

Synthesis and Crystal Structure of $[\text{Cu}_3(\text{dmpzm})_4(\mu\text{-}1,3\text{-dca})_2(\text{dca})_4]\cdot 2\text{H}_2\text{O}$ (dmpzm = 1,1'-Methylenebis-(3,5-dimethyl-1*H*-pyrazole), dca = dicyanamide)

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ABSTRACT The title compound, $[\text{Cu}_3(\text{dmpzm})_4(\mu\text{-}1,3\text{-dca})_2(\text{dca})_4]\cdot 2\text{H}_2\text{O}$ (dmpzm = 1,1'-methylenebis(3,5-dimethyl-1*H*-pyrazole), dca = dicyanamide) $\cdot 2\text{H}_2\text{O}$, was synthesized *via* the reaction of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ with dmpzm and $\text{Na}(\text{dca})$, and characterized by elemental analysis and IR spectra. $\text{1}\cdot 2\text{H}_2\text{O}$ crystallizes in the monoclinic system, space group $C2/m$ with $a = 13.578(3)$, $b = 16.769(3)$, $c = 14.769(3)$ Å, $\beta = 104.10(3)^\circ$, $V = 3261.4(11)$ Å³, $Z = 2$, $D_c = 1.466$ g/cm³, $T = 153(2)$ K, $\text{C}_{56}\text{H}_{68}\text{N}_{34}\text{O}_2\text{Cu}_3$, $M_r = 1440.09$, $F(000) = 1490$, $\mu(\text{MoK}\alpha) = 1.040$ mm⁻¹, $S = 1.150$, $R = 0.0553$ and $wR = 0.1123$ for 2744 observed reflections with $I > 2\sigma(I)$. The central copper atom is chelated by two dmpzm ligands and coordinated by two bridging dca anions, forming a slightly distorted octahedral geometry. The two external copper atoms adopt a square-pyramidal coordination geometry, coordinated by one chelating dmpzm ligand and one bridging and two terminal dca anions. Two intermolecular hydrogen bonding interactions result in the formation of a 2D (4,4) hydrogen-bonded network.

Keywords: copper(II) complex, 1,1'-methylenebis(3,5-dimethyl-1*H*-pyrazole), dicyanamide, synthesis, crystal structure

1 INTRODUCTION

Copper(II) coordination oligomers or polymers constructed by dicyanamide (dca) anions have attracted considerable interest due to their diverse structures and fascinating magnetic properties^[1-4]. In order to gain insights into the influence of co-ligands on the structures and magnetic properties of Cu(II)/dca complexes, some N-donor ligands like

pyridine, 2,2'-bipyridine, 4,4'-bipyridine, pyrimidine, 2,2'-bipyrimidine, pyrazine, 3,5-dimethylpyrazole, *etc.* have been introduced to the Cu(II)/dca systems. The resulting compounds showed that the co-ligands can not only modify the structures, but also adjust the magnetic properties^[5-11]. dmpzm is a bulky N-donor ligand and readily reacts with transition metals to form soluble complexes with interesting structures^[12-17]. However, no Cu(II)/dca com-

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plex with dmpzm as co-ligand has been reported so far. Herein, we report the synthesis and crystal structure of the title compound, $1 \cdot 2\text{H}_2\text{O}$, in which dmpzms acting as co-ligands were incorporated into the trinuclear Cu(II)/dca framework.

2 EXPERIMENTAL

2.1 Materials and methods

All the chemicals were obtained from commercial sources and used as received. The IR spectrum was recorded on a Varian 1000 FT-IR spectrometer ($4000 \sim 400 \text{ cm}^{-1}$). The elemental analyses for C, H and N were performed on a Carlo-Erba EA1110 CHNO-S microanalyzer.

2.2 Synthesis of the title complex

To a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (34 mg, 0.2 mmol) in MeCN (10 ml) was added dmpzm (80 mg, 0.4 mmol) and 2 mL aqueous solution of Na(dca) (18 mg, 0.2 mmol). The resulting bright green solution was stirred overnight at ambient temperature and then filtered. Slow evaporation of the filtrate gave rise to green block crystals of $1 \cdot 2\text{H}_2\text{O}$. Yield: 16 mg (33.75%). Anal. Calcd. (%) for $\text{C}_{56}\text{H}_{68}\text{N}_{34}\text{O}_2\text{Cu}_3$: C, 46.71; H, 4.76; N, 33.07. Found (%): C, 46.83; H, 4.71; N, 32.94. IR (KBr disc, cm^{-1}): 3567 (m), 3487 (m), 3441 (m), 3129 (w), 3058 (w), 2937 (w), 2289 (s), 2231 (s), 2214 (s), 2168 (s), 1658 (w), 1559 (s), 1468 (s), 1423 (m), 1392 (s), 1358 (s), 1289 (s), 1153 (w), 1049 (m), 927 (w), 837 (m), 819 (m), 800 (m), 682 (m), 625 (w), 519 (w), 479 (w).

2.3 Data collection, structure determination and refinement

All measurements were performed on a Rigaku Mercury CCD X-ray diffractometer (3KW, sealed tube) at 153(2) K by using a graphite-monochromatic $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. A green block crystal of $1 \cdot 2\text{H}_2\text{O}$ ($0.14 \text{ mm} \times 0.30 \text{ mm} \times 0.35 \text{ mm}$) was mounted on a glass fiber with grease. Diffraction data were collected using an ω scan mode with a detector distance of 35 mm to the crystal. Indexing was performed from 6 images, each of which was exposed for 4 s. A total of 15852

reflections ($R_{\text{int}} = 0.0897$) were measured in the range of $3.07 < \theta < 25.35^\circ$, of which 3089 were unique. The collected data were reduced by using the program *CrystalClear* (Rigaku and MSC, Ver. 1.3, 2001), and an absorption correction (multi-scan) was applied, resulting in transmission factors ranging from 0.712 to 0.868. The reflection data were also corrected for Lorentz and polarization effects.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques with SHELXTL97 program^[18]. All non-hydrogen atoms were refined anisotropically and the H atoms except those of water were placed in the geometrically idealized positions and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, while the hydrogen atoms of water molecules were located in difference Fourier syntheses and refined isotropically. The final refinement based on 2744 observed reflections with $I > 2\sigma(I)$ and 238 variable parameters converged to $R = 0.0553$, $wR = 0.1123$ ($w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 10.6528P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.150$, $(\Delta/\sigma)_{\text{max}} = 0.000$, $(\Delta\rho)_{\text{max}} = 0.737$ and $(\Delta\rho)_{\text{min}} = -0.350 \text{ e/\AA}^3$.

3 RESULTS AND DISCUSSION

3.1 Synthesis and spectral aspects

Reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with dmpzm and Na(dca) in MeCN and water at ambient temperature gave rise to $1 \cdot 2\text{H}_2\text{O}$ in 33.75% yield. Compound $1 \cdot 2\text{H}_2\text{O}$ is air- and moisture-stable. Elemental analysis of $1 \cdot 2\text{H}_2\text{O}$ was consistent with its chemical formula. In the IR spectrum of $1 \cdot 2\text{H}_2\text{O}$, peaks at $3400 \sim 3600 \text{ cm}^{-1}$ may be assigned to the O-H vibrations of water solvent molecules. Peaks at 2289, 2231, 2214 and 2168 cm^{-1} are assignable to the $\text{C}\equiv\text{N}$ vibrations of the dca anions^[19], while those at $3100 \sim 2900$ and $1700 \sim 1300 \text{ cm}^{-1}$ are assigned to the C-H and C=C, C=N and N=N vibrations of dmpzm ligands, respectively^[16]. The identity of $1 \cdot 2\text{H}_2\text{O}$ was further confirmed by X-ray analysis.

3.2 Structure description

Compound $1 \cdot 2\text{H}_2\text{O}$ crystallizes in the monoclinic

space group $C2/m$ and the asymmetric unit of $1 \cdot 2\text{H}_2\text{O}$ consists of one quarter of the $[\text{Cu}_3(\text{dmpzm})_4(\mu\text{-}1,3\text{-dca})_2(\text{dca})_4]$ molecule together with a half water solvent molecule. The molecular structure of $1 \cdot 2\text{H}_2\text{O}$ with atomic numbering scheme is

depicted in Fig. 1. The selected bond lengths and bond angles and the geometrical parameters of hydrogen bonds are given in Tables 1 and 2, respectively.

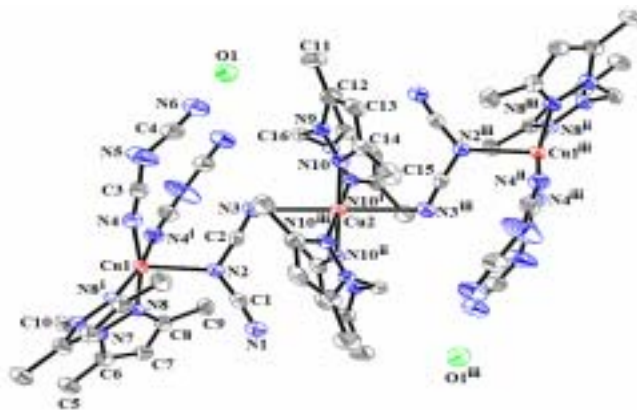


Fig. 1. Perspective view of $1 \cdot 2\text{H}_2\text{O}$ with atomic numbering scheme at 50% thermal ellipsoids. All H atoms have been omitted for clarity (Symmetry codes: (i) $x, -y, z$; (ii) $1 - x, y, 1 - z$; (iii) $1 - x, -y, 1 - z$)

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu(1)–N(4)	1.976(3)	Cu(1)–N(8)	2.005(3)	Cu(1)–N(2)	2.243(4)
Cu(2)–N(10)	2.027(3)	Cu(2)–N(3)	2.575(4)		
Angle	(°)	Angle	(°)	Angle	(°)
N(4)–Cu(1)–N(4 ⁱ)	87.93(19)	N(10)–Cu(2)–N(10 ⁱⁱ)	92.41(15)	C(2)–N(2)–C(1)	119.6(4)
N(4)–Cu(1)–N(8)	168.95(12)	N(10)–Cu(2)–N(10 ⁱⁱⁱ)	180.00(16)	C(3)–N(5)–C(4)	123.0(4)
N(4 ⁱ)–Cu(1)–N(8)	91.24(12)	N(10 ⁱⁱ)–Cu(2)–N(10 ⁱⁱⁱ)	87.59(15)	N(1)–C(1)–N(2)	174.4(5)
N(8)–Cu(1)–N(8 ⁱ)	87.46(16)	N(10)–Cu(2)–N(3 ⁱⁱ)	85.22(10)	N(3)–C(2)–N(2)	175.3(5)
N(4)–Cu(1)–N(2)	92.12(12)	N(10)–Cu(2)–N(3)	94.78(10)	N(4)–C(3)–N(5)	171.5(4)
N(8)–Cu(1)–N(2)	98.92(11)	N(3 ⁱⁱ)–Cu(2)–N(3)	180.0	N(6)–C(4)–N(5)	172.2(4)

Symmetry transformations used to generate the equivalent atoms: (i) $x, -y, z$; (ii) $-x+1, y, -z+1$; (iii) $-x+1, -y, -z+1$

Table 2. Hydrogen-bonding Geometry in the Title Compound (Length in Å and Angle in °)

D–H...A	d(D–H)	d(H...A)	d(D...A)	DHA
O(1)–H(1)...N(6)	0.84(2)	2.13(6)	2.910(5)	155(12)
C(16)–H(16A)...O(1)	0.99	2.46	3.364(6)	152
C(5)–H(5A)...N(1) ^{iv}	0.98	2.58	3.489(5)	154
C(10)–H(10B)...O(1) ^v	0.99	2.45	3.319(6)	146

Symmetry codes: (iv) $-x, y, -z$; (v) $-x+1, y, -z$

Compound $1 \cdot 2\text{H}_2\text{O}$ may be viewed as having a “seesaw” shaped structure in which a central $[\text{Cu}(\text{dmpzm})_2]^{2+}$ fragment and two outer $[\text{Cu}(\text{dmpzm})(\text{dca})_2]$ fragments are linked by a pair of $\mu\text{-}1,3\text{-dca}$ bridges. There is a two-fold axis located at the central copper atom while a crystallographic mirror

plane is running through Cu(1), Cu(2), Cu(1ⁱⁱⁱ), N(1), N(2), N(3), C(1), C(2), C(10) and C(16) atoms. The copper(II) atoms in $1 \cdot 2\text{H}_2\text{O}$ show two different coordination modes. The central Cu(2) is chelated by two dmpzm ligands and coordinated by two terminal N atoms from the axial $\mu\text{-}1,3\text{-dca}$ ligands, forming a

distorted octahedral coordination geometry. The axial dca shows a unique μ -1,3 bridging mode. To our knowledge, only one Cu(II)/ μ -1,3-dca example was reported^[20]. The mean Cu(2)–N (dmpzm) bond length (2.027(3) Å) is slightly longer than that in [Cu(MeCN)₂L₂] dication (2.020(3) Å, $L = 2,2'2''$ -tripyridylamine)^[21] and [Cu(N₃)₂L₂] molecule (2.010(2) Å, $L = \text{bis}(\text{pyrid-2-yl})\text{amine}$)^[22]. The mean axial Cu(2)–N(dca) distance (2.575(4) Å) is in-between those corresponding of Cu(en)₂[Mn(dca)₄] [en = ethylenediamine, 2.610(2) Å] or [Cu(pn)₂][Mn(dca)₄] (pn = 1,3-diaminopropane, 2.519(2) Å)^[23].

Each of the two external Cu²⁺ atoms is chelated by two N atoms from dmpzm and coordinated by one amide N atom from bridging dca together with two nitrile N atoms of two terminal dca ligands, thereby forming a square-pyramidal coordination geometry. For Cu(1) (or Cu(1ⁱⁱⁱ)), the basal plane is defined by the N(4), N(4ⁱ), N(8), N(8ⁱ) (or N(4ⁱⁱ), N(4ⁱⁱⁱ), N(8ⁱⁱ), and N(8ⁱⁱⁱ) for Cu(1ⁱⁱⁱ)) atoms, while the apical position is occupied by N(2) (or N(2ⁱⁱⁱ)). But, Cu(1) (or Cu(1ⁱⁱⁱ)) is not coplanar to the corresponding basal plane with the deviation of 0.1915 Å. The mean Cu(1)–N (or Cu(1ⁱⁱⁱ))–N (dmpzm) bond length (2.005(3) Å) is obviously shorter than that in [Cu₂(μ -dca)₂(dca)₂L]_n (2.069(2) Å, $L = 2,2'$ -bipyrimidine)^[24], and the mean Cu(1)–N (or Cu(1ⁱⁱ))–N (dca) distance located on the basal plane (1.976(3) Å) is slightly longer than that in [Cu₂(μ -dca)₂(dca)₂L]_n

(1.947(2) Å, $L = 2,2'$ -bipyrimidine)^[24].

Each dmpzm ligand in 1·2H₂O exhibits a twisted boat configuration. The intraligand dihedral angles between the five-membered rings are 64.41(1)° (located on the central Cu) and 57.62(1)° (located on the external Cu), which are larger than the literature value (56.34(2)°) in Cu(II)/dmpzm derivative^[25]. The dca anions in 1·2H₂O are bent with the C–N–C angles to be 119.6(4)° (for bridging dca anions) and 123.0(4)° (for terminal dca anions), and the N–C–N straight linear units have angles ranging from 171.5(4) to 175.3(5)° in both cases^[26].

In the crystal of 1·2H₂O, [Cu₃(dmpzm)₄(μ -1,3-dca)₂(dca)₄] and the solvate water molecule are held together by two kinds of intramolecular hydrogen bonds. One is between O(1) and N(6) (O(1)···N(6) 2.910(5) Å, O(1)–H(1)···N(6) 155°), while the other is between O(1) and C(16) (O(1)···C(16) 3.364(7) Å, C(16)–H(16A)···O(1) 152°). In addition, the molecules of 1·2H₂O are further connected by intermolecular hydrogen bonding interactions between dmpzm around the external Cu²⁺ ion and bridging dca anion (C(5)···N(1) 3.489(5) Å, C(5)–H(5A)···N(1) 154°, symmetry code: $-x, y, -z$) as well as between the water molecule and chelating dmpzm located on the external Cu²⁺ ion (C(10)···O(1) 3.319(6) Å, C(10)–H(10B)···O(1) 146°, symmetry code: $1-x, y, -z$), generating a 2D (4,4) layer framework extending along the ac plane (Fig. 2).

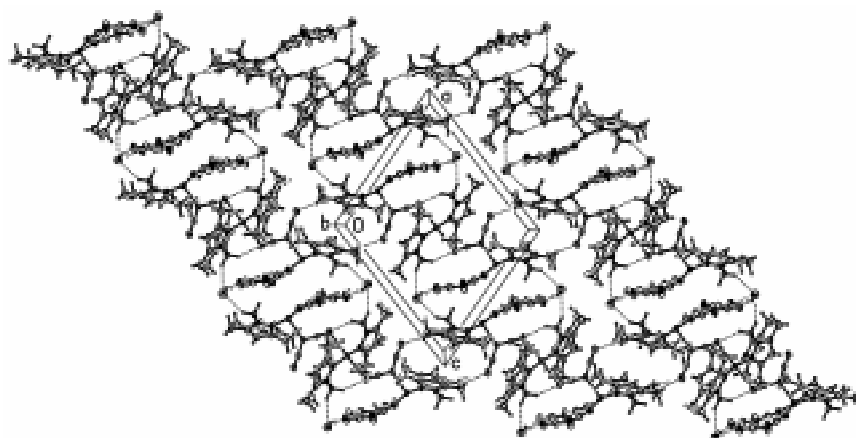


Fig. 2. Two-dimensional layer framework in 1·2H₂O extending along the ac plane

As shown in Fig. 3, the distances between adjacent central Cu^{2+} ions in one layer are 14.769 Å (between I and II) and 17.458 Å (between I and III), and the separation between sheets constructed by copper(II) atoms (the central Cu^{2+} ions and external

Cu^{2+} ions are coplanar in one layer) is 8.384 Å. No obvious interaction is found between the adjacent layers which show a unique "ABAB" staggered stacking.

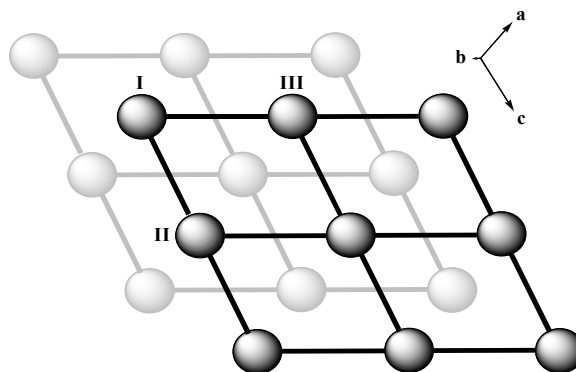


Fig. 3. Staggered stacking of layers in the three-dimensional crystal lattice. Every ball represents a central Cu^{2+} ion in one molecule of $1\cdot 2\text{H}_2\text{O}$

REFERENCES

- (1) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, 246, 103–130.
- (2) Ghoshal, D.; Jana, A. D.; Maji, T. K.; Mostafa, G. *Inorg. Chim. Acta* **2006**, 359, 690–694.
- (3) Gu, W.; Bian, H. D.; Xu, J. Y.; Liu, Z. Q.; Cheng, P.; Yan, S. P.; Liao, D. Z.; Jiang, Z. H. *Inorg. Chem. Commun.* **2003**, 6, 966–970.
- (4) Jones, L. F.; O'Dea, L.; Offermann, D. A.; Jensen, P.; Moubaraki, B.; Murray, K. S. *Polyhedron* **2006**, 25, 360–372.
- (5) Jensen, P.; Batten, S. R.; Moubaraki, B.; Murray, K. S. *J. Chem. Soc., Dalton Trans.* **2002**, 3712–3722.
- (6) Luo, J.; Zhou, X. G.; Hou, X. F.; Wu, H. X.; Weng, L. H.; Li, Y. R. *Chin. J. Chem.* **2005**, 23, 310–314.
- (7) Luo, J. H.; Hong, M. C.; Cao, R.; Liang, Y. C.; Zhao, Y. J.; Wang, R. H.; Weng, J. B. *Polyhedron* **2002**, 21, 893–898.
- (8) Luo, J. H.; Hong, M. C.; Weng, J. B.; Zhao, Y. J.; Cao, R. *Inorg. Chim. Acta* **2002**, 329, 59–65.
- (9) Manson, J. L.; Incarvito, C. D.; Rheingold, A. L.; Miller, J. S. *J. Chem. Soc., Dalton Trans.* **1998**, 3705–3706.
- (10) Riggio, I.; van Albada, G. A.; Ellis, D. D.; Spek, A. L.; Reedijk, J. *Inorg. Chim. Acta* **2001**, 313, 120–124.
- (11) Triki, S.; Thétiot, F.; Galán-Mascarós, J. R.; Pala, J. S.; Dunbar, K. R. *New J. Chem.* **2001**, 25, 954–958.
- (12) Cheng, M. L.; Li, H. X.; Zhang, Y.; Lang, J. P. *Acta Crystallogr., Sect. C* **2006**, 62, m74–m77.
- (13) Ding, N. N.; Zhang, W. H.; Chen, J. X.; Ren, Z. G.; Zhang, Y.; Lang, J. P. *Chin. J. Struct. Chem.* **2006**, 25, 557–561.
- (14) Li, Q. Y.; Zhang, W. H.; Li, H. X.; Ren, Z. G.; Zhang, Y.; Lang, J. P. *Chin. J. Chem.* **2006**, 24, 811–816.
- (15) Li, Q. Y.; Zhang, W. H.; Li, H. X.; Tang, X. Y.; Lang, J. P.; Zhang, Y.; Wang, X. Y.; Gao, S. *Chin. J. Chem.* **2006**, 24, 1716–1720.
- (16) Xu, Y.; Li, H. X.; Zhang, W. H.; Zhang, Y.; Lang, J. P. *Acta Crystallogr., Sect. C* **2005**, 61, m4–m6.
- (17) Xu, Y.; Ren, Z. G.; Li, H. X.; Zhang, W. H.; Chen, J. X.; Zhang, Y.; Lang, J. P. *J. Mol. Struct.* **2006**, 782, 150–156.
- (18) Sheldrick, G. M. *SHELXS-97 and SHELXL-97, Programs for Crystal Structure Refinement*, University of Göttingen, Germany **1997**.
- (19) He, Y.; Kou, H. Z.; Xiong, M.; Wang, R. J. *Chin. J. Struct. Chem.* **2004**, 23, 574–579.
- (20) Mohamadou, A.; van Albada, G. A.; Kooijman, H.; Wiczorek, B.; Spek, A. L.; Reedijk, J. *New J. Chem.* **2003**, 27, 983–988.
- (21) Dedert, P. L.; Thompson, J. S.; Ibers, J. A.; Marks, T. J. *Inorg. Chem.* **1982**, 21, 969–977.
- (22) Du, M.; Guo, Y. M.; Chen, S. T.; Bu, X. H.; Ribas, J. *Inorg. Chim. Acta* **2003**, 346, 207–214.
- (23) Wang, Z. M.; Sun, B. W.; Luo, J.; Gao, S.; Liao, C. S.; Yan, C. H.; Li, Y. *Inorg. Chim. Acta* **2002**, 332, 127–134.
- (24) Martin, S.; Barandika, M. G.; de Larramendi, J. I. R.; Cortes, R.; Font-Bardia, M.; Lezama, L.; Serna, Z. E.; Solans, X.; Rojo, T. *Inorg. Chem.* **2001**, 40, 3687–3692.
- (25) Zhang, L.; Bu, W. M.; Yan, S. P.; Jiang, Z. H.; Liao, D. Z.; Wang, G. L. *Polyhedron* **2000**, 19, 1105–1110.
- (26) Manson, J. L.; Lee, D. W.; Rheingold, A. L.; Miller, J. S. *Inorg. Chem.* **1998**, 37, 5966–5967.