View Article Online / Journal Homepage / Table of Contents for this issue

The first 2D trinuclear Cd(II)-complex with adenine nucleobase: hydrothermal synthesis, crystal structure and fluorescent properties†

En-Cui Yang, Hong-Kun Zhao, Bin Ding, Xiu-Guang Wang and Xiao-Jun Zhao*

Received (in Gainesville, FL, USA) 13th August 2007, Accepted 13th September 2007
First published as an Advance Article on the web 21st September 2007
DOI: 10.1039/b712387f

Downloaded by University of Belgrade on 01 January 2013
Published on 21 September 2007 on http://pubs.rsc.org | doi:10.1039/B712387F

The first 2D aggregate, $\{[Cd_3(\mu_3\text{-ade})_2(ap)_2(H_2O)_2]\cdot 1.5H_2O\}_n$ (1) (where adeH = adenine; H_2ap = adipic acid), with trinuclear Cd(II) as secondary building units, has been successfully synthesized, the compound shows scarce coordination modes (tridentate μ_3-N3,N7,N9 for ade and hexadentate $\eta^1:\eta^2:\eta^2:\eta^1$ for flexible ap) and a novel crystal packing arrangement, exhibiting strong fluorescent emission properties.

Recently, transition metal complexes with nucleobases have been investigated extensively owing not only to the biological importance of the metal–nucleobase bonds, the functions of nucleic acids and genetic information transfer but also to their structural diversity, molecular recognition behaviors and potential applications as advanced functional materials.[1–3] Many investigations have pointed out the binding preferences of a specific metal ion towards nucleic acids or their constituents depend essentially on the metal properties (main group or transition metal, charge, d-electron configuration, and hard- or softness), the basicity of the N/O donor site of the nucleobases and, sometimes, the auxiliary ligands that complete the metal coordination sphere.[4]

As one of the native nucleobases, adenine (adeH) can undergo a variety of acid–base reactions and exists as surprising tautomers, which thus offer the possibility of coordination as neutral and also as both anionic and cationic ligands. On the other hand, resulting from its three kinetically favored endocyclic sites (N1, N3, and N7) and potential H-bonding site (N6), adeH can potentially exhibit versatile binding modes upon coordination with metal ions. For example, it can easily bind with Mn(II), Co(II), and Zn(II) ions as a terminal ligand at room temperature, exhibiting common N7-, N1- and less common N3-, N9-, N6-monodentate fashions.[5] Whereas in adeH-based Cu(II)/Hg(II)-complexes, it presents unique N3–N7 and N7–N9 *et al.* bridging coordination modes by carefully controlling the reaction conditions.[5–8] Although many novel adeH-based metal complexes mentioned above have been well documented so far, to our best knowledge, the discrete and/or infinitely high-dimensional Cd(II) complexes with adeH are comparably less well investigated,[9] and specially the hydrothermal synthesis technique has been applied rarely to the construction of nucleobase-based metal complexes. Motivated by the great recent success of the hydrothermal method in the preparation of novel Cd(II)-complexes with intriguing structural motifs and potential applications,[10,11] in this paper, we initiate investigations into the preparation and coordination nature of metal complexes of adeH, especially with Cd(II), with the emphasis on binding modes of adeH under hydrothermal conditions as well as the crystal packing arrangement.

By the assembly of flexible adipic acid (H_2ap), adeH nucleobase and Cd(II) salts under hydrothermal conditions, herein, the first infinite 2D Cd(II) aggregates, $\{[Cd_3(\mu_3\text{-ade})_2(ap)_2(H_2O)_2]\cdot 1.5H_2O\}_n$ (**1**) (adeH = adenine; H_2ap = adipic acid), with trinuclear Cd(II) as secondary building units, have been successfully isolated. The preparation of **1** is independent of the molar ratio of the starting materials. Although the stoichiometric ratio of metal ion, ade and ap anions in **1** is 3 : 2 : 2, they preferably reacted with each other in a ratio of 2 : 1 : 1. In contrast, the assembly of **1** is highly sensitive to pH value. Thus, triethylamine was added into the mixture in order to tune the pH value of the reaction system to 5, otherwise only grey powders were obtained. Just as pointed out in previous investigations, the main reason is that the pH value can significantly affect the protonated and deprotonated degree of adeH, and further dominate the resulting framework structure.[12]

As shown in Fig. 1, crystal structure determination reveals that the basic building block of trinuclear Cd(II) in **1** contains three Cd(II) ions, two ap anions, two bridging ade, two coordinated water molecules (O5 and O5A) and two free lattice water molecules with 50% occupancy number for O6 and 25% for O7. Cd2, located at an inversion center of the

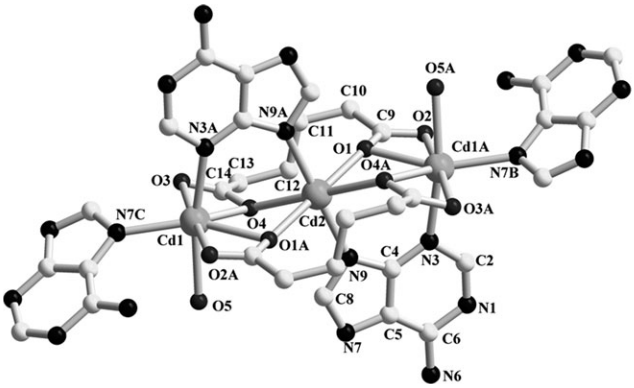


Fig. 1 View of the trinuclear Cd(II)-subunit in **1**.

College of Chemistry & Life Science, Key Laboratory of Molecular Structure and Materials Performance, Tianjin Normal University, 300387, P. R. China. E-mail: xiaojun_zhao15@yahoo.com.cn; Fax: +86 2223766556; Tel: +86 2223766556

† Electronic supplementary information (ESI) available: List of bond lengths, angles and hydrogen bonds, additional crystal diagrams and TG-DTA curves. See DOI: 10.1039/b712387f.

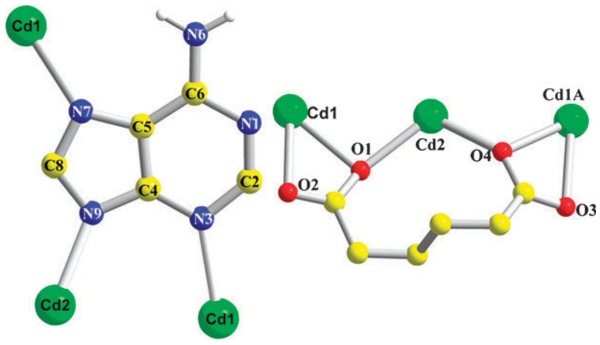
Downloaded by University of Belgrade on 01 January 2013
Published on 21 September 2007 on http://pubs.rsc.org | doi:10.1039/B712387F

trinuclear subunit, exhibits a distorted octahedral geometry formed by four carboxylate oxygen atoms from two ap anions and two ade imidazole nitrogen atoms (N9 and N9A), resulting in a CdN_2O_4 donor set. While symmetry-related Cd1 and Cd1A (symmetry code A: $2 - x$, $1 - y$, $-z$) are both seven-coordinated by four oxygen atoms from two chelated carboxylate groups, two ade nitrogen atoms (N7, N3, N7A, N3A) and one coordinated aqua molecule, building distorted pentagonal bipyramidal CdN_2O_5 surroundings. Cd1, Cd2 and Cd1A are strictly linear with a bond angle of 180.0°. The Cd1···Cd2 distance within the trinuclear subunit is 3.632(3) Å. In comparison, the Cd···Cd distance in **1** is 0.311 Å shorter than the previously reported trinuclear Cd(II)-complex with modified ade, $[\{Cd_2Cl_6(\text{A-Et-en})_2\}_n]$ (A-Et-enHCl: ethylenediamine-N9-ethyladenine hydrochloride), suggesting the potentially stronger intermetal ion interaction and seven-coordinated polyhedra around terminal Cd(II) ions are different from those in $[\{Cd_2Cl_6(\text{A-Et-en})_2\}_n]$.[9] On the other hand, the deprotonated ade in **1** adopts a μ_3-N3,N7,N9 tridentate coordination mode. While ap anions exhibit a new hexadentate η^1:η^2:η^2:η^1 binding fashion (see Scheme 1). To our best knowledge, such a simultaneously chelating and bridging μ_3-N3,N7,N9 tridentate binding mode by ade is unique except for several copper(II) and a few compounds of methylmercury(II) metalated adeninato (1−) derivatives.[7,13]

The linear trinuclear Cd(II) centers and the two ap anions are almost coplanar (Fig. S1†), which are spread by four bridging ade ligands into infinite 2D planes along the crystallographic *b*- and *c*-directions (Fig. 2). Unexpectedly, neighboring Cd(II) subunits within the 2D planes are arranged in a unique way, with specific dihedral angles of 78.11(9)° (calcd from the Cd–ap plane), and cannot be overlapped simply through rotation. (Fig. S2†) Thus these neighboring trinuclear subunits are arranged in a chiral Λ and Δ way. Each trinuclear Cd(II)-subunit with Λ geometry is linked to four neighboring Δ-shaped blocks. In turn, each trinuclear Cd(II)-block with Δ geometry is linked to four neighboring subunits with Λ geometry, ultimately resulting in a 2D neutral network with (4, 4) topology. A side view of the 2D plane suggests that trinuclear Cd(II)-subunits are parallel with each other just resulting from its unique arrangement, rather than being in a straight line.

It is also interesting to investigate the supramolecular architecture of **1** because previous examples have revealed that those supramolecular architectures based on ade can be correlated with the host framework and can be used as host molecules to recognize their complementary base pairs, which also affect the coordination modes of ade or adeH.[14] In the crystal packing of **1**, lattice water molecules are found to be trapped within 2D planes *via* classic O–H···O H-bonding interactions (O5···O6, 2.627(3) Å; O5···O3, 2.848(5) Å, see Fig. 3 and Table S3†). Furthermore, the neighboring 2D planes are stacked together in a parallel way by pairs of "head to tail" N–H···N (N6···N1, 2.932(1) Å, Fig. S3†) H-bonding interactions. Such an arrangement of H-bonds is different from those previously reported for 1D or 3D ade-based complexes,[15] and can be correlated with the unique trinuclear Cd(II)-subunit framework of **1**. Surprisingly, no direct interactions between ade and those lattice or coordinated aqua molecules can be observed. In particular, no π···π interactions are observed, and the nearest aromatic ring distance is 4.189(0) Å.

The FT-IR spectra of **1** display the following relevant peaks (cm^{-1}) for aqua (ν_{as} 3311), ap (ν_{as}(COO) 1599, ν_s(COO) 1542)



Scheme 1

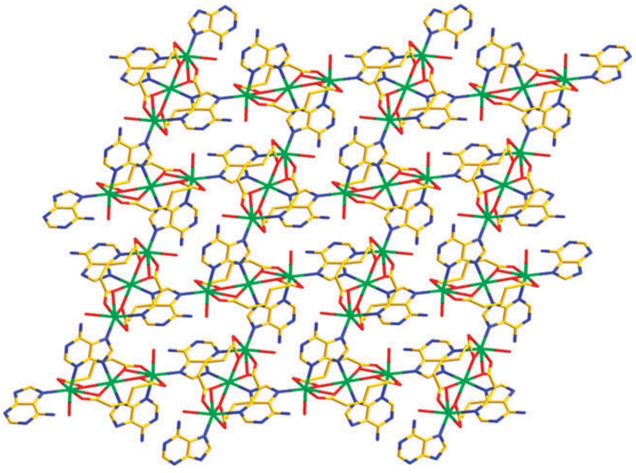


Fig. 2 2D neutral plane containing two alternative arrangements of trinuclear Cd(II)-subunits, namely Λ and Δ geometries.

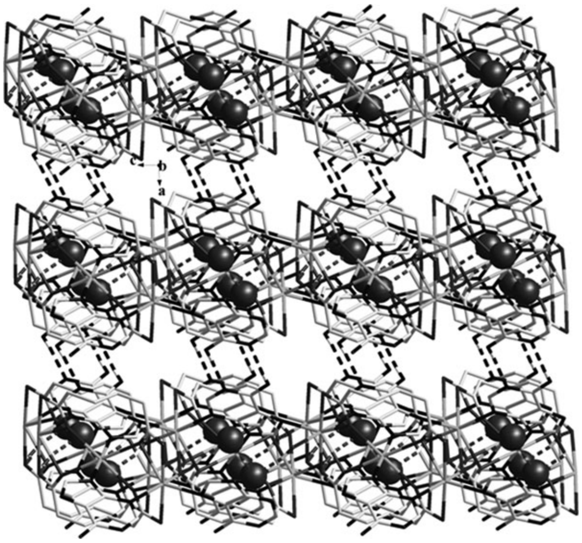


Fig. 3 3D supramolecular architecture constructed *via* pairs of interlayer N–H···N interactions with free lattice water molecules being trapped *via* strong O–H···O interactions.

Downloaded by University of Belgrade on 01 January 2013
Published on 21 September 2007 on http://pubs.rsc.org | doi:10.1039/B712387F

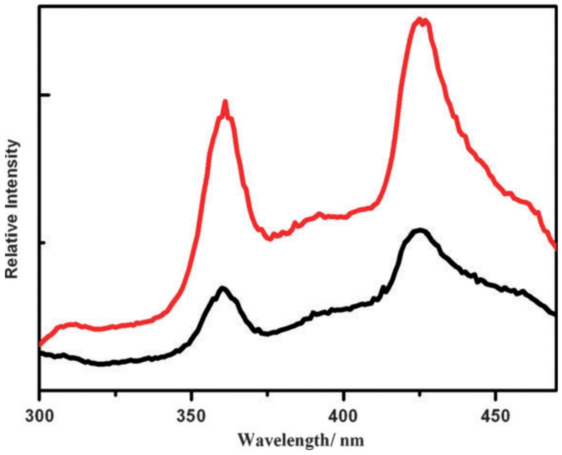


Fig. 4 Solid-state emission spectra of **1** (red) and adeH (black) at room temperature.

and ade ($\nu_{as}(NH_2)$ 3103, $\nu_s(NH_2)$ 1684, ν(C–H) 782 and 639). Additionally, the absence of bands around 1700 cm^{-1} indicates that the carboxylate groups in **1** are fully deprotonated.[16] Thermogravimetric results (Fig. S4†) exhibit two steps of slow decomposition of **1**. The first weight-loss, with a slight heat effect, is observed from 60 to 200 °C, corresponding to the removal of lattice and coordinated water molecules (expt 6.1%; calcd 6.6%). Then the next obvious weight-loss began at 210 °C and ended at 530 °C, ascribing to the consecutive decomposition of ade and ap anions. No remarkable changes appeared upon further heating of the sample to 800 °C, leaving CdO fragments as the final products (expt 39.6%, calcd 40.3%).

As a high-dimensional Cd(II) species, the solid-state photoluminescent spectrum of **1** has been investigated together with that of the free adeH ligand for comparison. As shown in Fig. 4, free adeH shows weak emission peaks at 359 and 424 nm upon excitation at 265 nm. And the same emissions with much stronger intensity are shown by **1**. The strong emission bands should be assigned tentatively to intraligand charge transfer, just as is observed in the previous literature. The enhancement of luminescence may be attributed to the ligand chelation to the metal center, which effectively increases the rigidity and reduces the loss of energy by radiationless decay.[17]

In conclusion, the first trinuclear Cd(II)-complex has been synthesized, using deprotonated ade and flexible ap ligands under hydrothermal conditions, and fully structurally characterized, in which ade and ap anions display rare tridentate μ_3-N3,N7,N9 and hexadentate $\eta^1:\eta^2:\eta^2:\eta^1$ bridging coordination modes, respectively. The arrangement of the trinuclear Cd(II)-subunit and H-bonding interactions is observed to dominate the overall stacking structure of **1**. These significant results provide us with some highly valuable clues for the preparation of novel metal complexes with nucleobases as ligands.

Experimental

Methods and materials

All reagents were purchased commercially and used without further purification. Doubly deionized water was used for the conventional synthesis. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a CE-440 (Leeman-Labs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken on an AVATAR-370 (Nicolet) spectrometer in a range of 4000–400 cm^{-1}. Thermogravimetric analysis (TGA) experiments were carried out on a Shimadzu simultaneous DTG-60A compositional analysis instrument from room temperature to 800 °C under a N_2 atmosphere at a heating rate of 5 °C min^{-1}. Fluorescence spectra of the polycrystalline powder samples were performed on a Cary Eclipse fluorescence spectrophotometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature.

Synthesis of $\{[Cd_3(\mu_3\text{-ade})_2(ap)_2(H_2O)_2]\cdot 1.5H_2O\}_n$ (1). An aqueous solution (10 ml) containing $Cd(NO_3)_2$ (30.85 mg, 0.1 mmol), adeH (6.75 mg, 0.05 mmol) and H_2ap (7.3 mg, 0.05 mmol) (two drops of triethylamine were added to the mixture) was placed in a Parr Teflon-lined stainless steel vessel (23 ml) with the maximum pressure supported up to 3 MPa, which was heated to 140 °C for 24 h and kept for 72 h under autogenous pressure, and then cooled to room temperature at a rate of 5 °C h^{-1}. The colorless block-shaped single crystals suitable for X-ray analysis were obtained directly in a 65% yield based on adeH, and were washed with ethanol and air-dried. Anal. Calcd for $C_{11}H_{15.5}Cd_{1.5}N_5O_{5.75}$: C, 27.62; H, 3.27; N, 14.64%. Found: C, 27.51; H, 3.30; N, 14.77%. FT-IR (cm^{-1}): 3311(m), 3103(m), 1684(m), 1599(m), 1542(s), 1406(m), 1355(w), 1320(w), 1227(m), 1148(m), 1040(m), 782(m), 639(m), 588(m).

X-Ray crystallography

Diffraction intensities for **1** were collected on a Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation with radiation wavelength 0.71073 Å by using the φ-ω scan technique at 293 K. There was no evidence of crystal decay during data collection. Semiempirical absorption corrections were applied (SADABS), and the program SAINT was used for integration of the diffraction profiles.[18] The structure was solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs.[19] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. The hydrogen atoms of the water molecules were located from difference maps and refined with isotropic temperature factors.

$C_{11}H_{15.5}N_5O_{5.75}Cd_{1.5}$, M_w = 478.38 g mol^{-1}, monoclinic space group $P2_1/c$, a = 9.250(2) Å, b = 12.011(3) Å, c = 14.326(4) Å, β = 92.618(3)°, V = 1590.0(7) Å^3, Z = 4, ρ_{calc} = 1.998 g cm^{-3}, λ(Mo-Ka) = 0.71073 Å, μ = 2.061 mm^{-1}, T = 293(2) K, 2.21° < θ < 25.00°, data set [h, k, l]: −10/11, −14/14, −17/9, 8203 reflections ($I > 2\sigma(I)$), 2788 unique (R_{int} = 0.0347), 224 parameters refined, R_1 = 0.0362, wR_2 = 0.0836, GoF = 1.034. CCDC reference number 656553. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712387f

Published on 21 September 2007 on http://pubs.rsc.org | doi:10.1039/B712387F
Downloaded by University of Belgrade on 01 January 2013

Acknowledgements

We gratefully acknowledge the National Natural Science Foundation of China (20571056, 20703030), the National Key Fundamental Research Project of China (2005CCA01200), Natural Science Foundation of Tianjin (06YFJMJC03900) and Tianjin Educational Committee (20060501).

References

1 (*a*) S. Sivakova and S. J. Rowan, *Chem. Soc. Rev.*, 2005, **34**, 9; (*b*) J. A. R. Navarro and B. Lippert, *Coord. Chem. Rev.*, 2001, **222**, 219.
2 (*a*) Y. Hisamatsu, K. Hasada, F. Amano, Y. Tsubota, Y. Wasada-Tsutsui, N. Shirai, S. Ikeda and K. Odashima, *Chem.–Eur. J.*, 2006, **12**, 7733; (*b*) T. Tekeste and H. Vahrenkamp, *Inorg. Chem.*, 2002, **41**, 6103; (*c*) C. Price, B. R. Horrocks, A. Mayeux, M. R. J. Elsegood, W. Clegg and A. Houlton, *Angew. Chem., Int. Ed.*, 2002, **41**, 1047.
3 (*a*) S. J. Berners-Price and P. J. Sadler, *Coord. Chem. Rev.*, 1996, **151**, 1; (*b*) D. Olea, S. S. Alexandre, P. Amo-Ochoa, A. Guijarro, F. De Jesus, J. M. Soler, P. J. De Pablo, F. Zamora and J. Gomez-Herrero, *Adv. Mater.*, 2005, **17**, 1761; (*c*) P. Amo-Ochoa, M. I. Rodriguez-Tapiador, O. Castillo, D. Olea, A. Guijarro, S. S. Alexandre, J. Gomez-Herrero and F. Zamora, *Inorg. Chem.*, 2006, **45**, 7642.
4 (*a*) B. Lippert, *Coord. Chem. Rev.*, 2000, **200–202**, 487; (*b*) E. Bugella-Altamirano, D. Choquesillo-Lazarte, J. M. González-Pérez, M. J. Sánchez-Moreno, R. J. D. Martín-Ramos, B. Covelo, R. Carballo, A. Castiñeiras and J. Niclós-Gutiérrez, *Inorg. Chim. Acta*, 2002, **339**, 160; (*c*) A. Marzotto, D. A. Clemente, A. Ciccarese and G. Valle, *J. Crystallogr. Spectrosc. Res.*, 1993, **23**, 119.
5 (*a*) J. P. Garcia-Teran, O. Castillo, A. Luque, U. Garcia-Couceiro, P. Román and F. Lloret, *Inorg. Chem.*, 2004, **43**, 5761; (*b*) A. Luque, U. Garcia-Couceiro, G. Beobide and P. Roman, *Dalton Trans.*, 2006, 902; (*c*) T. Suzuki, Y. Hirai, H. Monjushiro and S. Kaizaki, *Inorg. Chem.*, 2004, **43**, 6435; (*d*) D. B. Brown, J. W. Hall, H. M. Helis, E. G. Walton, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, 1977, **16**, 2675.
6 (*a*) M. Authier-Martin, J. Hubert, R. Rivest and A. L. Beauchamp, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1978, **B34**, 273; (*b*) C. S. Purohit and S. L. Verma, *J. Am. Chem. Soc.*, 2006, **128**, 400; (*c*) C. S. Purohit and S. L. Verma, *J. Am. Chem. Soc.*, 2007, **129**, 3488.
7 J. P. Garcia-Teran, O. Castillo, A. Luque, U. Garcia-Couceiro, P. Roman and L. Lezama, *Inorg. Chem.*, 2004, **43**, 4549.
8 (*a*) P. X. Rojas-González, A. Castiñeiras, J. M. González-Pérez, D. Choquesillo-Lazarte and J. Niclós-Gutiérrez, *Inorg. Chem.*, 2002, **41**, 6190; (*b*) L. Prizant, M. J. Olivier, R. Rivest and A. L. Beauchamp, *J. Am. Chem. Soc.*, 1979, **101**, 2765; (*c*) A.L. Beauchamp, *J. Cryst. Mol. Struct.*, 1980, **10**, 149; (*d*) J.-P. Charland, J. F. Britten and A. L. Beauchamp, *Inorg. Chim. Acta*, 1986, **124**, 161; (*e*) E. Bugella-Altamirano, D. Choquesillo-Lazarte, J. M. González-Pérez, M. J. Sanchez-Moreno, R. Marín-Sánchez, J. D. Martín-Ramos, B. Covelo, R. Carballo, A. Castiñeiras and J. Niclós-Gutiérrez, *Inorg. Chim. Acta*, 2002, **339**, 160; (*f*) P. X. Rojas-González, A. Castiñeiras, J. M. González-Pérez, D. Choquesillo-Lazarte and J. Niclós-Gutiérrez, *Inorg. Chem.*, 2002, **41**, 6190–6192.
9 M. A. Shipman, C. Price, A. E. Gibson, M. R. J. Elsegood, W. Clegg and A. Houlton, *Chem.–Eur. J.*, 2000, **6**, 4371.
10 (*a*) W. Ouellette, B. S. Hudson and J. Zubieta, *Inorg. Chem.*, 2007, **46**, 4887; (*b*) R. Wang, M. C. Hong, J. Luo, R. Cao and J. Weng, *Chem. Commun.*, 2003, 1018.
11 J.-C. Dai, S.-M. Hu, X.-T. Wu, Z.-Y. Fu, W.-X. Du, H.-H. Zhang and R.-Q. Sun, *New J. Chem.*, 2003, **27**, 914.
12 (*a*) M. A. Salam and K. Aoki, *Inorg. Chim. Acta*, 2001, **314**, 71; (*b*) A. Terzis, A. L. Beauchamp and R. Rivest, *Inorg. Chem.*, 1973, **12**, 1166; (*c*) P. de Meester and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1973, 424.
13 (*a*) E. Kimura, T. Ikeda, S. Aoki and M. Shionoya, *JBIC, J. Biol. Inorg. Chem.*, 1998, **3**, 259; (*b*) J. Hubert and A. L. Beauchamp, *Can. J. Chem.*, 1980, **58**, 1439; (*c*) J. P. Charl, J. F. Britten and A. L. Beauchamp, *Inorg. Chim. Acta*, 1986, **124**, 161; (*d*) J. M. González-Pérez, C. Alarcón-Payer, A. Castiñeiras, T. Pivetta. L. Lezama, D. Choquesillo-Lazarte, G. Crisponi and J. Niclós-Gutiérrez, *Inorg. Chem.*, 2006, **45**, 877.
14 D. Dobrzynska and L. B. Jerzykiewicz, *J. Am. Chem. Soc.*, 2004, **126**, 11118.
15 (*a*) P. Amo-Ochoa, S. S. Alexandre, C. Pastor and F. Zamora, *J. Inorg. Biochem.*, 2005, **99**, 2226; (*b*) D. Amantia, M. A. Shipman, C. Price, M. R. J. Elsegood, W. Clegg and A. Houlton, *Inorg. Chim. Acta*, 2006, **359**, 3515; (*c*) A. C. Morel, D. Choquesillo-Lazarte, C. Alarcon-Payer, J. M. Gonzalez-Perez, A. Castiñeiras and J. Niclos-Gutierrez, *Inorg. Chem. Commun.*, 2003, **6**, 1354.
16 G. B. Deacon and R. J. Philips, *Coord. Chem. Rev.*, 1980, **33**, 227.
17 B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, 2002.
18 *SAINT*, Bruker AXS, Madison, WI, 1998.
19 (*a*) G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.