

Structure of Bischloro tris(1,10-phenanthroline)copper(II) Dichloromethane Solvate Nonahydrate: [Cu(phen)₃]Cl₂·CH₂Cl₂·9H₂O

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The crystal and molecular structures of [Cu(phen)₃]Cl₂·CH₂Cl₂·9H₂O (PHEN = 1,10-phenanthroline) have been determined by X-ray crystallography. The complex crystallizes in triclinic system, space group *P* $\bar{1}$, with lattice parameters $a = 1.26000(3)$, $b = 1.37525(4)$, $c = 1.42750(3)$ nm, $\alpha = 85.2970(1)$, $\beta = 66.8400(1)$, $\gamma = 83.09(1)^\circ$, and $Z = 2$. The coordinated cations contain a six-coordinated copper atom chelated by three PHEN ligands, and the Jahn-Teller effect of the Cu(II) ion results in a distorted octahedral arrangement with the six Cu—N distances ranging from 0.2112(6) to 0.2265(7) nm. In addition to the copper coordinated cation, there are two chloride ions, one dichloromethane solvate and nine water molecules in its asymmetric unit. In the solid state, the title compound forms three dimensional network structures through hydrogen bonds. The intermolecular hydrogen bonds connect the [Cu(phen)₃]²⁺, chloride ion, dichloromethane solvate and H₂O moieties altogether.

Keywords Copper complexes, 1,10-phenanthroline ligands, hydrogen bonds, network

Introduction

Phenanthroline is well known as a bidentate ligand in coordination chemistry. Metal complexes of the type [M(LL)₃]ⁿ⁺ where LL is either 1,10-phenanthroline (PHEN) or a modified PHEN ligand, are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA.^{1,2} The ligands or the metal in these complexes can be changed in an easily controlled manner to facilitate an

individual application, thus providing an easy access for understanding the details involved in DNA-binding and cleavage.³ Some [M(phen)₂XY]ⁿ⁺ (M = Co, Ni, Cu and Zn) complexes are reported to show the DNA-binding and photochemical DNA cleavage characteristics.⁴ It has been suggested that under certain conditions copper phenanthroline complexes play an important role in the cleavage of DNA and the differences in the arrangement of the complexes can result in very striking differences in biopharmacological activity.⁵ These complexes have a potential application as a model for the interaction of enzyme-metal ion and substrate and may be related to a transport process of copper in human serum.⁶⁻⁸ Also, molecular recognition and self-assembly of molecules are generally based on strong (O—H···O and N—H···O hydrogen bonds), weak (van der Waals, π ··· π stacking) and potentially weak (C—H···Y hydrogen bonds, Y = O, N and Cl) intermolecular interactions.⁹⁻¹¹ Few organic-metal complexes were used as a host to recognize an organic guest molecules through hydrogen bonds.¹²⁻¹⁴ In this paper, we describe the crystal structure of bischloro-tris(1,10-phenanthroline)copper(II) dichloromethane solvate nonahydrate [Cu(phen)₃]Cl₂·CH₂Cl₂·9H₂O which displays strong hydrogen bond interactions.

Experimental

Materials

The reagents CuCl₂·6H₂O (A. R.) and PHEN

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Received December 19, 2000; revised April 10, 2001; accepted April 20, 2001.

Project supported by the Natural Science Foundation of Shandong Province (No. Q99B16) and the National Natural Science Foundation of China (No. 29775012).

(A.R.) were commercially available.

Preparation

To a warm solution of PHEN (2.97 g, 15 mmol) in EtOH (50 mL) was added $[\text{CuCl}_2 \cdot 6\text{H}_2\text{O}]$ (1.19 g, 5 mmol) with stirring and the mixture was refluxed for 20 min. The blue solution was filtered and the filtrate was heated to evaporate, a blue solid appeared and was separated by filtration. Crystals suitable for X-ray structure determination were obtained by slowly evaporating its dichloromethane and ethanol mixed solution in air. The C, H and N contents were determined by elemental analysis (calcd for C 48.16, H 4.77, N 9.11; found C 48.40, H 5.05, N 8.87).

Crystal structure analysis

A summary of the key crystallographic information is given in Table 1. The selected crystal of $[\text{Cu}(\text{phen})_3]\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2 \cdot 9\text{H}_2\text{O}$ was mounted on a SMART CCD diffractometer. Reflection data were measured at 20°C using graphite monochromated Mo K_α ($\lambda = 0.071073$ nm) radiation with a detector distance of 4 cm to the crystal and swing angle of -35° . A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle ($0^\circ, 88^\circ, 180^\circ$) and each exposure of 30s covered 0.3° in ω . The collected data were reduced by using the program SAINT¹⁵ and empirical absorption correction was done by using the SADABS¹⁶ ($T_{\min} = 0.7079$; $T_{\max} =$

Table 1 Summary of crystallographic results for $[\text{Cu}(\text{phen})_3]\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2 \cdot 9\text{H}_2\text{O}$

Empirical formula	$\text{C}_{37}\text{H}_{44}\text{Cl}_4\text{CuN}_6\text{O}_9$
Formula weight	922.13
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
a (nm)	1.26000(3)
b (nm)	1.37525(4)
c (nm)	1.42750(3)
α ($^\circ$)	85.2970(1)
β ($^\circ$)	66.8400(1)
γ ($^\circ$)	83.09(1)
V (nm^3)	2.2561(1)
Z	2
Calculated density (Mg/m^3)	1.334
Absorption coefficient (mm^{-1})	0.773
$F(000)$	890
Crystal size (mm^3)	$0.48 \times 0.40 \times 0.22$
Theta range for data collection ($^\circ$)	1.55—25.00
Limiting indices	$-13 \leq h \leq 13, -16 \leq k \leq 15, 0 \leq l \leq 16$
Reflections collected/unique	12038/7722 [$R(\text{int}) = 0.0587$]
Completeness to theta = 25.00	97.2%
Absorption correction	Empirical
Max. and min. transmission	0.8483 and 0.7079
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7722/2/514
Goodness-of-fit on F^2	1.559
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0691, wR_2 = 0.1013$
R indices (all data)	$R_1 = 0.1098, wR_2 = 0.1413$
Largest diff. peak and hole ($\text{e} \cdot \text{nm}^{-3}$)	1422 and -1490

0.8483) program. Reflections with $2\theta < 50^\circ$ were used for structure solution and refinement.

The structure was solved by direct method using SHELXTL.¹⁷ All the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method. All the hydrogen atoms were placed in the calculated positions assigned the fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in structure-factor calculations. The final least-square cycle gave $R = 0.0691$, $wR = 0.1013$ for 7173 reflections with $I > 2\sigma(I)$; the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-Ray Crystallography.¹⁸

Results and discussions

The X-ray structure of the complex $[\text{Cu}(\text{phen})_3]\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2 \cdot 9\text{H}_2\text{O}$ consists of the $[\text{Cu}(\text{phen})_3]^{3+}$ cation, two Cl^- anions, one dichloromethane solvate molecule and nine molecules of water. Fig. 1 shows a perspective view of the title compound with atomic numbering scheme, and Fig. 2 shows a perspective view of the crystal packing in the unit cell. Table 2 lists atomic coordinates and equivalent temperature factors for non-hydrogen atoms. Selected bond lengths and angles are

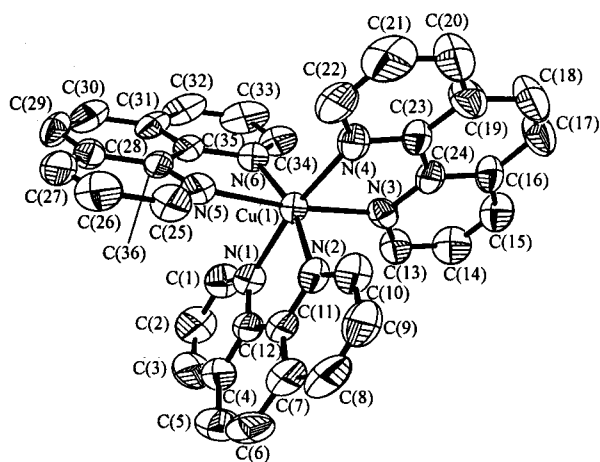


Fig. 1 Molecular structure of $[\text{Cu}(\text{phen})_3]\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2 \cdot 9\text{H}_2\text{O}$ with the atomic numbering scheme.

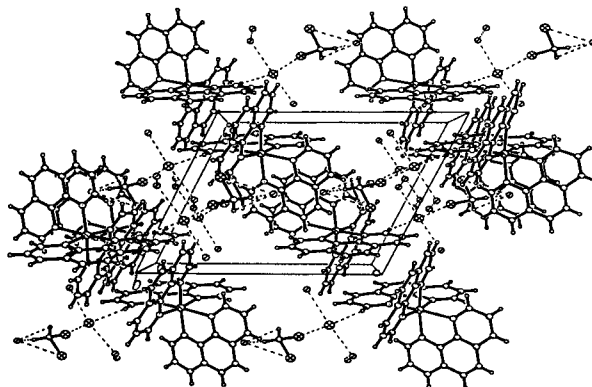


Fig. 2 A view of the crystal packing down the b axis for $[\text{Cu}(\text{phen})_3]\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2 \cdot 9\text{H}_2\text{O}$.

Table 2 Atomic coordinates (10^3) and equivalent isotropic displacement parameters ($\text{nm}^2 \times 10^2$). U (eq.) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U (eq.)
Cu(1)	2444(1)	2479(1)	-2509(1)	40(1)
Cl(1)	1839(3)	5464(2)	2721(2)	101(1)
Cl(2)	3305(4)	1056(3)	960(3)	126(1)
O(1W)	5431(9)	2025(8)	-757(8)	133(3)
O(2W)	469(6)	-737(6)	-3838(5)	85(2)
O(3W)	469(7)	6995(6)	4337(5)	94(2)
O(4W)	1056(7)	-1020(5)	-5983(5)	82(2)
O(5W)	3351(6)	-685(5)	-7558(5)	81(2)
O(6W)	-1137(9)	-2062(6)	-2621(6)	120(3)
O(7W)	-1510(7)	6574(6)	6106(6)	99(2)
N(1)	2893(6)	1755(5)	-4004(5)	49(2)
N(2)	4259(6)	2614(4)	-3260(5)	48(2)
N(3)	1926(6)	3885(5)	-2985(5)	50(2)
N(4)	2168(6)	3367(5)	-1199(5)	54(2)
N(5)	2734(6)	1069(5)	-1826(5)	49(2)
N(6)	752(5)	1988(4)	-1953(4)	44(2)
C(1)	2195(8)	1366(7)	-4378(7)	65(2)
C(2)	2643(10)	883(8)	-5309(8)	79(3)
C(3)	3848(11)	770(8)	-5860(8)	80(3)
C(4)	4611(8)	1172(6)	-5491(6)	58(2)
C(5)	5859(10)	1103(8)	-6027(7)	81(3)
C(6)	6515(8)	1536(8)	-5663(7)	72(3)
C(7)	6002(8)	2090(6)	-4725(7)	60(2)
C(8)	6653(9)	2598(8)	-4315(8)	77(3)
C(9)	6081(10)	3093(7)	-3430(8)	73(3)
C(10)	4907(9)	3095(6)	-2923(7)	61(2)
C(11)	4807(7)	2118(5)	-4170(6)	44(2)
C(12)	4087(7)	1659(5)	-4569(6)	45(2)

Continued				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq.)
C(13)	1824(9)	4134(6)	-3894(6)	63(2)
C(14)	1447(9)	5096(7)	-4125(7)	75(3)
C(15)	1164(9)	5810(7)	-3456(7)	70(3)
C(16)	1245(9)	5587(6)	-2467(7)	61(2)
C(17)	960(12)	6313(7)	-1694(8)	96(4)
C(18)	1152(13)	6064(7)	-833(8)	105(5)
C(19)	1554(10)	5055(7)	-617(7)	77(3)
C(20)	1745(12)	4761(8)	300(8)	94(4)
C(21)	2098(11)	3814(9)	452(9)	97(4)
C(22)	2305(9)	3099(7)	-301(7)	72(3)
C(23)	1770(7)	4338(5)	-1321(6)	52(2)
C(24)	1652(7)	4609(5)	-2291(6)	48(2)
C(25)	3701(7)	671(7)	-1705(6)	59(2)
C(26)	3785(9)	-309(8)	-1332(7)	76(3)
C(27)	2928(9)	-887(7)	-1129(6)	68(3)
C(28)	1871(9)	-493(6)	-1252(6)	59(2)
C(29)	857(10)	-1023(6)	-1022(6)	67(3)
C(30)	-162(10)	-552(7)	-1113(6)	77(3)
C(31)	-222(8)	453(6)	-1423(5)	55(2)
C(32)	-1273(8)	973(8)	-1446(6)	71(3)
C(33)	-1248(9)	1973(9)	-1716(7)	79(3)
C(34)	-236(8)	2447(7)	-1975(6)	59(2)
C(35)	762(7)	990(5)	-1661(5)	41(2)
C(36)	1831(7)	520(5)	-1590(5)	43(2)
O(8W)	4945(8)	4377(5)	-5974(6)	100(3)
C(38)	4614(14)	3756(14)	-7392(10)	306(19)
Cl(4)	5921(12)	4217(14)	-8310(9)	575(16)
Cl(5)	4303(6)	2896(4)	-8124(5)	198(2)
O(9W)	5980(20)	3962(18)	-788(15)	365(16)

presented in Table 3, and potentially weak intermolecular interaction in Table 4.

The title compound crystallized with one [Cu(phen)₃]²⁺ cation and two Cl⁻ anion, one CH₂Cl₂ solvent molecule and nine molecules of water. There was no evidence of covalent bonding interactions between the chloride anions and cation, however, there are close contacts, probably indicative of hydrogen bonding between the hydrates and chloride, and also between chlorides and the surrounding phenanthroline C atoms. The Cu atom exhibits a slightly distorted octahedral geometry in which the Cu atom is coordinated to six N atoms from three phenanthrolines. The three PHEN ligands are bidentately bonded to Cu, forming five-member chelate rings. The bond distances of Cu—N are in the range of

0.2112(6)—0.2265(6) nm. These lengths are longer than those found in the similar structures with usual octahedral coordination environment of Cu(II) complexes, such as Cu(bpy)[ClO₄]₂ (0.1948(2)—0.1996(2) nm)¹⁹ and [Cu(phen)(Sa)(ClO₄)₂] (0.1999(2)—0.2005(2) nm).²⁰ The bite angles between the PHEN chelate rings and Cu atom are almost the same (~78°) which are in good agreement with those phenanthroline metal complexes.^{21,22} However, there are significant deviations from linearity for the *trans* atoms with angles N(1)-Cu-N(4), N(2)-Cu-N(6) and N(3)-Cu-N(5) at 171.0(2)°, 165.0(2)° and 171.4(2)°, respectively. The rigidity of the PHEN ligand has been cited to afford 'slightly bent metal-ligand bonds'.²³ Therefore, in this report, the bite angles should not be taken as an indication of distortion with the PHEN ligand itself. Rather the bite angle appears to correlate well with the metal-to-N-atom distance: 82.6(4)° and 0.1978(3) nm in [Fe(phen)₃]²⁺,²⁴ 81.0(2)° and 0.205(1) nm in [Cr(phen)₃]³⁺,²⁵ 78.1(3)° and 0.213(1) nm in [Co(phen)₃]³⁺,²⁶ 70.2(2)° and 0.2400(6) nm in [Hg(phen)₃]²⁺,²⁷ 78.2(2)° and 0.2167(2) nm in this study. This can be described by the equation $y = -298.18x + 141.75$, where *y* represents the bite angle and *x* is the metal-to-N-atom bond distance. It is noteworthy that the bond distances of Cu—N(1) and Cu—N(4) [0.2265(6) and 0.2207(7) nm] are longer than those of other Cu—N, which can be attributed to the Jahn-Teller distortion of the Cu(II) ion.²⁸ The bond lengths of C(1)—N(1) and C(22)—N(4) [0.13704(2) and 0.13753(2) nm] are longer than other C—N bond lengths [0.13367(3)—0.13660(2) nm]. The bond distances of C—C and other C—N in the title compound all fall within the range of the literature values.²⁹

The two aromatic ring systems in each PHEN are coplanar within the experimental error. The three PHEN ligand planes have dihedral angles of 78.37, 76.08 and 73.15° between each two of them, respectively.

The most interesting structural feature of the complex is the intramolecular and intermolecular hydrogen bonds and potentially weak (C—H···Y hydrogen bonds, Y = O, N and Cl) intermolecular interactions. The nine lattice water molecules are hydrogen bonded to each other, and O(1w) form the strongest hydrogen bond with O(9w). The O(1w)—O(9w) distance is 0.28229 nm, which is little shorter than that of pure water

Table 3 Selected bond distances (nm) and bond angles ($^{\circ}$) of the title compound

Cu—N(3)	0.2112(6)	Cu—N(2)	0.2134(7)	Cu—N(6)	0.2136(6)	Cu—N(5)	0.2155(6)
Cu—N(4)	0.2207(7)	Cu—N(1)	0.2265(6)	N(1)—C(1)	0.1370(9)	N(2)—C(10)	0.1351(9)
N(3)—C(13)	0.1366(9)	N(5)—C(25)	0.1343(9)	N(4)—C(22)	0.1375(9)	N(6)—C(34)	0.1337(9)
N(2)—Cu(1)—N(6)		165.0(2)		N(3)—Cu(1)—N(5)		171.4(2)	
N(4)—Cu(1)—N(1)		171.0(2)		N(2)—Cu(1)—N(1)		77.7(2)	
N(3)—Cu(1)—N(4)		77.8(2)		N(6)—Cu(1)—N(5)		78.9(2)	

Symmetry transformations used to generate equivalent atoms: # : $-x, -y, -z$.

Table 4 Intermolecular interaction distances (nm) of the title compound

D	H	A	Symm.	D—H	H \cdots A	D \cdots A	D—H \cdots A
C(22)	H(22A)	Cl(2)	$x, y, 1+z$	0.09300	0.27438	0.35802	150.10
C(19)	H(19A)	Cl(4)	$1-x, 1-y, 1-z$	0.09383	0.22148	0.31871	163.30
O(5w)	H	Cl(2)	$x, -1+y, z$	0.09500	0.27225	0.30733	104.68
O(6w)	H	Cl(2)	$1-x, 1-y, -z$	0.09500	0.27964	0.31807	156.58
O(3w)	H	Cl(1)	x, y, z	0.09500	0.27138	0.30864	125.94
O(2w)	H	O(6w)	$1+x, y, z$			0.28354	131.75
O(4w)	H	O(2w)	$1+x, -1+y, z$			0.29018	125.94
O(3w)	H	O(7w)	$-x, 1-y, 1-z$			0.28428	162.82
O(1w)	H	O(9w)	x, y, z			0.28229	160.77

D: Donor; A: Acceptor; Symm.: Symmetry applied in acceptor.

(0.283 nm).³⁰ The two Cl⁻ anions form hydrogen bond network with O(3w), O(5w), O(6w) and O(9w) water molecules and the Cl(4) atom in dichloromethane solvate molecule forms hydrogen bond with O(8w). The Cl(2), Cl(4) and O(8w) with C atoms in PHEN ligands form potentially weak (C—H \cdots Y hydrogen bonds, Y = O and Cl) intermolecular interactions as shown in Table 3. All above hydrogen bonds in this structure connect [Cu(phen)₃]³⁺, H₂O moieties, chloride anion and dichloromethane solvate molecule altogether and form three dimensional hydrogen bond network which stabilizes the structure.

References

- Barton, J. K. *Science* **1986**, *233*, 727.
- Naing, K.; Takashani, M.; Taniguchi, M.; Yamagishi, A. *Inorg. Chem.* **1995**, *34*, 350.
- Sammes, P. C.; Yahioğlu, G. *Chem. Soc. Rev.* **1994**, 327.
- Arounaguirri, S.; Maiya, B. G. *Inorg. Chem.* **1996**, *35*, 4267.
- Yang, Y.; Pogni, R.; Basosi, R. *J. Chem. Soc., Faraday Trans.* **1989**, 3995.
- Simmons, C. J.; Lundeen, M.; Seff, K. *Inorg. Chem.* **1978**, *17*, 1429.
- Desphande, S. V.; Srivastava, T. S. *Inorg. Chim. Acta* **1883**, *78*, 75.
- Battaglin, L. P.; Corradi, M. A.; Zoroddu, M. A.; Manca, G.; Basosi, R.; Solinas, C. *J. Chem. Soc., Dalton Trans.* **1991**, 2109.
- Whitesides, G. M.; Mathisa, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312.
- Hunter, C. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1584.
- Kotera, M.; Lehn, J. M.; Vigneron, J. P. *J. Chem. Soc., Chem. Commun.* **1994**, 197.
- Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1995**, *117*, 1401.
- Fugita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151.
- Xu, L. Z.; Zhao, P. S.; Zhang, S. S. *Chin. J. Chem.* **2001**, *19*, 436.
- Sheldrick, G. M. *SHELXTL5*, Ed: Siemens, A. G., Analytical Systems Aut37, D76181 Karlsruhe 21, Germany, **1995**.
- Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
- Sheldrick, G. M. *SHELXTL93*, University of Gottingen, Germany, **1993**.
- Wilson, A. J. *International Table for X-ray Crystallography*,

- Vol. C, Kluwer Academic Publishers, 1992, Dordrecht: Tables 6.1.1.4 (pp. 500—5502) and 4.2.6.8 (pp. 219—222) respectively.
- 19 Fu, Y. J.; Yang, H.; Wang, D. F.; Tang, W. X.; Wu, B. M.; Mak, T. M. C. *Polyhedron* 1997, 16, 1505.
- 20 Li, M.; Zou, J. Z.; Xu, Z., You, X. Z.; Huang, X. Y. *Polyhedron* 1995, 14, 642.
- 21 Ye, B. H.; Chen, X. M.; Zeng T. X.; Ji, L. N. *Polyhedron* 1994, 13, 2185.
- 22 Kom, Y. *Koord. Khim.* 1982, 8, 225.
- 23 Goodwin, H. A.; Kepert, D. L.; Patrick, J. M.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* 1984, 34, 1817.
- 24 Koh, L. L.; Xu, Y.; Hsieh, A. K.; Song, B.; Wu, F.; Ji, L. *Acta Crystallogr.* 1994, C50, 884.
- 25 Luck, R. L.; Gawryszewska, P.; Riehl, J. P. *Acta Crystallogr.* 2000, C56, 238.
- 26 Boys, D.; Escobar, C.; Wittke, O. *Acta Crystallogr.* 1984, C40, 1359.
- 27 Deacon, G. B.; Raston, C. L.; Tunaley, D.; White, A. H. *Aust. J. Chem.* 1979, 32, 2195.
- 28 Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3th. John Wiley & Sons, Inc. London, 1972, pp. 502—508.
- 29 Tian, Y. P.; Duan, C. Y.; Xu, X. X.; You, X. Z. *Acta Crystallogr.* 1995, C51, 2309.
- 30 Xiong, R. G.; Liu, C. M.; Zuo, J. L.; Li, H. Z.; You, X. Z.; Fun, H. K.; Sivakumar, K. *Polyhedron* 1997, 16, 2315.

(E200012284 SONG, J.P.; DONG, L.J.)