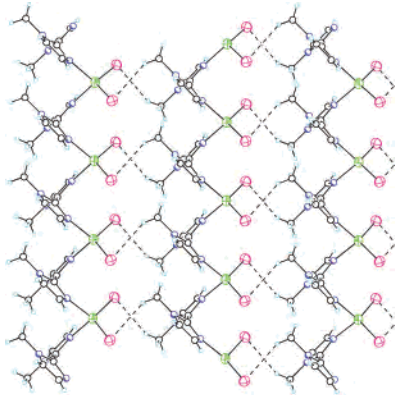


Figure 5. Head-to-tail stacking of the chains of **4**.

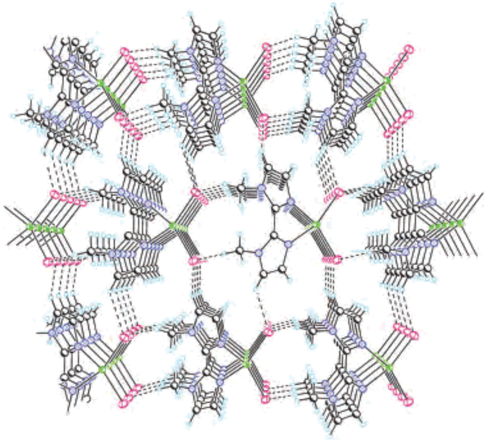


Figure 6. Supermolecular open framework of **3**.

"head-to-tail" arrangement of the infinite chains directed by the CH_3···Cl hydrogen-bonds. The H···Cl distances are 2.743 (∠C−H···Cl = 145°) and 2.892 Å (∠C−H···Cl = 148°), respectively, within the reported range of C−H···Cl hydrogen bonds.[9] Significantly, the C−H···Cl hydrogen bonds (2.784 and 2.832 Å) between the layers are observed in **5**, which leads to the formation of the supramolecular open framework of **5** as displayed in Figure 6.

(D) $[Zn_2(\mu\text{-}Me_2biim)_3(H_2O)_2](NO_3)_4\cdot H_2O$ (6). The numbering scheme of the cation of **6** and the selected bond lengths and angles are given in Figure 7 and Table 2, respectively. The crystal structure consists of the cationic dimmer $[Zn_2(\mu\text{-}Me_2biim)_3(H_2O)_2]^{4+}$, four nitrate ions and one water molecule. Each zinc atom has rather rigorous $[ZnON_3]$ tetrahedral coordination geometry. Unlike **2**, **6** has two apical Zn−O bonds along the Zn−Zn axis. The axial Zn−O bonds (1.948(5), 1954(4) Å) are shorter than in the pentacoordinate (2.006(3) Å)[1a] and hexacoordinate (2.150(3) Å)[1n] zinc complexes. The Zn−N bonds (average 2.009(5) Å) are not significantly different from those in **2**. The bond angles in the $[ZnON_3]$ tetrahedron range from 106.5(2) to 111.8(2)° (N−Zn−N) and from 102.2(2) to 118.9(2)° (O−Zn−N). The C−C distances between the imidazol rings are 1.464(9), 1.482(9), and 1.466(10) Å, similar to those in **2** but significantly longer than those in the chelating compounds.[5] The two imidazol rings of the bridging Me_2biim form dihedral angles of 67−76° so that the two $[ZnON_3]$ tetrahedrons are perfectly staggered around the Zn−Zn axis by

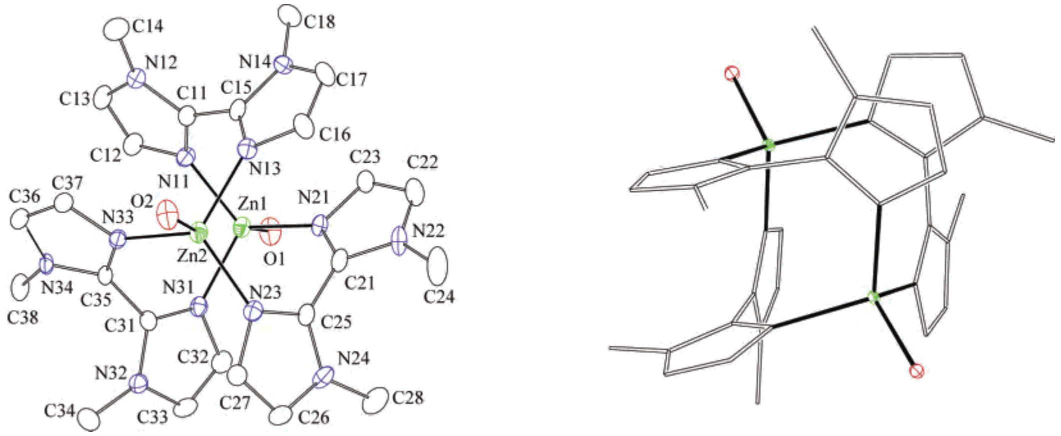


Figure 7. ORTEP drawing of $[Zn_2(\mu\text{-}Me_2biim)_3]^{4+}$ of **6** with 30% thermal ellipsoids.

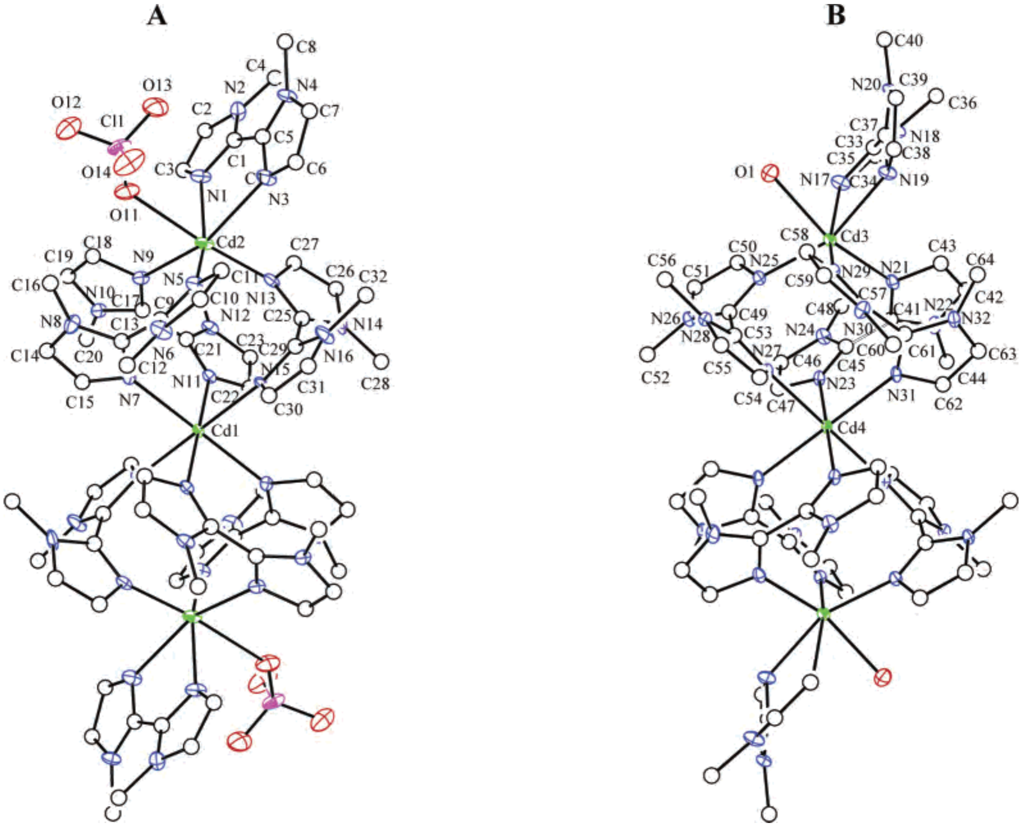


Figure 8. ORTEP drawing of the cationic clusters of **7** with 30% thermal ellipsoids.

about 60°. As illustrated in Figure 7, there are three pairs of the appropriately parallel imidazole rings (dihedral angles 9−11°) with the distances ranging from 3.1 to 3.6 Å presumably driven by the π-stacking.

(E) $[Cd_3(Me_2biim)_8]_2(ClO_4)_{12}(H_2O)_6$ (7). The unprecedented hexa Me_2biim-bridged trinuclear cluster **7** is displayed in Figure 8. The crystal structures consist of the 2 independent cationic trimers, $[Cd_3(Me_2biim)_8(ClO_4)_2]^{4+}$ (trimer A) and $[Cd_3(Me_2biim)_8(H_2O)_2]^{6+}$ (trimer B), 10 perchlorate ions, and 4 water molecules. Both are centrosymmetric with the central Cd^{2+} atoms lying at invention center. The Cd1 atom is bonded to six bridging Me_2biim in a rather rigorous $[CdN_6]$ octahedral geometry ($\angle$N−Cd−N = 90 ± 2.5°). The Cd1−N distances (2.360(3), 2.395(4), 2.418(4), average 2.391(4) Å) are longer than in the tetracoordinate **3** (2.274(9) Å) but similar to the hexacoordinate $[CdBr_2(H_2biim)]$ (2.337(8) Å)[1b] and $[Cd(imidazole)_6]^{2+}$ (2.361(3) Å).[6] The Cd2 atom is coordinated to three bridging and one chelating Me_2biim and one ClO_4^- with a distorted $[CdON_5]$ octahedron. The Cd2−O distance (2.622(5) Å) is much longer than normal value (2.20 Å), indicative of weak bonding to perchlorate. The Cd2−N3 distance (2.476(5) Å) is significantly longer than the other Cd−N bonds (2.242(4)-2.329(4) Å) presumably as a consequence of the deviation of the C−N3−Cd2 angles (143.1(4) and 109.5(3)°) from the optimum value. The chelating angle (N1−Cd2−N3) is 72.0(1)°, similar to that in $[CdBr_2(H_2biim)]$ (72.2(4)°)[1d] but smaller than in $PtI_2(Me_2biim)$ (78.2(2)°).[5] The chelating Me_2biim is nonplanar with the dihedral angle of 21.1°(cf. 0.9(3)° in $PtI_2(Me_2biim)$[5]). The bridging Me_2-

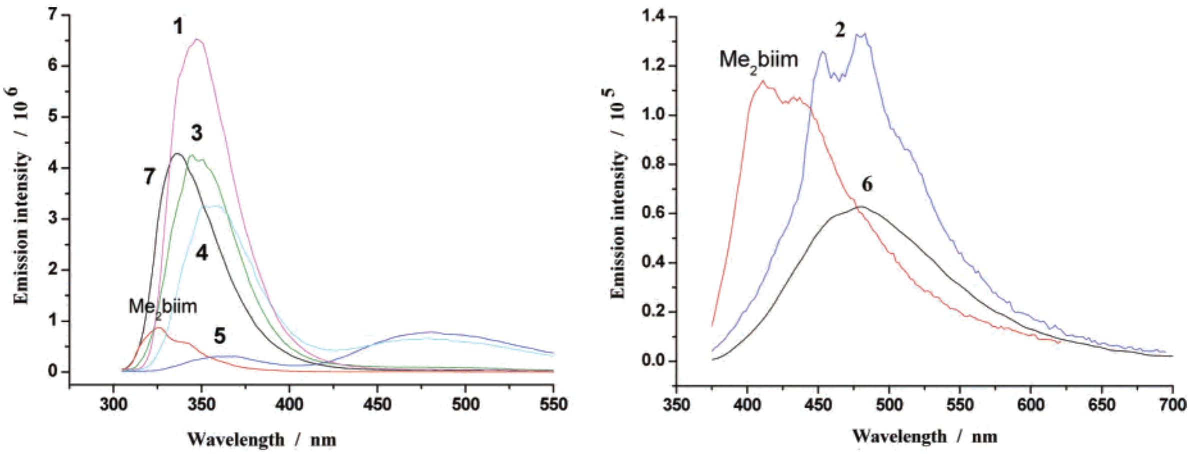


Figure 9. Emission spectra of Me$_2$biim and **1**−**7**.

biim have dihedral angles ranging from 67 to 76° because of steric demands. Trimer B has similar structural parameters around the central Cd4 atom (N−Cd4−N, 90±1°, Cd4−N, 2.365(4)-2.402(4) Å). The Cd3−OH$_2$ distance (2.467(4) Å) is shorter than Cd2−OClO$_3$. It is interesting to note that the dihedral angle of the bidentate Me$_2$biim in trimer B (43.0-(1)°) is considerably greater than in trimer A, presumably due to the smaller water molecule that imposes less barriers for the conformational inversion of the bidentate Me$_2$biim. The resultant poor coordination of the Cd3 to the bidentate Me$_2$biim (the deviation from the imidazole rings is about 1.2 Å, cf. 0.55Å in trimer A and 0.1−0.4 Å for Cd3-μ-Me$_2$-biim) is believed to be responsible for the longer Cd3−N distances (2.456(4) and 2.476(5) Å) than the Cd3-μ-Me$_2$-biim bond lengths (2.278(4), 2.279(4), 2.290(4) Å).

Fluorescence Properties. Metal complexes are promising luminescent materials for their potential applications such as light-emitting materials (LEDs) owing to their ability to enhance, shift and quench luminescent emission of organic ligands by metal coordination. The solid-state emission spectra of Me$_2$biim and complexes **1**−**7** were shown in Figure 9. A comparison of the fluorescence spectra of Me$_2$-biim and its metal complexes **1**−**7** is suggestive of the emission origin. Free Me$_2$biim exhibits an emission maximum at 330 nm when excited at 305 nm (λ_{ex} = 305 nm). It is interesting that **1** showed highly enhanced fluorescence intensity with similar emission maximum (345 nm) presumably due to the aromaticity induced by the protonation of Me$_2$biim in **1**. However, this fluorescence emission was quenched by coordination to Zn^{2+} in **2** and **6**, suggestive of strong ineteraction between the π-system and Zn^{2+}. It was also strongly enhanced in the cadmium compounds **3**, **4**, and **7** with similar emission maximum (330 ± 10 nm). An exception is the iodide compound **5** that had slightly lower emission intensity. It is noteworth that the other emission at about 410 nm of Me$_2$biim (λ_{ex} = 440 nm) was not observed for **3** and **7** but considerably enhanced in **4** and **5**. It also appeared in the zinc compounds **2** and **6** with similar emission intensity. An bathochromic shift of the emission at 410 nm was observed for **2** and **4**−**6**. It is obvious that the insoluble **3**−**5** and **7** possess strong fluorescent intensity, suggestive of potential application in solvent-resistant fluorescent material.

Conclusions

A series of single, double, and triple Me$_2$biim-bridged di-, trinuclear, and polymeric complexes with diverse structural topologies were prepared. The repulsion between the methyl groups plays more important role than resonance delocalization. Thus, Me$_2$biim has the two imidazole rings out of coplanarity with the dihedral angles ranging from 20 to 89° depending on specific steric requirements. As a consequence, Me$_2$biim prefers to be bridging rather than chelating ligands, showing potential in preparing polynuclear or polymeric metal complexes. The fluorescence emission of Me$_2$biim can be effectively enhanced, shifted, or quenched by metal coordination, indicating that these complexes have potential applications in fluorescence materials.

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Supporting Information Available: X-ray crystallographic files in CIF format for compouds **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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