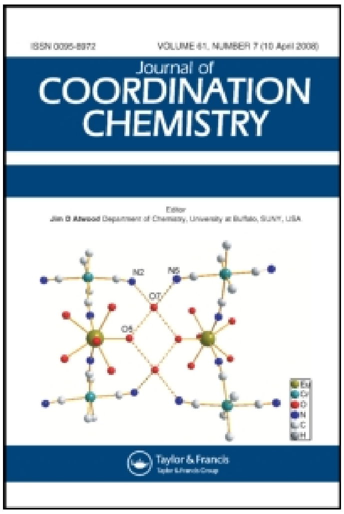

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Syntheses, structures and luminescent properties of two Zn(II) complexes of N-2-nitrobenzenesulfonyl-glycine acid

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Syntheses, structures and luminescent properties of two Zn(II) complexes of N-2-nitrobenzenesulfonyl-glycine acid

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Two luminescent zinc coordination complexes $[Zn_2(2\text{-NBS-gly})_4(H_2O)_4]\cdot 2H_2O$ (**1**), and $Zn(Im)_2(2\text{-NBS-gly})_2$ (**2**), (2-NBS-glyH = N-2-nitrobenzenesulfonyl-glycine acid, Im = imidazole) have been synthesized and their crystal structures determined by X-ray crystallography. The Zn(II) in **1** is a five-coordinate geometry and can be described as a slightly distorted square-pyramid; complex **2** is four-coordinate, forming a distorted tetrahedron. Through hydrogen bonding, complex **1** forms a 2-D network and complex **2** forms a zigzag chain. Fluorescent analyses show that both **1** and **2** exhibit photoluminescence in the solid state and may be potential candidates for photoactive materials.

Keywords: N-2-nitrobenzenesulfonyl-glycine; Crystal structure; Zinc complex; Fluorescent properties

1. Introduction

Amino acids are fundamental units of biomacromolecules, such as proteins and enzymes. Moreover, N-sulfonyl-amino acids were found to reproduce the coordination behavior of peptides and their selectivity towards metal ions [1–4]. Substitution of an Ar–SO_{2-} group on amine increase the coordination donors' behavior of amino acids to three types of ON donors from carboxyl, sulfoxyl and amine respectively, which may result in different coordination modes [5–9] and thus is of great interest in studying the coordination chemistry of N-sulfonyl-amino acids [10, 11].

Luminescent coordination compounds with amino acids have attracted much attention due to their performance in sensor technologies and electroluminescent devices. Several d^{10} metal-organic complexes have been found to exhibit interesting photoluminescent properties. Luminescent zinc complexes with nitrogen-containing ligands have been considerably investigated as potential luminescent materials [12–18].

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Herein we report the preparation, X-ray crystal structure and luminescent properties of two new zinc complexes $[Zn_2(2\text{-NBS-gly})_4(H_2O)_4] \cdot 2H_2O$ (**1**) and $Zn(Im)_2(2\text{-NBS-gly})_2$ (**2**).

2. Experimental

2.1. *General*

All reagents used in the syntheses were of analytical grade. C, H and N analysis were determined on a Perkin-Elmer 2400 elemental analyzer. The IR spectra were recorded in KBr discs on a Shimadzu IR-408 IR spectrophotometer in the 4000–600 cm^{-1} range. Fluorescence experiments used a HITACHI F-4500 Fluorescence Spectrophotometer and were measured in solid state at room temperature.

2.2. *Preparation of the ligand*

N-2-nitrobenzenesulfonyl-gly acid was prepared according to the method reported in the literature [19], and characterized by elemental analysis, and IR.

2.3. *Synthesis of $[Zn_2(2\text{-NBS-gly})_4(H_2O)_4] \cdot 2H_2O$ (1)*

The mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.5 mmol, 0.110 g) and 2-NBS-glyH (1 mmol, 0.259 g) was stirred into 10 mL water for 10 min to give a clear solution at room temperature. Then the pH value of the reaction mixture was adjusted to 6 by slow addition of 0.1 M NaOH solution. The reaction mixture was then heated on a water bath for 6 h at 65°C and filtered. Colorless crystals were separated from the mother liquor during slow evaporation at room temperature after 7 days. Anal. Calcd (%) for $C_{16}H_{20}N_4O_{15}S_2Zn$: C, 30.12; H, 3.16; N, 8.78. Found: C, 30.07; H, 3.23; N, 8.67. IR (KBr disc): υ (cm^{-1}) 3330 (s), 1608 (vs), 1537 (s), 1405 (w), 1160 (s).

2.4. *Synthesis of $Zn(Im)_2(2\text{-NBS-gly})_2(2)$*

The mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.5 mmol, 0.110 g) and 2-NBS-glyH (1 mmol, 0.259 g) was stirred into 10 mL of water for 10 min to give a clear solution at room temperature. Then the pH value of the reaction mixture was adjusted to 8 by slow addition of 0.1 M NaOH solution. After 3 h of stirring at 65°C, 3 mL ethanol solution of imidazole (0.5 mmol, 0.034 g) was added and the solution was stirred for another 3 h at 65°C and filtered. Colorless crystals separated from the mother liquor by slow evaporation at room temperature after 5 days. Anal. Calcd (%) for $C_{22}H_{22}N_4O_{12}S_2Zn$: C, 39.80; H, 3.34; N, 8.44. Found: C, 39.69; H, 3.43; N, 8.34. IR (KBr disc): υ (cm^{-1}) 3434 (s), 1637 (s), 1539 (s), 1417 (w), 1160 (s).

Table 1. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Bonds			
Zn(1)-O(7)^a	1.9550(2)	Zn(1)-O(3)^b	1.9674(1)
Zn(1)-O(1)	1.9680(2)	Zn(1)-O(3)	1.9674(1)
Zn(1)-O(14)	2.022(3)	Zn(1)-N(3)^b	1.9932(2)
Zn(1)-O(13)	2.098(2)	Zn(1)-N(3)	1.9933(2)
Zn(1)-O(7)	2.2552(2)	S(1)-N(2)	1.6072(2)
Angles			
O(7)^a-Zn(1)-O(1)	127.49(1)	O(3)^b-Zn(1)-O(3)	116.16(9)
O(7)^a-Zn(1)-O(1)	112.87(1)	O(3)^b-Zn(1)-N(3)^b	118.74(6)
O(1)-Zn(1)-O(1)	116.80(1)	O(3)-Zn(1)-N(3)^b	97.44(6)
O(7)^a-Zn(1)-O(1)	109.11(9)	O(3)^b-Zn(1)-N(3)	97.44(6)
O(1)-Zn(1)-O(1)	91.84(9)	O(3)-Zn(1)-N(3)	118.74(6)
O(14)-Zn(1)-O(1)	84.40(1)	N(3)^b-Zn(1)-N(3)	109.51(1)
O(7)^a-Zn(1)-O(7)	76.53(7)	O(6)-S(1)-O(5)	120.24(1)
O(1)-Zn(1)-O(7)	88.34(8)	O(6)-S(1)-N(2)	108.31(9)
O(14)-Zn(1)-O(7)	88.79(1)	O(5)-S(1)-N(2)	105.80(9)
O(13)-Zn(1)-O(7)	172.47(1)	N(2)-S(1)-C(1)	109.67(9)

Symmetry codes: a $= -x+1, -y+1, -z+1$; b $= -x, y, -z+(3/2)$.

2.5. *X-ray determination*

X-ray single-crystal data collection for **1** and **2** was performed with a Bruker SMART APEX II CCD diffractometer equipped with graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073\,1$ Å) by using ω–2θ scan technique at room temperature. The structures were solved by direct methods with SHELXS-97. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [20, 21].

Crystal data of **1**: $C_{16}H_{20}N_4O_{15}S_2Zn$, Mr = 637.85. Unit cell dimensions: $a = 7.8808(7)$, $b = 7.9227(7)$, $c = 19.8857(2)$ Å, $V = 1211.14(2)$ Å^3, $Z = 2$, $D_c = 1.749\,\mathrm{g\,cm^{-3}}$. Data were collected by an ω–2θ scan technique in the range of $2.60 \le \theta \le 27.49°$ with index ranges $-10 \le h \le 10$, $-10 \le k \le 10$, $-25 \le l \le 16$ with a total of 7362 reflections collected including 5354 independent ($R_{\mathrm{int}} = 0.0081$). The final agreement factor values are $R_1 = 0.0392$, $wR_2 = 0.1097$ ($I > 2\sigma(I)$). $w = 1/[\sigma^2(F_o)^2 + (0.0638P)^2 + 0.7284P]$ where $P = (F_o^2 + F_c^2)/3$, $S = 0.963$, $(\Delta\rho)_{\max} = 0.752$ and $(\Delta\rho)_{\min} = -0.596\,\mathrm{e}\,$Å^3. Crystal dimensions: $0.45 \times 0.35 \times 0.28\,\mathrm{mm}^3$.

Crystal data of **2**: $C_{22}H_{22}N_4O_{12}S_2Zn$, Mr = 719.96. Unit cell dimensions: $a = 15.0299(1)$, $b = 8.0684(5)$, $c = 24.3213(2)$ Å, $V = 2949.4(3)$ Å^3, $Z = 8$, $D_c = 1.621\,\mathrm{g\,cm^{-3}}$. Data were collected by an ω–2θ scan technique in the range of $2.71 \le \theta \le 27.50°$ with index ranges $-13 \le h \le 19$, $-10 \le k \le 9$, $-31 \le l \le 31$ with a total of 16,728 reflections collected including 3388 independent ($R_{\mathrm{int}} = 0.0183$). The final agreement factor values are $R_1 = 0.0316$, $wR_2 = 0.0841$ ($I > 2\sigma(I)$). $w = 1/[\sigma^2(F_o)^2 + (0.0437P)^2 + 1.5131P]$ where $P = (F_o^2 + F_c^2)/3$, $S = 0.996$, $(\Delta\rho)_{\max} = 0.407$ and $(\Delta\rho)_{\min} = -0.361\mathrm{e}\,$Å^3. Crystal dimensions: $0.38 \times 0.27 \times 0.18\,\mathrm{mm}^3$. Selected bond distances and angles for **1** and **2** are given in table 1.

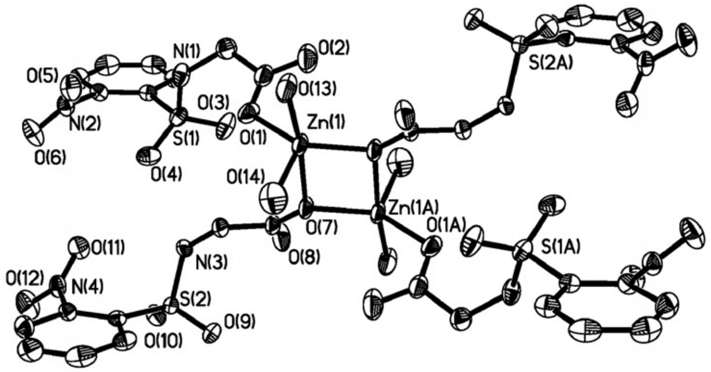

Figure 1. The structure of $[Zn_2(2\text{-NBS-gly})_4(H_2O)_4] \cdot 2H_2O$ (**1**).

3. Results and discussion

3.1. *Description of crystal structure of 1*

The molecular structure and atom numbering of complex **1** are shown in figure 1. Selected bond distances and angles are given in table 1.

Complex **1** crystallizes in the triclinic, space group $P\bar{1}$.

The symmetry unit in **1** is composed of two crystallographically independent Zn(II) ions, four 2-NBS-gly anions, and four water molecules. Each Zn(II) ion is five-coordinate, coordinated by five oxygen atoms, three from three 2-NBS-gly carboxylate groups, and two from water. The Zn–O bond lengths are all different, ranging from 1.9550(2) to 2.2552(2) Å (table 1). The Zn–O bond length formed by water (Zn–O(w): 2.022(3), 2.098(2) Å, respectively) are slightly longer than those formed by the carboxylate group of the 2-NBS-gly ligands (Zn–O: 1.9550(2), 1.9680(2) Å) except for Zn(1)–O(7) bond, which is the longest. So the coordination environment around the Zn(II) ion can be described as a slightly distorted square-pyramid.

The O–Zn–O angles vary from 76.53(7)° (O(7)–Zn(1)–O(7)#1) to 127.49(1)° (O(7)^{a}–Zn(1)–O(1)) (table 1). The Zn–O–Zn angle is 103.47°; the nonbonding intramolecular Zn $\cdots$ Zn distance is 3.311 Å, typical for the bis(μ-carboxylate-O) dimetal core without direct metal–metal bonding. The intradimeric metal–metal distance (3.311 Å) is identical to that found in the enzyme phospholipase C from *Bacillus cereus* (3.3 Å) and the serine/threonine protein phosphatase-1 (3.3 Å), suggesting that the μ-carboxylate-O group may play a similar role as a hydroxyl or an aqua bridge, since the intradimeric metal–metal length is primarily determined on the nature and mode of coordination of the bridging groups [9, 22]. Two Zn(II) ions are bridged by μ-carboxylate-O of the 2-NBS-gly to form a four-membered ring, as shown in figure 1.

Hydrogen bonding interactions exist involving the 2-NBS-gly as well as coordinated and lattice water molecules (as shown in table 2). The crystal packing is mainly due to two different hydrogen bonds O $\cdots$ O (including carboxyl oxygen atoms, oxygen atoms of water molecules and lattice water molecules) and N $\cdots$ O (N atoms of 2-NBS-gly ligands) in the range of 2.657(6) to 3.406(5) Å. An extended two-dimensional network structure via hydrogen bonds is formed, contributing to the stability of the structure (figure 2).

Table 2. Hydrogen bonds (Å, °) for **1** and **2**.

D–H···A	H–A	D–A	∠D–H···A
1			
O(15)–H(6W)···O(8)^{b}	2.15(2)	3.044(5)	169(5)
O(15)–H(5W)···O(2)^{a}	2.10(8)	2.857(7)	137(10)
O(13)–H(2W)···O(9)^{c}	2.03(3)	2.889(3)	157(5)
O(14)–H(4W)···O(15)	2.20(3)	2.657(6)	114(2)
O(13)–H(1W)···O(2)	2.633(2)	3.406(5)	145.1(2)
N(3)–H(3)···O(11)	2.58	3.037(3)	114.3
N(3)–H(3)···O(4)	2.12	2.865(3)	144.7
N(1)–H(1)···O(5)	2.50	3.046(3)	122.2
N(1)–H(1)···O(10)^{c}	2.15	2.924(3)	149.0
2			
N(4)–H(4′)···O(4)^{d}	1.90	2.699(2)	153.9

Symmetry codes: a = $-x+1$, $-y+1$, $-z+1$; b = $x+1$, y, z; c = x, $y+1$, z; d = $-x+(1/2)$, $y+(1/2)$, z.

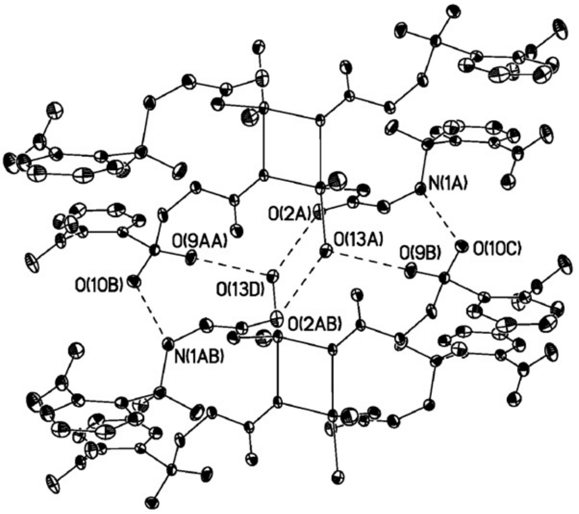

Figure 2. A sketch of the intermolecular interaction of **1**.

3.2. *Description of crystal structure of 2*

The molecular structure and atom numbering of **2** are shown in figure 3. Selected bond distances and angles are given in table 1. A single crystal X-ray analysis shows that complex **2** crystallizes in the orthorhombic, space group Pbcn. Each Zn ion is four-coordinate, two N atoms from two imidazole molecules and two oxygen atoms from two 2-NBS-gly ligands. The coordination geometry of zinc(II) is a distorted tetrahedron with angles varying from 97.44(6)°(O(3)–Zn(1)–N(3)^{b}) to 118.74(6)° (O(3)–Zn(1)–N(3)) (table 1). The Zn–O bond length, 1.9674(2) Å, is within the range reported for tetrahedral complexes [23, 24]. The Zn–N bond lengths, 1.9932(2) and 1.9933(2) Å, are similar to those found in tetrahedral zinc complexes of imidazole [10, 25].

A remarkable feature of **2** is that it consists of a 1-D zigzag chain via intermolecular hydrogen bonds (figure 4), composed of uncoordinated carboxylate oxygen atoms of

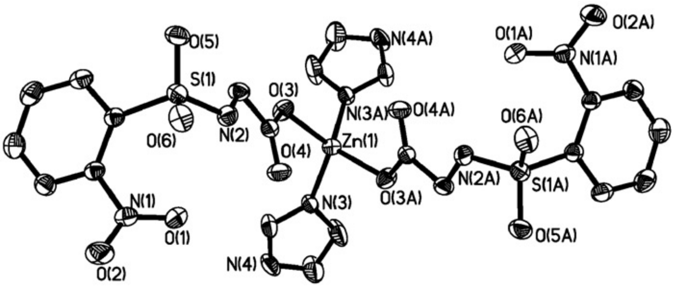

Figure 3. The structure of $Zn(Im)_2(2\text{-NBS-gly})_2$ (**2**).

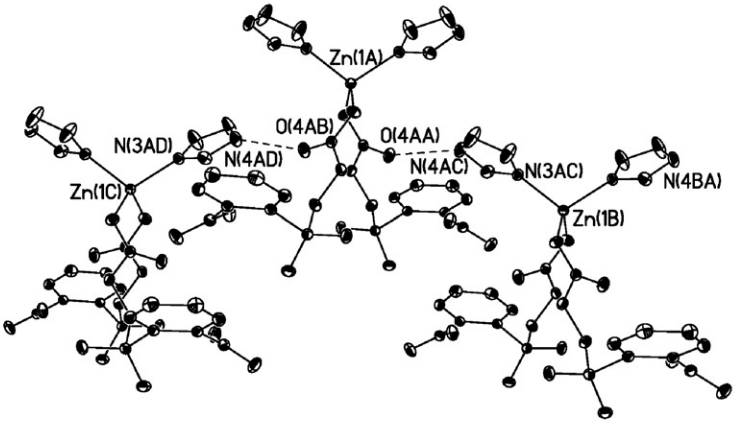

Figure 4. A sketch of the intermolecular interaction of complex **2**.

2–NBS–gly ligands and nitrogen atoms of imidazole molecules [(N(4)–H(4′)O(4)^{d}), symmetry code: d $= -x + (1/2), y + (1/2), z$] with bond distance of 2.699(2) Å.

3.3. *Fluorescent properties of 1 and 2*

Coordination frameworks are promising luminescent materials owing to their higher thermal stability than the free organic ligand and the ability to affect the emission wavelength of the organic material by metal coordination. Combinations of organic groups and transition metals are promising to luminescent materials as light-emitting diodes (LEDS) [26–27]. The luminescent properties of **1** and **2** were investigated in the solid state at room temperature. Figures 5 and 6 show the excitation and emission spectra of **1** and **2** in solid state measured at room temperature. The one intense fluorescent emission with maxima at 391 and 397 nm can be observed for **1** and **2** when excited at wavelengths 245 and 246 nm. Because the free carboxylate ligand displays no luminescence in the solid state at room temperature, the fluorescence may be due to intraligand fluorescent emission [28, 29]. Enhanced luminescent efficiency is probably due to coordination of 2-NBS-gly ligand to Zn(II) increasing the ligand conformational rigidity, reducing the loss of the energy by non-radiative decay of the intraligand excited state [30–33].

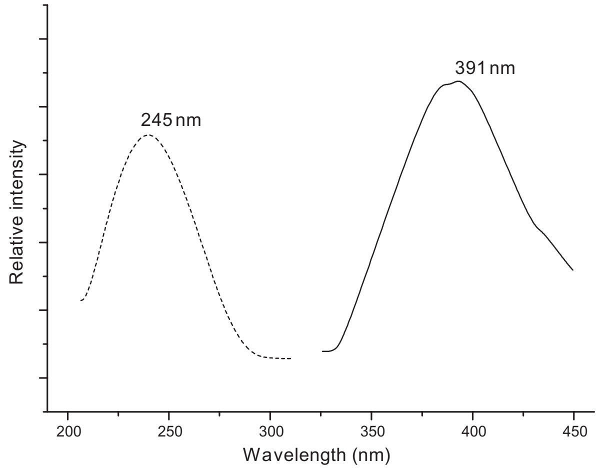

Figure 5. The solid-state excitation (dash line) and emission (solid line) spectra of **1** at room temperature.

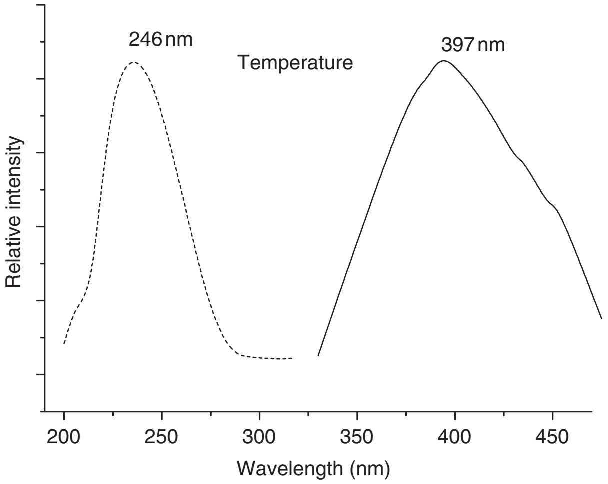

Figure 6. The solid-state excitation (dash line) and emission (solid line) spectra of **2** at room temperature.

4. Conclusion

Two new zinc 2-NBS-gly complexes $[Zn_2(2\text{-NBS-gly})_4(H_2O)_4]\cdot 2H_2O$ (**1**) and $Zn(Im)_2(2\text{-NBS-gly})_2$ (**2**) were synthesized and characterized by single X-ray diffraction. The X-ray analyses show that the coordination environment around the Zn(II) in **1** can be described as a slightly distorted square-pyramid with a metal–metal distance of 3.3 Å. This observation may provide some information to further understand the enzyme phospholipase C from *B. cereus* and the serine/threonine protein phosphatase-1. Complex **2** is in a distorted tetrahedral environment and a 1-D zigzag chain is formed through hydrogen bonds. Luminescence studies **1** and **2** show strong photoluminescence mainly as the result of fluorescence from the intraligand emission excited state. Those complexes may be potential luminescent materials.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 605550 for compound **1** and 605551 for compound **2**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] H. Sigel, R.B. Martin. *Chem. Rev.*, **82**, 385 (1982).
[2] T.G. Appleton, J.R. Hall, P.D. Prenzler. *Inorg. Chem.*, **28**, 815 (1989).
[3] G. Battistuzzi, M. Borsari, L. Menabue, M. Saladini. *Inorg. Chem.*, **35**, 4239 (1996).
[4] A.B. Corradi, G. Lusvardi, L. Menabue. *Polyhedron*, **18**, 1975 (1999).
[5] M. Saladini, L. Menabue, E. Ferrari, D. Lacopino. *J. Chem. Soc., Dalton. Trans.*, 1513 (2001).
[6] F.P. Liang, M.S. Cheng, R.X. Hu, Z.L. Chen. *Acta Cryst.*, **C60**, m269 (2004).
[7] L. Menabue, M. Saladini. *Inorg. Chem.*, **30**, 1651 (1991).
[8] D. Iacopino, L. Menabue, M. Saladini. *Aust. J. Chem.*, **52**, 741 (1999).
[9] G. Battistuzzi, M. Borsari, L. Menabue, M. Saladini. *Inorg. Chem.*, **35**, 4239 (1996).
[10] G.B. Gavioli, M. Borsari, G.C. Pellacani, L. Menabue, M. Sola, A.B. Corradi. *Inorg. Chem.*, **27**, 1587 (1988).
[11] A.B. Corradi, E. Gozzoli, L. Menabue, M. Saladini, L.P. Battaglia, P. Sgarabotto. *J. Chem. Soc., Dalton Trans.*, 273 (1994).
[12] L.Y. Zhang, G.F. Liu, S.L. Zheng, B.H. Ye, X.M. Zhang, X.M. Chen. *Eur. J. Inorg. Chem.*, 2965 (2003).
[13] X.L. Wang, Q. Chao, E.B. Wang, L. Xu. *Eur. J. Inorg. Chem.*, 3418 (2005).
[14] Q. Chao, X.L. Wang, E.B. Wang, L. Xu. *J. Mol. Struct.*, **738**, 91 (2005).
[15] H. Kunkely, A. Vogler. *Chem. Commun.*, 1204 (1990).
[16] Y. Kang, C. Seward, D. Song, S. Wang. *Inorg. Chem.*, **42**, 2789 (2003).
[17] G. Yu, S.W. Yin, Y.Q. Liu, Z.G. Shuai, D.B. Zhu. *J. Am. Chem. Soc.*, **125**, 14816 (2003).
[18] J. Li, J.H. Zhou, Y.Z. Li, L.H. Weng, X.T. Chen, Z. Yu, Z.L. Xue. *Inorg. Chem. Commun.*, **7**, 538 (2004).
[19] E.W. McChesney, W.K. Swann. *J. Am. Chem. Soc.*, **59**, 1116 (1937).
[20] G.M. Sheldrick. *SHELXL 97*, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
[21] G.M. Sheldrick. *SHELXS 97*, *Program for the Solution of Crystal Structures*, University of Göttingen, Germany (1997).
[22] L.S. Long, K.Y. Ding, X.M. Chen, L.N. Ji. *Inorg. Chem. Commun.*, **3**, 65 (2000).
[23] A.Z. Thomas, G. Helmar, D. Eckhard. *Polyhedron*, **17**, 2199 (1998).
[24] Y. Yukawa, N. Yasukawa, Y. Inomata, T. Takeuchi. *Bull. Chem. Soc. Jpn*, **58**, 1591 (1985).
[25] C.D. Wu, C.Z. Lu, D.M. Wu, H.H. Zhuang, J.S. Huang. *Inorg. Chem. Commun.*, **4**, 561 (2001).
[26] C. Jiang, Z.P. Yu, C. Jiao, S.J. Wang, J.M. Li, Z.Y. Wang, Y. Cui. *Eur. J. Inorg. Chem.*, 4669 (2004).
[27] H.F. Bunz. *Chem. Rev.*, **100**, 1605 (2000).
[28] J. Li, J.H. Zhou, Y.Z. Li, L.H. Weng, X.T. Chen, Z. Yu, Z.L. Xue. *Inorg. Chem. Commun.*, **7**, 538 (2004).
[29] C.X. Wang, C.X. Du, Y.H. Li, Y.J. Wu. *Inorg. Chem. Commun.*, **8**, 379 (2005).

[30] L.Z. Zhang, Y. Xiong, P. Cheng, G.Q. Tang, L.J. Wang, D.Z. Liao. *J. Mater. Chem.*, **11**, 2903 (2001).
[31] L.Z. Zhang, P. Cheng, W. Shi, D.Z. Liao, Y. Xiong, G.Q. Tang. *Inorg. Chem. Commun.*, **5**, 361 (2002).
[32] L.N. Zhu, L.Z. Zhang, W.Z. Wang, D.Z. Liao, P. Cheng, Z.H. Jiong, S.P. Yan. *Inorg. Chem. Commun.*, **5**, 1017 (2002).
[33] X.L. Wang, C. Qin, E.B. Wang, L. Xu, Z.M. Su, C.W. Hu. *Angew. Chem. Int. Ed.*, **43**, 5036 (2004).