Synthesis, Crystal Structures and Luminescent Properties of a New Family of Cubane Complexes Self-Assembled by Metal Carboxylates and Di-2-pyridyl Ketone in Gem-Diol Form

Ming-Liang Tong, Hung Kay Lee,*† Shao-Liang Zheng, and Xiao-Ming Chen*
School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, P.R. China
†*Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, P.R. China*

(Received June 30, 1999; CL-990579)

Five cubane-type complexes comprising similar $[M_4O_4]^{n+}$ cores (M = Zn(II), Cd(II), Mn(II), Co(II) or Ni(II)) synthesised in a facile route utilizing the *gem*-diol form of di-2-pyridyl ketone have been characterised by X-ray structural analysis. Both Zn(II) and Cd(II) complexes show room-temperature emission upon photo-excitation at 300 nm.

Recently, considerable research effort has been focused on studies of cubane-type polynuclear complexes due to their relevance to multi-electron transfer centres in biological systems,[1] and to their interesting magnetic and optical properties,[2,3] as well as to their potential relevance to inorganic solids.[4] Although cubane-type complexes of the tpye Fe_4S_4 or Mn_4O_4 and their derivatives have been extensively investigated,[1,5] reports on complexes containing Zn_4 and Cd_4 cubane cores are unprecedented. Only a few unstable cubane Zn_4 and Cd_4 organometallic compounds containing metal-carbon bonds have been documented.[6] On the other hand, although di-2-pyridyl ketone [$(2\text{-py})_2CO$] and its hydrolyzed derivative [$(2\text{-py})_2C(OH)_2$, designated as H_2L] are good chelating ligands, and a few polynuclear complexes of $(2\text{-py})_2C(O)(OH)^-$ (HL^-) obtained from metal carboxylates and $(2\text{-py})_2CO$ have been isolated and structurally characterized,[7] no systematic reaction has yet been shown before our work. The metal carboxylates are only limited to $Cu(O_2CMe)_2$ and $Co(O_2CMe)_2$.[8] We present herewith a facile synthetic route to a family of discrete cubane-type Zn(II), Cd(II), Ni(II), Mn(II) and Co(II) complexes self-assembled by the anion of H_2L as a ligand, namely, $[M_4(HL)_4(O_2CMe)_m(H_2O)_n](ClO_4)_{4-m}\cdot xH_2O$ (**1**: M = Zn^{2+}, $m = n = 2$; **2**: M = Cd^{2+}, $m = 3$, $n = 1$; **3**: M = Mn^{2+}, $m = 3$, $n = 1$; **4**: M = Co^{2+}, $m = 3$, $n = 1$; and **5**: M = Ni^{2+}, $m = 3$, $n = 0$). Among these compounds, to our knowledge, the Zn(II) and Cd(II) complexes are the first examples of the cubane Zn(II) or Cd(II) complexes.

Complexes **1-5** were prepared by self-assembly of $(2\text{-py})_2CO$ and $M(O_2CMe)_2$ in the MeCN-H_2O solvent with molar ratio of 1:2 at room temperature. The resulting solution were allowed to stand in air at room temperature for two weeks, yielding polyhedral crystals [*ca.* 85% yield based on $(2\text{-py})_2CO$ ligand]. The elemental analysis confirmed their formula.[9]

X-Ray crystallography[10] has established that the crystal of **1** is made up of cubane-type $[Zn_4(HL)_4]$ species, perchlorate anions and lattice water molecules. As illustrated in Figure 1, each cubane core is constructed by four zinc atoms and four oxygen atoms from the HL^- ligands each at alternating corners, where each zinc atom is coordinated in a distorted octahedral geometry by two nitrogen atoms each from a $(2\text{-py})_2CO$ ligand and four oxygen atoms. Except three oxygen atoms each from a HL^- ligand, being acting in the μ_3-O mode, the fourth oxygen atom is from a monodentate acetate group for the Zn(1) and Zn(2) atoms, and is from an aqua ligand for the Zn(3) and Zn(4) atoms.

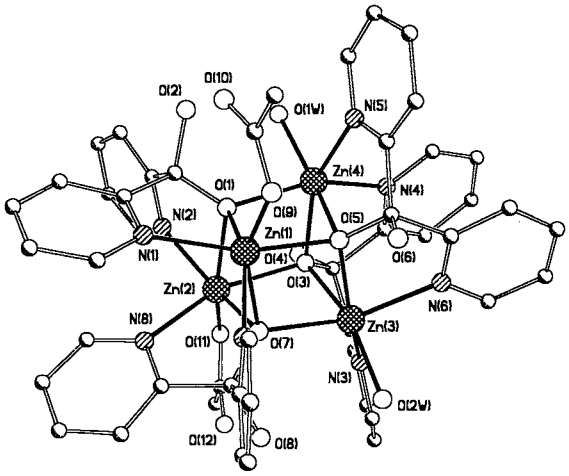

Figure 1. Structure of the cubane core in **1**. Selected distances (Å): Zn(1)-O 2.022(5)-2.264(5), Zn(1)-N 2.100(6)-2.117(6), Zn(2)-O 2.040(5)-2.220(4), Zn(2)-N 2.096(6)-2.116(6), Zn(3)-O 2.074(4)-2.224(5), Zn(3)-N 2.088(6)-2.125(6), Zn(4)-O 2.072(4)-2.216(5), Zn(4)-N 2.081(6)-2.133(6).

Another oxygen atom of each HL^- ligand remains protonated and unbound to metal ions. Hence the resulting monoanion acts as a $\eta^1:\eta^3:\eta^1:\mu_3$ ligation mode, which has recently been reported in a double cubane complex,[7a] but different from those found in most metal-HL^- complexes.[7]

The zinc atoms in **1** are in a slightly distorted octahedral coordination geometry. In contrast, both zinc and oxygen atoms possess highly distorted tetrahedral geometry, and the external angles are accordingly higher than those within the cube in common organometallic $[RZn(OR')]_4$ cubanes.[6]

The structures of **2**, **3** and **4** are similar to **1**, which also contains a cubane $[M_4O_4]$ core, perchlorate anions and lattice water molecules. In **2**, a minor difference lies in the seven-coordination geometry of the Cd(4) atom, which is bidentately chelated by an acetate group.

The structure of **5** also contains similar cubane-type $[Ni_4(HL)_4]$ species, perchlorate anions and lattice water molecules, but the cubane core is different from those in **1-4** and other nickel(II) cubane-type complexes.[9] As shown in Figure 2, the Ni(1) and Ni(2) atoms are connected by a μ_2-O_2CMe bridge, and further ligated by a nitrogen atom from a HL^- ligand, three oxygen atoms from different HL^- ligands and a monodentate acetate ion; while the Ni(3) and Ni(4) atoms are coordinated by three nitrigen atoms and three oxygen atoms from different HL^- ligands.

Both **1** and **2** show room-temperature emission upon photo-excitation at 300 nm. They can emit a moderate intense photo-

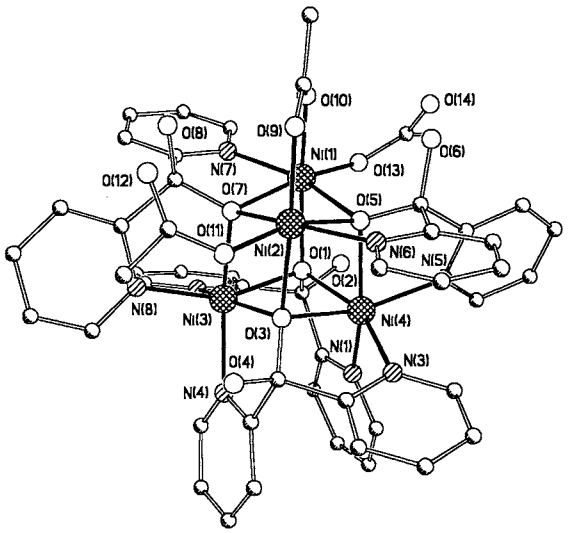

Figure 2. Structure of the cubane core in **5**. Selected distances (Å): Ni(1)···Ni(2) 2.9440(13), Ni(1)-O, 2.003(5)-2.165(4), Ni(1)-N(7) 2.056(6), Ni(2)-O 2.001(5)-2.158(4), Ni(2)-N(6) 2.068(5), Ni(3)-O 2.016(4-2.094(4), Ni(3)-N 2.030(5)-2.073(5), Ni(4)-O 2.011(4)-2.103(4), Ni(4)-N 2.012(6)-2.059(5).

luminescence with maximum at *ca.* 335 nm in MeCN solution. This high energy emission may be comparable to that of a very recently reported zinc(II) complex.[11] Further study on their other physical properties are in progress.

This work was supported by the NSFC (No. 29625102) and a Direct Grant from the Chinese University of Hong Kong.

References and Notes

1 R. H. Holm, S. Ciurli, and J. A. Weigel, In "Progress in Inorganic Chemistry: Bioinorganic Chemistry", ed by S. J. Lippard, John & Sons: New York (1990), Vol. 38, p 1; P. Zanello, *Coord. Chem. Rev.*, **83**, 199 (1988); D. Sellmann, *Angew. Chem. Int. Ed. Engl.*, **32**, 64 (1993); W. F. Ruettinger, D. M. Ho, and G. C. Dismukes, *Inorg. Chem.*, **38**, 1037 (1999), and the references cited therein.

2 "Magnetic Molecular Materials", ed by D. Gatteschi, O. Kahn, J. S. Miller, and F. Palacio; Kluwer Academic Publishers, Dordrecht, The Netherlands (1991), NATO ASI Series E, Vol. 198; S. M. J. Aubin, N. R. Dilley, L. Pardi, J. Krzystek, M. W. Wemple, L.-C. Brunel, M. B. Maple, G. Christou, and D.N. Hendrickson, *J. Am. Chem. Soc.*, **120**, 4991 (1998); K. Dimitrou, A. D. Brown, K. Folting, and G. Christou, *Inorg. Chem.*, **38**, 1834 (1999), and the references cited therein.

3 S.-W. Lai, K.-K. Cheung, M. C.-W. Chan, and C.-M. Che, *Angew. Chem., Int. Ed.*, **37**, 182 (1998); Y. Ma, H.-Y. Chao, Y. Wu, S. T. Lee, W.-Y. Yu, and C.-M. Che, *J. Chem. Soc., Chem. Commun.*, **1998**, 2491.

4 K. Isobe and A. Yagasaki, *Acc. Chem. Res.*, **26**, 524 (1993).

5 K. Dimitrou, K. Folting, W. E. Streib, and G. Christou, *J. Am. Chem. Soc.*, **115**, 6432 (1993); K. L. Taft, A. Caneschi, L. E. Pence, C. D. Delfs, G. C. Papaefthymiou, and S. J. Lippard, *J. Am. Chem. Soc.*, **115**, 11753 (1993), and the references cited therein.

6 F. Schindler, H. Schmidbaur, and U. Kruger, *Angew. Chem., Int. Ed. Engl.*, 4, 876 (1965); H. M. M. Shearer and C. B. Spencer, *Chem. Commun.*, **1966**, 194; H. M. M. Shearer and C. B. Spencer, *Acta Crystallogr., Sect. B*, **36**, 2046 (1980); M. M. Olmstead, P. P. Power, and S. C. Shoner, *J. Am. Chem. Soc.*, **113**, 3379 (1991).

7 V. Tangoulis, S. Paschalidou, E. G. Bakalbassis, S. P. Perlepes, C. P. Raptopoulou, and A. Terzis, *J. Chem. Soc., Chem. Commun.*, **1996**, 1297; V. Tangoulis, C. P. Raptopoulou, S. Paschalidou, E. G. Bakalbassis, S. P. Perlepes, and A. Terzis, *Angew. Chem., Int. Ed. Engl.*, **36**, 1083 (1997); V. Tangoulis, C. P. Raptopoulou, S. Paschalidou, A. E. Tsohos, E. G. Bakalbassis, A. Terzis, and S. P. Perlepes, *Inorg. Chem.*, **36**, 5270 (1997); S. R. Breeze, S. Wang, J. E. Greedan, and N. P. Raju, *Inorg. Chem.*, **35**, 6944 (1996), and the references cited therein.

8 A. Tsohos, S. Dionyssopoulou, C. P. Raptopoulou, A. Terzis E. G. Bakalbassis, and S. P. Perlepes, *Angew. Chem., Int. Ed.*, **38**, 983 (1999).

9 Anal. Found: C, 37.6; H, 3.5; N, 7.1%. Calc. for $C_{48}H_{57}N_8O_{27.5}Cl_2Zn_4$ **1**: C, 38.0; H, 3.8; N, 7.4%. Found: C, 38.1; H, 3.0; N, 7.0%. Calc. for $C_{50}H_{49}N_8O_{20}ClCd_4$ **2**: C, 38.3; H, 3.2; N, 7.2%. Found: C, 44.9; H, 3.6; N, 8.3%. Calc. for $C_{50}H_{49}N_8O_{20}Cl_2Mn_4$ **3**: C, 44.9; H, 3.7; N, 8.4%. Found: C, 43.8; H, 3.6; N, 8.1%. Calc. for $C_{50}H_{50.6}N_8O_{20.8}Cl_2Co_4$ **4**: C, 43.9; H, 3.7; N, 8.2%. Found: C, 40.5; H, 4.2; N, 7.5%. Calc. for $C_{50}H_{62.5}N_8O_{27.25}Cl_2Ni_4$ **5**: C, 40.5; H, 4.3; N, 7.6%.

10 Crystal data for **1**: $C_{48}H_{57}N_8O_{27.5}Cl_2Zn_4$, Mr = 1518.40, monoclinic, space group $P2_1/n$, a = 15.328(6), b = 24.181(12), c = 16.060(8) Å, β = 97.25(1)°, V = 5905(5) Å^3, Z = 4, D_c = 1.708 g cm^{-3}, μ(MoKα) = 17.91 cm^{-1}. **2**: $C_{50}H_{49}N_8O_{20}ClCd_4$, Mr = 1567.02, triclinic, space group P-1, a = 13.065(4), b = 14.315(8), c = 16.082(8) Å, α = 90.53(1)°, β = 108.10(1), γ = 93.94(1)°, V = 2851(2) Å^3, Z = 2, D_c = 1.826 g cm^{-3}, μ(MoKα) = 16.00 cm^{-1}. Data collections ($2 \le \theta \le 25$ for **1** and $2 \le \theta \le 26°$ for **2**) were performed at 293 K on a Siemens R3m diffractometer (Mo-$K\alpha$ = 0.71073 Å). The structures were solved with direct methods using SHELXS-97 (G. M. Sheldrick, University of Göttingen, 1997) and refined with full-matrix least-squares technique using SHELXL-97 (G. M. Sheldrick, University of Göttingen, 1997), giving for **1** a final R_1 value of 0.0637 for 812 parameters, 5626 unique reflections with $I \ge 2\sigma(I)$ and wR_2 of 0.1533 for all 10386 reflections, for **2** a final R_1 value of 0.0896 for 748 parameters 7500 unique reflections with $I \ge 2\sigma(I)$ and wR_2 of 0.2674 for all 11210 reflections.

11 K. Kimura, T. Kimura, I. Kinoshita, N. Nakashima, K. Kitano, T. Nishioka, and K. Isobe, *Chem. Commun.*, **1999**, 497.

12 Crystal data for **3**: $C_{50}H_{49}N_8O_{20}ClMn_4$, M_r = 1337.18, triclinic, space group P-1, a = 12.927(8), b = 14.245(10), c = 15.943(7) Å, α = 89.84(1), β = 72.58(1), γ = 86.02(1)°, V = 2794(3) Å^3, Z = 2. R_1 = 0.0464, wR_2 = 0.1255 (for all data). **4**: $C_{50}H_{50.6}N_8O_{20.8}ClCo_4$, Mr = 1367.45, triclinic, space group P-1, a = 12.893(11), b = 14.228(11), c = 16.048(8) Å, α = 89.43(1), β = 72.39(1), γ = 86.61(1)°, V = 2801(4) Å^3, Z = 2. R_1 = 0.0431, wR_2 = 0.1070 (for all data). **5**: $C_{50}H_{62.5}N_8O_{27.25}ClNi_4$, M_r = 1481.87, monoclinic, space group $P2_1/c$, a = 11.943(3), b = 24.582(8), c = 21.892(9) Å, β = 100.61(1)°, V = 6317(4) Å^3, Z = 4. R_1 = 0.0738, wR_2 = 0.2259 (for all data).