

Unique formation of two high-nuclearity metallamacrocycles from a mononuclear complex $[\text{Zn}(\text{dmpzdtc})_2]$ (dmpzdtc = 3,5-dimethylpyrazole-1-dithiocarboxylate) via CS_2 elimination†

Hong-Xi Li,^a Hua-Zhou Wu,^a Wen-Hua Zhang,^a Zhi-Gang Ren,^a Yong Zhang^a and Jian-Ping Lang^{*ab}

Received (in Cambridge, UK) 16th July 2007, Accepted 10th September 2007

First published as an Advance Article on the web 27th September 2007

DOI: 10.1039/b710787k

Dissolution of a mononuclear complex $[\text{Zn}(\text{dmpzdtc})_2]$ in $\text{BrCH}_2\text{CH}_2\text{Br}$ or DMF saturated with water followed by CS_2 elimination led to the formation of two unique high-nuclearity metallamacrocyclic complexes, $[\text{Zn}_4(\mu\text{-dmpz})_6(\mu\text{-OH})_2]_2$ and $[\text{Zn}_4(\mu\text{-dmpz})_6(\mu\text{-OH})_4]$.

In the past decades, much interest in the construction of polynuclear metallamacrocycles continues to be motivated by their aesthetically interesting structures, their magnetic and luminescent properties and their potential applications in catalysis.¹ These complexes are usually assembled from reactions of metal ions with various bridging ligands such as carboxylates, alcoholates, cyanides.² Among the polydentate N-donor ligands, pyrazolates are frequently employed in the assembly of polynuclear pyrazolate-bridged metallamacrocyclic structures.³ These pyrazolate-bridged metallamacrocycles were mostly prepared through reactions of metal ions with pyrazole under the presence of bases,^{3b,e,g} or oxidation reactions of low-valence metal pyrazolates,^{3c} or protonolysis reactions of metal carboxylate complexes with pyrazole,^{3d} or self-assembly reactions from cyclic or polymeric metal pyrazolates.^{3f,3h} However, only a few examples of cyclic zinc/pyrazolate complexes have been reported.⁴

On the other hand, alkali metal^{5a} and transition metals^{5b} of pyrazoledithiocarboxylates were observed to undergo CS_2 elimination in the solid state. Up to 2001, $[\text{Ni}(\text{dmpzdtc})_2]$ was reported to yield a dmpz-bridged dinuclear complex $[\text{Ni}_2(\mu\text{-dmpz})_2(\text{dmpzdtc})_2]$ (dmpz = 3,5-dimethylpyrazolate) via partial loss of CS_2 when recrystallized in CH_2Cl_2 -*n*-hexane.⁶ In the process of our preparing polynuclear oligomers or polymers from preformed complexes or clusters,⁷ the aforementioned intriguing properties for $[\text{M}(\text{dmpzdtc})_2]$ (M = Cu, Ni, etc.) attracted our attention: could the way of the CS_2 loss from these complexes be employed in the construction of dmpz-bridged metal complexes or even high-nuclearity metallamacrocycles? To this end, we prepared a zinc complex $[\text{Zn}(\text{dmpzdtc})_2]$ (**1**) and investigated its CS_2 elimination reactions in several organic solvents. In this communication, we report the isolation and structural characterization‡ of two unique

metallamacrocyclic complexes, $[\text{Zn}_4(\mu\text{-dmpz})_6(\mu\text{-OH})_2]_2$ (**2**) and $[\text{Zn}_4(\mu\text{-dmpz})_6(\mu\text{-OH})_4]$ (**3**) derived from CS_2 cleavage from **1** in $\text{BrCH}_2\text{CH}_2\text{Br}$ or DMF saturated with water.

Complex **1** was prepared in an almost quantitative yield from reaction of ZnCl_2 with two equiv. of $\text{K}[\text{dmpzdtc}]$ in $\text{MeOH-H}_2\text{O}$. **1** crystallizes in the monoclinic $P2_1/n$ space group and the asymmetric unit contains two independent $[\text{Zn}(\text{dmpzdtc})_2]$ molecules. The Zn center in each molecule is chelated by two dmpzdtc ligands through an N,S coordination mode, forming a ZnN_2S_2 tetrahedral geometry (Fig. 1). The adjacent molecules are stacked in a face-to-face fashion with a separation of 3.638 Å between the centroids of the two pyrazolyl rings, indicating the existence of the significant intermolecular π - π interactions.

Complex **1** is readily soluble in CH_2Cl_2 , CHCl_3 and DMF, but insoluble in H_2O and MeOH. Treatment of **1** in $\text{BrCH}_2\text{CH}_2\text{Br}$ or DMF saturated with water followed by slow diffusion of Et_2O into the yellow solution produced colorless prisms of $2:2(\text{BrCH}_2\text{CH}_2\text{Br})$ in 56% yield or greenish crystals of $3:4\text{DMF}$ in 67% yield. The IR spectra of **2** and **3** did not exhibit the characteristic C=S and C-S stretching vibrations at 1317, 869 and 985 cm^{-1} of **1**, suggesting the dmpzdtc ligands in **1** lost CS_2 molecules during the crystallization. However, treatment of **1** in freshly dried solvents did not produce **2** or **3**. For example, recrystallization of **1** in dried CH_2Cl_2 - Et_2O afforded a trinuclear complex $[\text{Zn}_3(\mu\text{-dmpz})_4(\text{dmpzdtc})_2]\cdot\text{CH}_2\text{Cl}_2$ (**4**- CH_2Cl_2). Evidently, the presence of water in solvents was essential for the formation of these metal cyclic complexes. Although the mechanism of formation of **2** and **3** are not clear, **3** was likely to be formed by dmpzH and CS_2 cooperative elimination from **4** and **1** via H_2O nucleophilic attack. The formation of **2** may be derived from the nickel analogue⁶ “[$(\text{dmpzdtc})\text{Zn}(\mu\text{-dmpz})_2$]” by loss of dmpzH and CS_2 (see ESI†). Intriguingly, recrystallization of **1** in pure CS_2 did not form crystals of **1**, but gave rise to **4**- CS_2 (see ESI†). The orange prismatic crystals of **1** were finally obtained from diffusion

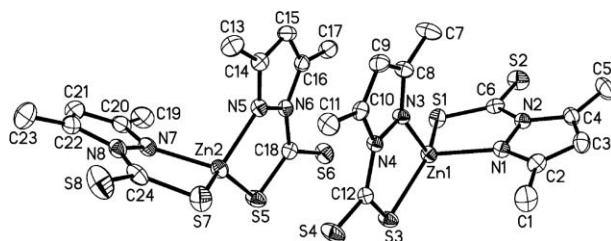


Fig. 1 View of **1** showing 50% thermal probability ellipsoids. All hydrogen atoms are omitted for clarity.

^aSchool of Chemistry and Chemical Engineering, Suzhou University, Suzhou, Jiangsu, P. R. China 215123. E-mail: jplang@suda.edu.cn; Fax: 86-512-65880089

^bState Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, Jiangsu, P. R. China 210093

† Electronic supplementary information (ESI) available: Synthesis of **1-4**, suggested mechanism of formation of **3** and **4**, the emission spectra of $\text{K}[\text{dmpzdtc}]$ and **1-4**, the positive-ion ESI mass spectra of **1-4**, ¹H NMR spectra of **1** and **4**, and selected bond lengths and angles of **1-4**. See DOI: 10.1039/b710787k

of Et₂O into the saturated solution of **1** in CHCl₃ within one day. The positive ion ESI mass spectrum of **1** in CH₂Cl₂ showed the parent molecular ion [M + H]⁺ along with a number of unidentified peaks. Although **2** and **3** are virtually insoluble in common organic solvents, some signals at *m/z* = 1765.0 for [M + 2H₂O + H]⁺ (**2**) or *m/z* = 3569.3 for [M + DMF + MeOH + H]⁺ (**3**) in the ESI-MS spectra of their mother liquors may be originated from their corresponding parent molecule (see ESI[†]).

2·2(BrCH₂CH₂Br) crystallizes in the triclinic *P* $\bar{1}$ space group and the asymmetric unit contains half of a [Zn₈(μ-dmpz)₁₂(μ-OH)₄] molecule and one BrCH₂CH₂Br solvent molecule. Complex **2** is composed of four [Zn₂(μ-dmpz)(μ-OH)] fragments linked by four pairs of μ-dmpz anions, forming a centrosymmetric metallamacrocyclic crown structure (Fig. 2). The four [Zn₂(μ-dmpz)(μ-OH)] fragments are approximately locating in a plane while four pairs of dmpz anions are symmetrically standing above or below the plane. In each fragment, the two tetrahedrally-coordinated Zn centers are bridged by one OH⁻ group and one dmpz to form a five-membered ZnN₂ZnO ring with Zn···Zn contacts of 3.267(2)–3.279(2) Å. The Zn···Zn contacts between two fragments are quite different: 3.267(2) and 3.520(2) Å. It is noted that there are two BrCH₂CH₂Br solvent molecules hovering above or below this crown molecule, and each is surrounded by four dmpz groups with the same orientation *via* four O–H···Br hydrogen bonding interactions.

3·4DMF crystallizes in the tetragonal *P4nc* space group and the asymmetric unit consists of one-fourth of a discrete [Zn₁₆(μ-dmpz)₂₄(μ-OH)₈] molecule and two one-half DMF solvent molecules. **3** consists of four [Zn₄(μ-dmpz)₆(μ-OH)₂] fragments linked by sharing pairs of μ-dmpz and μ-OH⁻ anions, forming another metallamacrocyclic crown structure with a crystallographic four-fold axis running through the centre of the structure (Fig. 3). This Zn₁₆ complex appears to be the largest pyrazolate-bridged zinc macrocyclic complex known to date. In each fragment, the four Zn centres are tetrahedrally coordinated by one OH⁻ and three dmpz (Zn1 and Zn3), or by two OH⁻ and two dmpz (Zn2), or by four dmpz ligands (Zn4). Within the fragment the Zn···Zn contacts vary from 3.192(1) to 3.612(1) Å while that between two fragments is 3.207(1) Å. However the Zn···Zn contacts in **2** and **3** are shorter than that found in

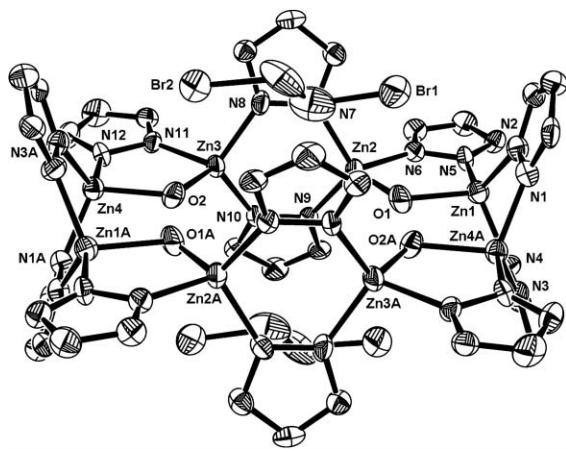


Fig. 2 Perspective view of 2·2(BrCH₂CH₂Br) showing 50% thermal probability ellipsoids. All methyl groups and hydrogen atoms are omitted for clarity.

[{Zn(Hdmpz)(dmpz)}₂(μ-dmpz)(μ-OH)] (3.747 Å).⁸ The edge distance (Zn2 and Zn2A) and diagonal distance (Zn2 and Zn2B) of this metallacycle are *ca.* 15.7 and 18.0 Å, which indicates that **3** is a nanosized molecular crown. Within the molecule, four halves of DMF solvent molecules are symmetrically “fixed” through four O2–H···O3 hydrogen-bonding interactions, while another four halves of DMF molecules are held outside the crown framework through four O1–H···O4 hydrogen bonds. It is estimated⁹ that there are very large voids in the structure of 3·4DMF, some 1016 Å³ centered at (0, 0, 0.132) and (0.5, 0.5, 0.632).

4·CH₂Cl₂ crystallizes in the triclinic *P* $\bar{1}$ space group. The structure of **4** consists of a linear array of three zinc ions connected by two pairs of μ-dmpz anions (Fig. 4). The Zn···Zn contacts are in the range 3.645(1)–3.657(1) Å, which excludes any metal–metal interaction. Each Zn atom adopt a tetrahedral coordination geometry, coordinated by four N atoms from four μ-dmpz anions (Zn2) or by one dmpzdtc through the N, S coordination mode and two N atoms from two μ-dmpz anions (Zn1 or Zn3). The average Zn–S bond distance (2.3342(13) Å) is longer than that of **1**. The mean Zn–N(dmpzdtc) length (2.028(4) Å) is slightly longer than that of the Zn–N(dmpz) length (1.987(3) Å), but almost the same as that of **1**.

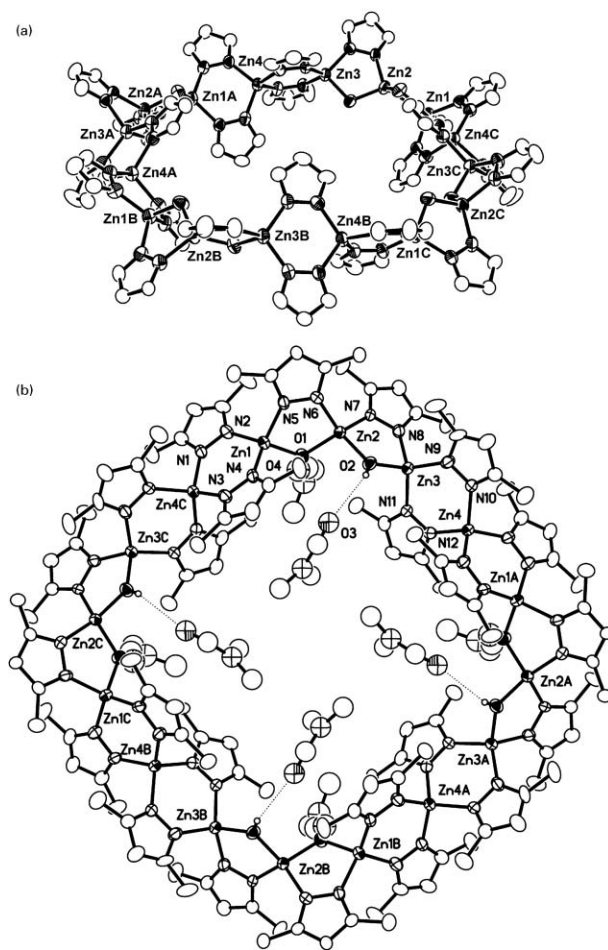


Fig. 3 Side view (upper) of 3·4DMF showing 50% thermal probability ellipsoids. All methyl groups, DMF molecules, and hydrogen atoms are omitted for clarity. Top view (down) of 3·4DMF showing 50% thermal probability ellipsoids.

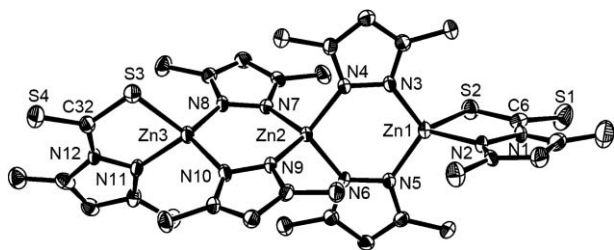


Fig. 4 Perspective view of **4** showing 50% thermal probability ellipsoids. All hydrogen atoms are omitted for clarity.

Complexes **1–4** showed interesting photoluminescent properties in solid state at ambient temperature. Excitation of **1** or **4** at 350 nm resulted in a strong emission band at 418 nm (**1**) or 421 nm (**4**) along with two weak bands at 484/541 nm (**1**) or 485/539 nm (**4**), which are similar to those of the free ligand K[dmpzdtc]. On the other hand, upon excitation at 293 nm, **2** and **3** showed a very similar emission band at 423 nm (**2**) or 421 nm (**3**) with a shoulder peak at 484 nm (see ESI†). These emissions observed in **2** and **3** are tentatively assigned to the π - π^* intraligand fluorescence due to their close resemblance of the emission bands.¹⁰

In summary, the present work demonstrated that for the first time, complete elimination of CS₂ from **1** in different solvents under the presence of water resulted in two high-nuclearity metallamacrocyclic Zn₈ and Zn₁₆ crown complexes **2** and **3**. It is anticipated that the synthetic methodology may be a promising approach to high-nuclearity pyrazolate-bridged metalla-macrocycles. Studies on this respect are under way in our laboratory.

This work was supported by the NNSF of China (20525101), the NSF of Jiangsu Province (BK2004205), the Specialized Research Fund for the Doctoral Program of Higher Education (20050285004), the State Key Laboratory of Coordination Chemistry of Nanjing University in China. Prof. Z.-N. Chen of FJIRSM was highly appreciated for his assistance in measuring photoluminescence and ESI-MS spectra of the four compounds. The authors also thank the helpful comments from the reviewers.

Notes and references

† X-Ray single-crystal diffraction data collections: **1–4** were collected on a Rigaku Mercury CCD at 193 K. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs. **1**: C₁₂H₁₄N₄S₄Zn, $M_r = 407.88$, monoclinic, space group $P2_1/n$, $a = 8.8341(18)$, $b = 14.938(3)$, $c = 24.781(5)$ Å, $\beta = 94.72(3)^\circ$, $V = 3259.1(11)$ Å³, $Z = 8$, $D_c = 1.663$ g cm⁻³, $\mu = 2.016$ mm⁻¹, 30647 reflections measured, 5937 unique reflections ($R_{\text{int}} = 0.0360$), 5496 observed reflections ($I > 2\sigma(I)$), 386 parameters, $R_1 = 0.0422$, $wR_2 = 0.0912$, $S = 1.278$. **2-2**(BrCH₂CH₂Br): C₆₄H₉₆Br₄N₂₄O₄Zn₈, $M_r = 2108.37$, triclinic, space group $P\bar{1}$, $a = 10.577(2)$, $b = 14.267(3)$, $c = 16.194(3)$ Å, $\alpha = 64.53(3)$, $\beta = 81.38(3)$, $\gamma = 68.43(3)^\circ$, $V = 2051.6(10)$ Å³, $Z = 1$, $D_c = 1.707$ g cm⁻³, $\mu = 4.303$ mm⁻¹, 20246 reflections measured, 7469 unique reflections ($R_{\text{int}} = 0.0700$), 5297 observed reflections ($I > 2\sigma(I)$), 500 parameters, $R_1 = 0.0830$, $wR_2 = 0.1828$, $S = 1.113$. **3-4**DMF: C₁₃₂H₂₀₄N₅₂O₁₂Zn₁₆, $M_r = 3757.71$, tetragonal, space group $P4nc$, $a = 27.083(4)$, $b = 27.083(4)$, $c = 14.675(3)$ Å, $V = 10764(3)$ Å³, $Z = 2$,

$D_c = 1.159$ g cm⁻³, $\mu = 1.799$ mm⁻¹, 37253 reflections measured, 9648 unique reflections ($R_{\text{int}} = 0.0870$), 8684 observed reflections ($I > 2\sigma(I)$), 480 parameters, $R_1 = 0.0624$, $wR_2 = 0.1615$, $S = 1.113$. **4-CH₂Cl₂**: C₃₃H₄₄Cl₂N₁₂S₄Zn₃, $M_r = 1004.15$, triclinic, space group $P\bar{1}$, $a = 12.1532(13)$, $b = 13.5228(12)$, $c = 14.3299(18)$ Å, $\alpha = 81.603(8)$, $\beta = 86.174(8)$, $\gamma = 63.810(5)^\circ$, $V = 2090.6(4)$ Å³, $Z = 2$, $D_c = 1.595$ g cm⁻³, $\mu = 2.077$ mm⁻¹, 20557 reflections measured, 7624 unique reflections ($R_{\text{int}} = 0.0370$), 6319 observed reflections ($I > 2\sigma(I)$), 500 parameters, $R_1 = 0.0511$, $wR_2 = 0.1039$, $S = 1.094$. In **2-2**(BrCH₂CH₂Br), two C atoms of the BrCH₂CH₂Br molecule were found to be disordered into two positions with the occupancy ratio of 0.68/0.32 for C31/C31A and C32/C32A. In the case of **3-4**DMF, the C, N, O atoms of the DMF molecule was refined with 50% occupancy due to their relatively higher thermal parameters. CCDC 649469, 649471, 649472, 649470. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710787k

- S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; A. Müller and C. Serain, *Acc. Chem. Res.*, 2000, **33**, 2; R. E. P. Winpenny, in *Comprehensive Coordination Chemistry II*, ed. T. J. Meyer and J. McCleverty, Elsevier-Peramon, New York, 2004, vol. 7, p. 125; M. A. Omary, A. A. Mohamed, M. A. Rawashdeh-Omary and J. P. Fackler, Jr., *Coord. Chem. Rev.*, 2005, **249**, 1372; H. V. R. Dias, H. V. K. Diyabalanage, M. A. Rawashdeh-Omary, M. A. Franzman and M. A. Omary, *J. Am. Chem. Soc.*, 2003, **125**, 12072; K. Singh, J. R. Long and P. Stavropoulos, *J. Am. Chem. Soc.*, 1997, **119**, 2942; S. X. Liu, S. Lin, B. Z. Lin, C. C. Lin and J. Q. Huang, *Angew. Chem., Int. Ed.*, 2001, **40**, 1084.
- C. P. Raptopoulou, V. Tangoulis and E. Devlin, *Angew. Chem., Int. Ed.*, 2002, **41**, 2386; K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi and S. J. Lippard, *J. Am. Chem. Soc.*, 1994, **116**, 823; Z. H. Ni, H. H. Kou, L. F. Zhang, C. Ge, A. L. Cui, R. J. Wang, Y. Li and O. Sato, *Angew. Chem., Int. Ed.*, 2005, **44**, 7742; B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022.
- M. Enomoto, A. Kishimura and T. Aida, *J. Am. Chem. Soc.*, 2001, **123**, 5608; G. A. Ardizzoia, S. Cenini, G. L. Monica, N. Masciocchi, A. Maspero and M. Moret, *Inorg. Chem.*, 1998, **37**, 4284; R. W. M. t. Hoedt, F. B. Hulsbergen, G. C. Verschoor and J. Reedijk, *Inorg. Chem.*, 1982, **21**, 2369; C. D. Nicola, Y. Y. Karabach, A. M. Kirillov, M. Monari, L. Pandolfo, C. Pettinari and A. J. L. Pombeiro, *Inorg. Chem.*, 2007, **46**, 221; N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia and G. L. Monica, *J. Am. Chem. Soc.*, 1994, **116**, 7668; A. A. Mohamed, A. Burini, R. Galassi, D. Paglialunga, J. Galán-Mascarós, K. R. Dunbar and J. P. Fackler, Jr., *Inorg. Chem.*, 2007, **46**, 2348; L. F. Jones, C. A. Kilner, M. P. d. Miranda, J. Wolowska and M. A. Halcrow, *Angew. Chem., Int. Ed.*, 2007, **46**, 4073; G. Mezei, P. Baran and R. G. Raptis, *Angew. Chem., Int. Ed.*, 2004, **43**, 574; A. L. Dearden, S. Parsons and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2001, **40**, 152.
- D. T. Puerta and S. M. Cohen, *Chem. Commun.*, 2003, 1278; V. Chandrasekhar, S. Kingsley, B. Rhatigan, M. K. Lam and A. L. Rheingold, *Inorg. Chem.*, 2002, **41**, 1030; B. Bauer-Siebenlist, F. Meyer, E. Farkas, D. Vidovic, J. A. Cuesta-Seijo, R. Herbst-Irmer and H. Pritzkow, *Inorg. Chem.*, 2004, **43**, 4189.
- S. Trofimenko, *J. Org. Chem.*, 1968, **33**, 890; R. D. Bereman, G. D. Shields and D. Nalewajek, *Inorg. Chem.*, 1978, **17**, 3713.
- S. Mukhopadhyay, U. Mukhopadhyay, T. C. W. Mak and D. Ray, *Inorg. Chem.*, 2001, **40**, 1057.
- H. X. Li, Z. G. Ren, Y. Zhang, W. H. Zhang, J. P. Lang and Q. Shen, *J. Am. Chem. Soc.*, 2005, **127**, 1122.
- M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson and J. Trotter, *Can. J. Chem.*, 1990, **68**, 1494.
- Volumes were estimated by using the PLATON program. PLATON: A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.
- C. M. Che, C. W. Wan, W. Z. Lin, W. Y. Yu, Z. Y. Zhou, W. Y. Lai and S. T. Lee, *Chem. Commun.*, 2001, 721.