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A Zn^{II}-Based Chiral Crystalline Nanotube

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A novel metal-organic chiral nanotube, $\{[Zn(C_{14}H_{10}N_2O_4)\cdot(H_2O)_4]_2\cdot H_2O\}_n$ (**1**), with the walls consisting of homochiral triple-stranded right-handed (*P*) helices has been constructed by the reaction of acyclic ligands and zinc ions. All guest water molecules are arranged in a helical fashion inside the hydrophilic channel of the nanotube. This coordination polymer shows blue-emitting fluorescence and displays a second harmonic generation (SHG) response in the solid state.

Introduction

Nanotubular supramolecular architectures are currently of intense interest in chemistry, biology, and materials science, owing to their potential applications in mimicking ion channels, water channels, and as small molecule transport systems.[1,2] The construction of synthetic nanotubes is achieved through the self-assembly of suitable cyclic building blocks such as cyclic peptides[3] and cyclic oligoureas.[4] Another motif in the formation of nanotubes is achieved by the self-assembly of acyclic oligopeptides which, like cyclic peptides, are building blocks that can also result in chiral tubular structures.[5] However, most of the previously reported nanotubes are made up of synthetic organic molecules and to date, the construction of metal-containing nanotubular structures has received scant attention.[6] In forming channel structures, the coordination polymer approach has the advantage of preparative convenience, functionalization, and thermal stability.[7] The metal-organic nanotubes could be generated through the self-assembly of metal ions with organic ligands and such metal-organic nanotubes might display opto-electronic or magnetic properties induced by the coordination moiety. Furthermore, the employment of chiral organic molecules can induce a noncentrosymmetric structure in the resulting nanotubes which may be useful in the field of nonlinear optics (NLO) applications.[8] In view of the above, we present herein the construction of a novel metal-organic chiral nanotube, ZnL (**1**) [L = (2*S*,2′*S*)-2,2′-(benzene-1,4-dicarboxamido)dipropionate], with the walls consisting of homochiral triple-stranded right-handed (*P*) helices and its optical properties.

Results and Discussion

Crystal Structure

Compound **1** was obtained by the reaction of zinc acetate with the chiral ligand H_2L. The crystal structure of **1** reveals that, there is one zinc ion, one ligand dianion, and two coordination water molecules as well as half of one guest water molecule in the asymmetric unit. Crystallographic data of **1** is summarized in Table 1. As shown in Figure 1, the coordination motif of the zinc ion has a trigonal-bipyramidal geometry. Two coordinated water O atoms (O1 and O2) occupy an axial position of the Zn trigonal

Table 1. Crystallographic data for complex **1**.

	1
Empirical formula	$C_{28}H_{38}N_4O_{17}Zn_2$
Formula mass	833.36
Crystal system	monoclinic
Space group	$P\ 2_1$
Temperature [K]	298(2)
a [Å]	11.755(2)
b [Å]	4.9670(10)
c [Å]	14.654(3)
β [°]	92.27(3)
V [Å^3]	854.9(3)
Z	1
$D_{\text{calcd.}}$ [$\mathrm{mg\,m^{-3}}$]	1.619
μ [$\mathrm{mm^{-1}}$]	1.485
R_{int}	0.0208
Reflections collected	3396
Unique reflections	2959
N(parameters/restraints)$_{\text{refined}}$	237/1
Goodness-of-fit on F^2	1.047
R_1 [$I > 2\sigma(I)$][a]	0.0544
wR_2 [$I > 2\sigma(I)$][b]	0.1145
R_1 (all data)[a]	0.0633
wR_2 (all data)[b]	0.1166

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w(|F_o{}^2|)^2]^{1/2}$.

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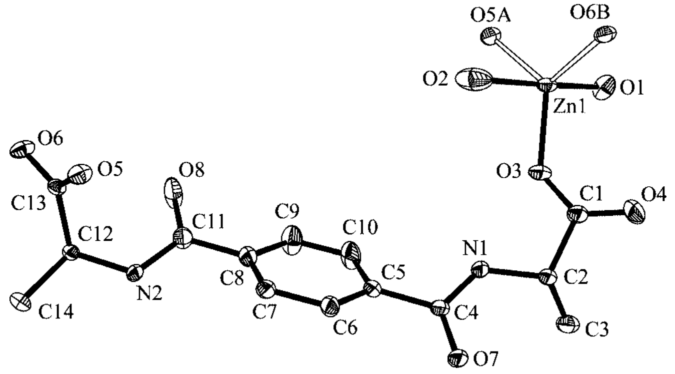

Figure 1. ORTEP view of compound **1** showing 30% probability displacement ellipsoids. All H atoms and the guest water molecule are omitted for clarity. Symmetric codes: A: –*x*, *y* – 1/2, –*z* + 1; B: –*x*, *y* – 3/2, –*z* + 1.

Table 2. Selected bond lengths [Å], angles [°], and torsion angles [°] for **1**.

Zn(1)–O(3)	1.952(4)	Zn(1)–O(6)[a]	1.976(5)
Zn(1)–O(5)[b]	1.982(4)	Zn(1)–O(1)	2.071(4)
Zn(1)–O(2)	2.252(4)	O(3)–Zn(1)–O(6)[a]	119.07(17)
O(3)–Zn(1)–O(5)[b]	125.79(18)	O(6)[a]–Zn(1)–O(5)[b]	113.21(18)
O(3)–Zn(1)–O(1)	97.38(18)	O(6)[a]–Zn(1)–O(1)	94.22(19)
O(5)[b]–Zn(1)–O(1)	92.03(17)	O(3)–Zn(1)–O(2)	83.90(17)
O(6)[a]–Zn(1)–O(2)	87.6(2)	O(5)[b]–Zn(1)–O(2)	84.95(19)
O(1)–Zn(1)–O(2)	176.9(2)	C(4)–N(1)–C(2)–C(3)	81.1(7)
C(4)–N(1)–C(2)–C(1)	–155.8(6)	C(11)–N(2)–C(12)–C(14)	176.8(6)
C(11)–N(2)–C(12)–C(13)	–62.2(7)	N(1)–C(2)–C(1)–O(3)	–6.2(8)
N(2)–C(12)–C(13)–O(5)	–34.3(7)	N(2)–C(12)–C(13)–O(6)	145.5(4)

[a] Symmetry transformations used to generate equivalent atoms: –*x*, *y* – 3/2, –*z* + 1. [b] Symmetry transformations used to generate equivalent atoms: –*x*, *y* – 1/2, –*z* + 1.

bipyramid, while three carboxylato O atoms (O3, O5A, and O6B) bond to the equatorial positions. At one end of the ligand, the side methyl group C14 is almost coplanar with the amide group O8/C11/N2 with a torsion angle of 176.8(6)° for C11–N2–C12–C14, while the carboxyl group O5/C13/O6 is almost perpendicular to the amide plane. At the other end of the ligand, the methyl group C3 is vertical on the amide plane O7/C4/N1 with a torsion angle of 81.1(7)° for C4–N1–C2–C3. The carboxyl group O4/C1/O3 lies slightly out of the plane of the amide group O7/C4/N1 with a torsion angle of –6.2(8)° for N1–C2–C1–O3 (selected bond lengths, angles, and torsion angles are listed in Table 2). Thus, the two sides of the phenyl ring are not equivalent with each other, owing to the different coordination modes of the two carboxylate groups (O3/C1/O4 as a monodentate ligand and O5/C13/O6 as a carboxyl bridge) and their conformations. Consequently, two ligands connect a pair of zinc ions in a head-to-tail fashion through the O3 and O6 atoms, thus forming a right-handed twofold single-

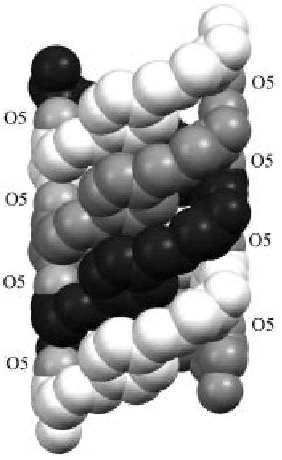

Figure 2. Triple-stranded right-handed helix. All water molecules, amide O atoms, H atoms, and the side α-methyl groups are omitted for clarity.

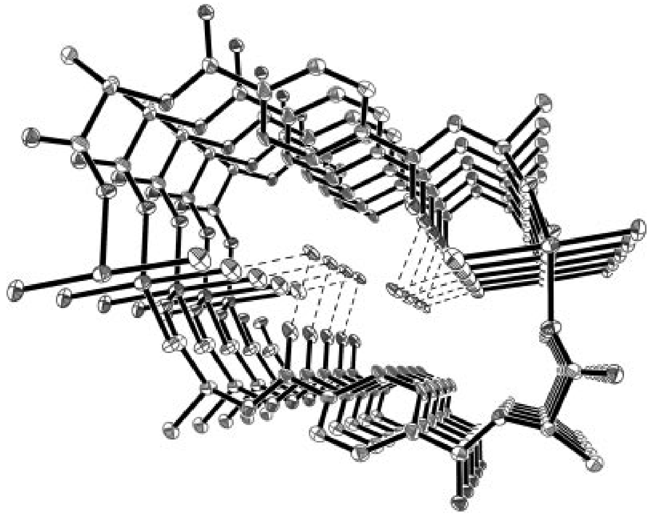

Figure 3. 1D tube-like coordination polymer with hydrophilic channel including water molecules.

Figure 4. Guest water molecules are arranged in a helical fashion inside the polymeric structure.

Table 3. Hydrogen bonds for **1**.

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D···A) [Å]	<(D–H···A) [°]
N(2)–H(6)···O(7)[c]	0.86	2.19	3.004(7)	158.8
O(1)–H(1B)···O(4)[d]	0.96	1.92	2.620(6)	127.4
O(1)–H(1A)···O(1)[d]	0.96	1.99	2.943(4)	170.8
O(2)–H(2B)···O(1W)[e]	0.96	1.82	2.500(10)	125.3
O(1W)–H(1WC)···O(8)[e]	0.85	2.39	3.094(9)	141.1
O(2)–H(2B)···O(8)[b]	0.96	2.49	3.430(7)	167.6
O(2)–H(2C)···O(8)[a]	0.96	1.82	2.776(6)	171.0

[a] Symmetry transformations used to generate equivalent atoms: $-x$, $y - 3/2$, $-z + 1$. [b] Symmetry transformations used to generate equivalent atoms: $-x$, $y - 1/2$, $-z + 1$. [c] Symmetry transformations used to generate equivalent atoms: $-x + 1$, $y + 1/2$, $-z + 1$. [d] Symmetry transformations used to generate equivalent atoms: $-x$, $y + 1/2$, $-z + 2$. [e] Symmetry transformations used to generate equivalent atoms: $-x + 1$, $y - 1/2$, $-z + 1$.

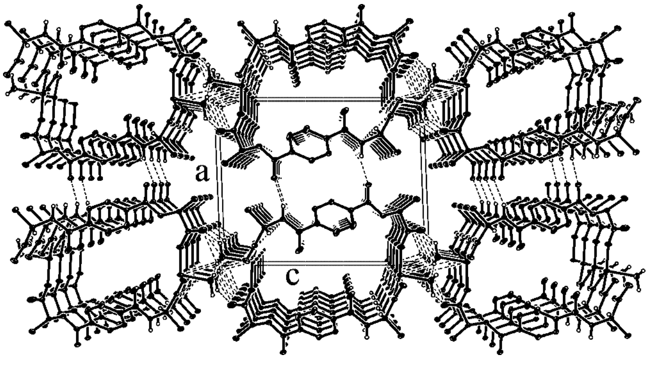

Figure 5. The nanotube arrays in complex **1**. The guest water molecules and H atoms except for the amide H atoms are omitted for clarity.

stranded helix propagating along the *b*-axis. The O5 atoms at "the head" and at "the tail" link two zinc ions from different single-stranded helices, respectively, thus constructing a homochiral triple-stranded (*P*) helix as depicted in Figure 2. In the previously reported triple helical coordination polymers, the interwoven helices just form rod-like structures owing to the small screw diameter.[9] However, in complex **1**, the triple-stranded helix around the screw axis generates an open-ended tube with an average internal diameter of 5 Å including the van der Waals contact (approximately 3 Å excluding the van der Waals contact), which is attributed to the expansion of the screw diameter by the phenyl ring. The interior of the channel is hydrophilic owing to the presence of the guest water molecules as shown in Figure 3. All guest water molecules are arranged in a helical fashion inside the polymeric structure (Figure 4). In the lattice, as depicted in Figure 5, all nanotubes are packed together to produce three-dimensional arrays by means of the inter-tubular hydrogen-bonding interactions between amide groups, coordination water molecules and guest water molecules as well as carboxylate groups (for details see Table 3).

Thermal and Optical Properties

The TGA performed under flowing N_2 shows a gradual weight loss of 1.95% in the temperature range of 30–64 °C corresponding to the guest water molecule's liberation from the channels (calcd. 2.16%). The weight loss of 8.29% in the range 64–135 °C is attributed to the removal of coordination water molecules (calcd. 8.64%) and the decomposition of compound **1** starts at 386 °C. A crystal of compound **1** was stable at room temperature; however, it cracked when it had been left to stand at 45 °C for 14 d in order to release guest water molecules. Compound **1** is insoluble in water and common organic solvents such as methanol, ethanol, acetone, acetonitrile, DMF, and DMSO.

As shown in Figure 6, compound **1** exhibits a blue-fluorescent emission around 439 nm upon excitation at 338 nm in the solid state at room temperature. This has a blue shift and an enhancement of intensity in comparison with the emission of the ligand (a very weak emission is observed for the free ligand around 450 nm upon excitation at 348 nm in the solid state). This indicates that the emission is neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in nature and can thus be tentatively assigned to intraligand fluorescent emission.[10] The significant enhancement of fluorescent intensity is probably ascribed to the coordination of ligand to the Zn ion, increasing the ligand conformational rigidity, thereby reducing the nonradiative decay of the intraligand $^1(\pi\text{-}\pi^*)$ excited state.[11]

Given that **1** crystallizes in a noncentrosymmetric space group, its powder second harmonic generation (SHG) measurement was performed according to the method previously reported by Kurtz.[12] When a beam at $\lambda = 1064$ nm fundamental wavelength from a Q-switched Nd:YAG laser falls onto compound **1**, a green light can be seen with the naked eye. The preliminary experimental result shows that the powder SHG intensity of **1** is about 0.6 times that of urea. This intensity is comparable to the previously reported helical coordination polymers.[13]

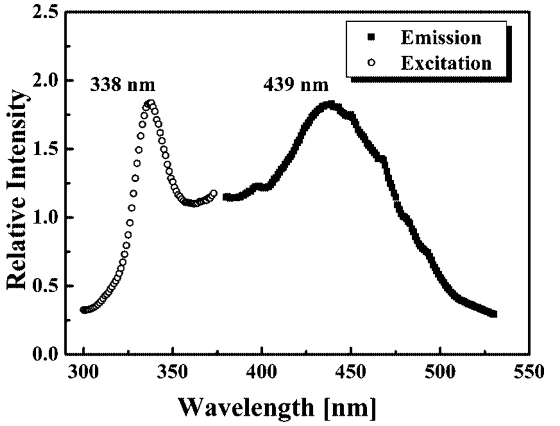

Figure 6. Fluorescent spectra of **1** in the solid state at room temperature.

Conclusions

In conclusion, the reported nanotubular coordination polymer **1** has hydrophilic channels surrounded by homochiral triple helices, emits an enhanced blue fluorescence, and exhibits a second harmonic generation response. The transparency of the complex and its insolubility in common solvents, such as water, methanol, and ethanol among others, makes it an attractive candidate for blue-emitting fluorescent materials and in nonlinear optics (NLO) applications. Therefore, it can be developed towards a new motif in the formation of chiral nanotubes with opto-electronic properties.

Experimental Section

General: Elemental analyses were carried out with a Perkin–Elmer 240C elemental analyzer. IR spectra were recorded with a Bruker VECTOR22 FT-IR spectrometer using the KBr pellet technique. Thermogravimetric analyses (TGA) were performed with a TA-SDT 2960 thermal analyzer at a heating rate of 10 °C min^{-1} from room temperature to 600 °C under flowing nitrogen. The solid-state excitation-emission spectrum was acquired with an AMINCO Bowman Series AB2 Luminescence Spectrometer at room temperature. Approximate estimations of second-order NLO intensity were obtained by a comparison of the results from a powdered sample, in the form of a pellet (Kurtz powder test),[12] with those obtained for urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate an SHG signal from samples. The backward-scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation.

$\{[Zn(C_{14}H_{10}N_2O_4)\cdot(H_2O)_4]_2\cdot H_2O\}_n$ (1): The diacid, (2*S*,2′*S*)-2,2′-(benzene-1,4-dicarboxamido)dipropionic acid (H_2L), was synthesized by treating 1,4-benzenedicarbonyl dichloride with L-alanine ethyl ester according to a published procedure.[14] The ligand H_2L (31.0 mg, 0.1 mmol) and zinc acetate dihydrate (22.0 mg, 0.1 mmol) were dissolved in water (10 mL). The resulting solution was left to stand for several weeks at room temperature. Colorless block crystals that formed were collected by filtration (16.0 mg, yield 40%). $C_{28}H_{38}N_4O_{17}Zn_2$ (833.36): calcd. C 40.35, H 4.60, N 6.72; found C 40.30, H 4.68, N 6.69. IR (KBr): $\tilde{\nu}$ = 3392 (m), 3268 (m), 2994 (w), 1654 (s), 1619 (s), 1578 (s), 1550 (s), 1490 (s), 1396 (m), 1320 (m), 1176 (w), 1055 (w), 870 (w), 746 (w), 594 (w) cm^{-1}.

Crystallography: A single crystal with dimensions 0.6 × 0.4 × 0.3 mm was used for structural determination with an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) using a ω-2θ scan mode at 298 K. Intensity data were collected in the θ range of 1.39–25.97°, data reduction was made with the MolEN package.[15] Absorption corrections from ψ scans were applied. The structure was solved by direct methods using SHELXS-97[16] and refined by least-squares treatment on F^2 by full-matrix least squares using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms.[17] The guest water molecule O1W was refined as occupancy disorder. CCDC-279580 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) D. T. Bong, T. D. Clark, J. R. Granja, M. R. Ghadiri, *Angew. Chem. Int. Ed.* **2001**, *40*, 989–1011; b) J. G. Moralez, J. Raez, T. Yamazaki, R. K. Motkuri, A. Kovalenko, H. Fenniri, *J. Am. Chem. Soc.* **2005**, *127*, 8307–8309.

[2] a) J. Sánchez-Quesada, H. S. Kim, M. R. Ghadiri, *Angew. Chem. Int. Ed.* **2001**, *40*, 2503–2506; b) M. Engels, D. Bashford, M. R. Ghadiri, *J. Am. Chem. Soc.* **1995**, *117*, 9151–9158.

[3] a) K. Rosenthal-Aizman, G. Svensson, A. Unden, *J. Am. Chem. Soc.* **2004**, *126*, 3372–3373; b) S. Leclair, P. Baillargeon, R. Skouta, D. Gauthier, Y. Zhao, Y. L. Dory, *Angew. Chem. Int. Ed.* **2004**, *43*, 349–353.

[4] a) L. S. Shimizu, A. D. Hughes, M. D. Smith, M. J. Davis, B. P. Zhang, H.-C. zur Loye, K. D. Shimizu, *J. Am. Chem. Soc.* **2003**, *125*, 14972–14973; b) V. Semetey, C. Didierjean, J. P. Briand, A. Aubry, G. Guichard, *Angew. Chem. Int. Ed.* **2002**, *41*, 1895–1898.

[5] a) S. Ray, D. Haldar, M. G. B. Drew, A. Banerjee, *Org. Lett.* **2004**, *6*, 4463–4465; b) C. H. Görbitz, *Chem. Eur. J.* **2001**, *7*, 5153–5159.

[6] a) Z. Fei, D. Zhao, T. J. Geldbach, R. Scopelliti, P. J. Dyson, S. Antonijevic, G. Bodenhausen, *Angew. Chem. Int. Ed.* **2005**, *44*, 5720–5725; b) T. Yamaguchi, S. Tashiro, M. Tominaga, M. Kawano, T. Ozeki, M. Fujita, *J. Am. Chem. Soc.* **2004**, *126*, 10818–10819; c) F. Chang, Z.-M. Wang, H.-L. Sun, S. Gao, G.-H. Wen, X.-X. Zhang, *Dalton Trans.* **2005**, 2976–2978.

[7] a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; b) B. F. Abrahams, M. Moylan, S. D. Orchard, R. Robson, *Angew. Chem. Int. Ed.* **2003**, *42*, 1848–1851; c) S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375.

[8] a) O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–522; b) P. A. Maggard, C. L. Stern, K. R. Poeppelmeier, *J. Am. Chem. Soc.* **2001**, *123*, 7742–7743.

[9] a) M. Elhabiri, J. Hamacek, J. C. G. Bünzli, A. M. Albrecht-Gary, *Eur. J. Inorg. Chem.* **2004**, 51–62; b) D. M. Ciurtin, N. G. Pschirer, M. D. Smith, U. H. F. Bunz, H.-C. zur Loye, *Chem. Mater.* **2001**, *13*, 2743–2745; c) M. Cantuel, G. Bernardinelli, G. Muller, J. P. Riehl, C. Piguet, *Inorg. Chem.* **2004**, *43*, 1840–

1849; d) B. Venkataramanan, Z. Ning, J. J. Vittal, S. Valiyaveettil, *CrystEngComm* **2005**, *7*, 108–112.

[10] a) For a recent review on luminescent Zn^{II} coordination complexes see: S.-L. Zheng, X.-M. Chen, *Aust. J. Chem.* **2004**, *57*, 703–712; b) R. Bertoncello, M. Bettinelli, M. Casarin, A. Gulino, E. Tondello, A. Vittadini, *Inorg. Chem.* **1992**, *31*, 1558–1565; c) W. Yang, H. Schmider, Q. Wu, Y.-S. Zhang, S. Wang, *Inorg. Chem.* **2000**, *39*, 2397–2404; d) Y.-P. Tong, S.-L. Zheng, X.-M. Chen, *Eur. J. Inorg. Chem.* **2005**, 3734–3741; e) C. Jiang, Z. Yu, C. Jiao, S. Wang, J. Li, Z. Wang, Y. Cui, *Eur. J. Inorg. Chem.* **2004**, 4669–4674; f) J. Pang, E. J.-P. Marcotte, C. Seward, R. S. Brown, S. Wang, *Angew. Chem., Int. Ed.* **2001**, *40*, 4042–4045; g) X.-L. Wang, C. Qin, E.-B. Wang, Z.-M. Su, *Chem. Eur. J.* **2006**, *12*, 2680–2691.

[11] C. Seward, J. Pang, S. Wang, *Eur. J. Inorg. Chem.* **2002**, 1390–1399.

[12] S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* **1986**, *39*, 3798–3813.

[13] a) B. Yan, M. D. Capracotta, P. A. Maggard, *Inorg. Chem.* **2005**, *44*, 6509–6511; b) R. Fu, H. Zhang, L. Wang, S. Hu, Y. Li, X. Huang, X. Wu, *Eur. J. Inorg. Chem.* **2005**, 3211–3213.

[14] B. Gong, C. Zheng, Y. Yan, *J. Chem. Crystallogr.* **1999**, *29*, 649–652.

[15] C. K. Fair, *MolEN, Structure Solution Procedures*, Enraf–Nonius, Delft, Holland, **1990**.

[16] G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, **1990**.

[17] G. M. Sheldrick, *SHELXS-97, Program for the Refinement of Crystal Structure from Diffraction Data*, University of Göttingen, Göttingen, Germany, **1997**.

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