J. Braz. Chem. Soc., Vol. 16, No. 4, 796-800, 2005.
Printed in Brazil - ©2005 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Synthesis, X-ray Crystal Structure and Thermal Decomposition Mechanism of $[Zn(MCZ)_3](NO_3)_2 \cdot H_2O$ (MCZ=Methyl Carbazate)

Guixia Ma[a], *Tonglai Zhang*[*,a] *and Kaibei Yu*[b]

[a] *State Key Lab of Prevention and Control of Explosion, Beijing Institute of Technology, Beijing 100081, P. R. China*

[b] *Chengdu Center of Analysis and Measurement, Chinese Academy of Sciences, Chengdu 610041, P. R. China*

Um novo complexo de coordenação, $[Zn(MCZ)_3](NO_3)2 \cdot H_2O$, foi sintetizado através da reação de soluções aquosas de nitrato de zinco(II) e metilcarbazato. O complexo foi caracterizado por espectroscopia IV, análise elementar e por um estudo de difração de raios X. Cristaliza no grupo espacial monoclínico *P2*$_1$*/n*. O íon metálico central é hexa-coordenado, com geometria octaédrica distorcida e se encontra ligado aos ligantes bidentados MCZ através dos átomos de oxigênio das carbonilas e dos átomos de nitrogênio terminais. Os cátions $[Zn(MCZ)_3]^{2+}$, os anions NO_3^- e as moléculas de água do retículo encontram-se interconectadas por forças eletrostáticas e por ligações de hidrogênio em um arranjo tridimensional. O mecanismo da decomposição térmica foi sugerido pelos estudos de DSC e TG-DTG. O composto $[Zn(MCZ)_3](NO_3)2 \cdot H_2O$ começa a decompor-se a 181,9 °C, e o resíduo final, a 300,0 °C é ZnO.

A new coordination complex, $[Zn(MCZ)_3](NO_3)_2 \cdot H_2O$, was synthesized by the reaction of the aqueous solutions of zinc(II) nitrate and methyl carbazate. The complex was characterized by IR spectroscopy, elemental analysis and X-ray diffraction. It crystallizes in the monoclinic space group *P2*$_1$*/n*. The central metal ion has distorted octahedral six-coordination environment, and is coordinated to bidentate MCZ ligands through carbonyl oxygen atoms and the terminal nitrogen atoms. $[Zn(MCZ)_3]^{2+}$ cations, NO_3^- anions and lattice water molecules are interconnected by electrostatic forces and hydrogen bonds into a 3-D network. The thermal decomposition mechanism was suggested by DSC and TG-DTG studies under the linear heating rates. $[Zn(MCZ)_3](NO_3)_2 \cdot H_2O$ begins to decompose at 181.9 °C, and the final solid residue at 300 °C is ZnO.

Keywords: zinc(II) complex, methyl carbazate, crystal structure, thermal decomposition

Introduction

Methyl carbazate (MCZ) is an important intermediate in organic synthesis, and is widely used in medicines, pesticides, fine chemicals and petroleum chemicals.[1-5] MCZ molecule consists of a hydrazine group, a carbonyl and a methoxy group, which determine its lively chemical reactivity. For example, it can substitute phosgene to be used as carbonylating reagent, and also can be used as replacer of dimethyl sulfate in methylating reaction.[6] In addition, all the hydrazine N and carbonyl O are potential coordination atoms, and the similar structure character to carbohydrazide, which is a widely used ligand in coordination compounds,[7-9] determine MCZ a promising coordination ligand. But till now, only a few studies on MCZ coordination compounds have been carried out.[10] Here the crystal structure and thermal decomposition mechanism of $[Zn(MCZ)_3](NO_3)_2 \cdot H_2O$ are described.

Results and Discussion

Infrared spectra of $[Zn(MCZ)_3](NO_3)_2 \cdot H_2O$

The complex has been characterized by analytical and spectroscopic data (see experimental). Selected bands from the spectra were tentatively assigned by comparison with previous study of MCZ metal(II) complex.[10] The band observed at 3323 cm^{-1} supports the fact that the H_2O molecule in the complex is lattice water, of which the bands are around 3400 cm^{-1}. The bands around 3200 cm^{-1} were assigned to the stretching vibration of the N-H group, and that at 1686 cm^{-1} was assigned to the C=O group. Both bands were shifted to lower wavenumber compared to the free ligand,[11] and this was interpreted as the evidence of coordination through the nitrogen atom of the hydrazine

---

* e-mail: ztlbit@public.bta.net.cn

group and the carbonyl oxygen atom. Finally, the bands observed in the 1300-700 cm^{-1} region were assigned to the N-O and C-O stretching vibrations.

Crystal structure of [Zn(MCZ)$_3$](NO$_3$)$_2$·H$_2$O

A single unit cell with the atomic numbering scheme and atom connectivity is shown in Figure 1. There are one [Zn(MCZ)$_3$]$^{2+}$ coordination cation, two NO$_3^-$ anions and a lattice H$_2$O molecule in the asymmetric unit, and they are linked through electrostatic forces and extensive hydrogen bonds into a 3-D network.

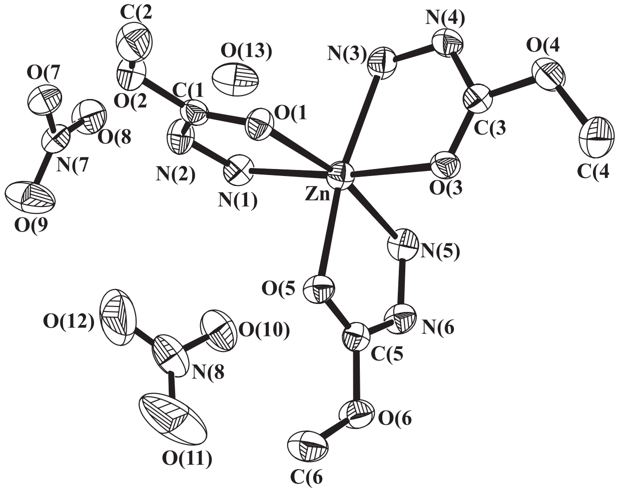

Figure 1. Molecular structure and atomic numbering scheme of [Zn(MCZ)$_3$](NO$_3$)$_2$·H$_2$O.

The zinc(II) center is in six-coordinate sites, and is coordinated to three MCZ ligands with bonding through carbonyl O atoms and terminal N atoms of the hydrazine group. This is almost the same coordination mode as observed in the carbohydrazide complexes.[12,13] The six coordinating atoms (3N, 3O) form a considerable distorted [ZnN$_3$O$_3$] octahedron with the O(1) and N(5) atoms at the apical positions, which is a normal coordination geometry of zinc(II) coordination complex.[14] The coordination bonds vary with donor type and position with the Zn-O(5) 2.109(2) Å, Zn-O(1) 2.131(2) Å, Zn-O(3) 2.132(2) Å, Zn-N(1) 2.141(3) Å, Zn-N(5) 2.146(3) Å and Zn-N(3) 2.150(3) Å, so distortion from ideal octahedral geometry is evident. Although there are no closely related octahedral zinc(II) compounds, the Zn-N bond distances are similar to the corresponding values observed in the bis(tripod) zinc(II) complex.[15] Whereas, the Zn-O bond distances are a little longer than the typical value in octahedral complexes (2.098 Å).[16] The longer Zn-O bond distances may be attributed to the bidentate coordination of the MCZ ligand and the double bond character of carbonyl group. More significant distortion from octahedral symmetry is observed in the coordination bond angles with the chelating MCZ ligand, O(1)-Zn-N(5) of 167.43(10)°, N(1)-Zn-O(3) of 171.45(10)° and O(5)-Zn-N(3) of 166.49(10)°, obviously deviating from the ideal angle of 180°.

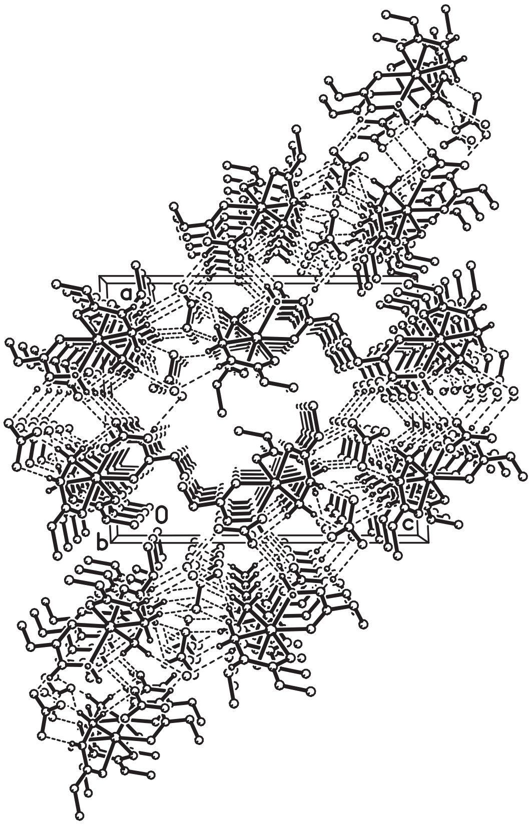

Figure 2. Packing arrangement of [Zn(MCZ)$_3$](NO$_3$)$_2$·H$_2$O.

Table 1. Crystal data and structure refinement parameters for [Zn(MCZ)$_3$](NO$_3$)$_2$·H$_2$O

Empirical formula	$C_6H_{20}N_8O_{13}Zn$
Formula weight/(g mol^{-1})	477.67
Color	colorless
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	13.609(2)
b/Å	8.270(1)
c/Å	16.187(3)
β/°	92.48(1)
V/Å^3	1820.2(4)
Z	4
D_c/(g cm^{-3})	1.743
μ (Mo K±)/mm^{-1}	1.433
F (000)	984
Crystal size/mm	0.52×0.42×0.34
θ/°	1.91-25.50
Measured reflections	3922
Independent reflections (R_{int})	3369 [R_{int}=0.0180]
Max & min transmission	0.9823, 0.8197
Final R indices ($I>2\sigma(I)$)	R_1=0.0360; wR_2=0.1014
R indices (all data)	R_1=0.0534; wR_2=0.1067

Table 2. Selected bond distances and angles for $[Zn(MCZ)_3](NO_3)_2{\cdot}H_2O$

Bond distances (Å)			
Zn-O(5)	2.109(2)	O(1)-C(1)	1.227(4)
Zn-O(1)	2.131(2)	O(2)-C(1)	1.314(4)
Zn-O(3)	2.132(2)	O(2)-C(2)	1.451(4)
Zn-N(1)	2.141(3)	N(1)-N(2)	1.402(4)
Zn-N(5)	2.146(3)	N(2)-C(1)	1.337(4)
Zn-N(3)	2.150(3)		
Bond angles (°)			
O(5)-Zn-O(1)	89.57(8)	O(5)-Zn-N(3)	166.49(10)
O(5)-Zn-O(3)	89.32(8)	O(1)-Zn-N(3)	89.80(11)
O(1)-Zn-O(3)	94.68(8)	O(3)-Zn-N(3)	77.28(10)
O(5)-Zn-N(1)	95.49(10)	N(1)-Zn-N(3)	97.60(11)
O(1)-Zn-N(1)	78.33(10)	N(5)-Zn-N(3)	102.76(12)
O(3)-Zn-N(1)	171.45(10)	N(2)-N(1)-Zn	107.41(18)
O(5)-Zn-N(5)	78.36(10)	C(1)-N(2)-N(1)	118.8(3)
O(1)-Zn-N(5)	167.43(10)	O(1)-C(1)-N(2)	123.5(3)
O(3)-Zn-N(5)	88.77(10)	C(1)-O(2)-C(2)	117.3(3)
N(1)-Zn-N(5)	99.11(11)	C(1)-O(1)-Zn	111.7(2)

In the asymmetric unit, three five-membered chelating rings, including a zinc(II) cation, are formed (see Figure 1), and all the non-hydrogen atoms of each ring are coplanar with the deviation less than 0.0276 Å. The dihedral angles between the rings are 93.7°, 91.3° and 97.8°, leading to minimum steric hindrance. The dihedral angle of the methoxy group outside each chelating plane is less than 10°. The stability of the five-membered chelating rings and minimum steric hindrance contribute to the high thermal stability of the complex, as verified by the DSC study described below. The possibility that there is delocalisation within the MCZ ligand was ruled out by the double bond character of the carbonyl groups of C(1)-O(1), C(3)-O(3) and C(5)-O(5), 1.227(4) Å, 1.223(4) Å and 1.220(4) Å, only a little longer than the normal C=O bond distance of 1.203 Å.[17]

One lattice H_2O molecule and two NO_3^- anions are also located within the asymmetric unit. The coordination cations, NO_3^- anions and lattice H_2O molecules are linked together through electrostatic forces and intermolecular hydrogen bonds. The hydrogen bond distances and angles are summarized in Table 3. The lattice water oxygen atom, O(13), acts as an acceptor in hydrogen bonds to MCZ ligands through N1 and N4 with distances of 2.991(4) and 3.159(5) Å, and angles of 163.5 and 140.1°. Furthermore, all the O atoms of NO_3^- anions, except O(11), act as acceptors in hydrogen bonds with all the MCZ N atoms as donors with bond distances of 2.922(4)-3.131(5) Å, and angles of 158.6-170.2°. The overall result of the interactions is the formation of a complicated 3-D hydrogen bond network. These extensive hydrogen bonds also make an important contribution to the stability of the complex.

Table 3. Hydrogen bond distances (Å) and angles (°) for $[Zn(MCZ)_3](NO_3)_2{\cdot}H_2O$

D-H...A	D-H	H...A	D...A	D-H...A
N(1)-H(1NB)...O(10)	0.90	2.20	3.083(5)	166.7
N(1)-H(1NA)...O(13)	0.90	2.12	2.991(4)	163.5
N(2)-H(2N)...O(7)	0.86	2.12	2.967(4)	168.1
N(3)-H(3NA)...O(9)	0.90	2.16	3.049(5)	170.2
N(3)-H(3NB)...O(7)	0.90	2.17	3.026(4)	158.6
N(4)-H(4N)...O(13)	0.86	2.45	3.159(5)	140.1
N(5)-H(5NA)...O(10)	0.90	2.26	3.131(5)	163.4
N(5)-H(5NB)...O(12)	0.90	2.12	3.014(6)	170.1
N(6)-H(6N)...O(8)	0.86	2.09	2.922(4)	162.4

Thermal decomposition mechanism of $[Zn(MCZ)_3](NO_3)_2{\cdot}H_2O$

In order to investigate the thermal decomposition of $[Zn(MCZ)_3](NO_3)_2{\cdot}H_2O$, the DSC and TG experiments were carried out. The DSC and TG-DTG curves are shown in Figures 3 and 4, respectively. The infrared spectra of the solid residues at different temperatures were used to determine their compositions, see Figure 5. Under linear

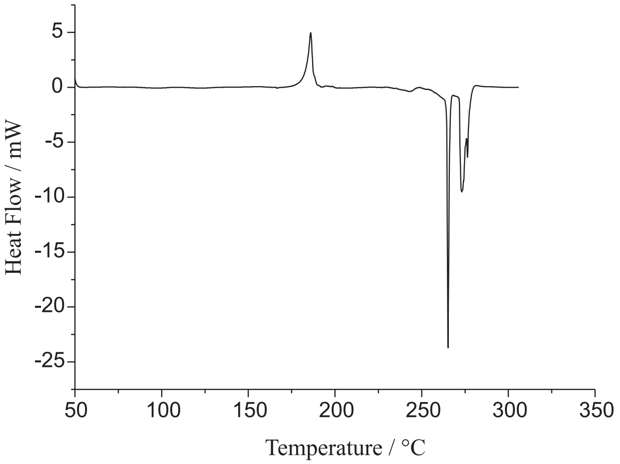

Figure 3. DSC curve of $[Zn(MCZ)_3](NO_3)_2{\cdot}H_2O$.

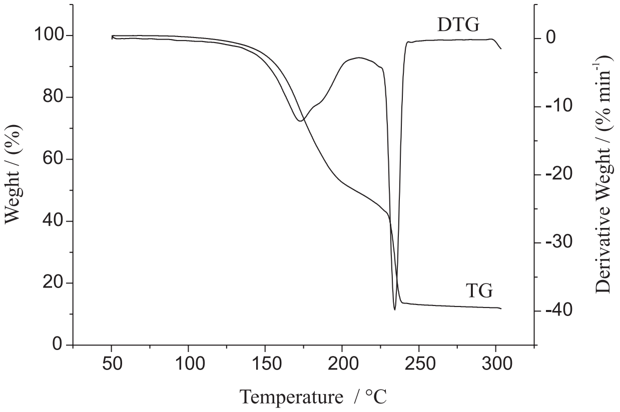

Figure 4. TG-DTG curves of $[Zn(MCZ)_3](NO_3)_2{\cdot}H_2O$.

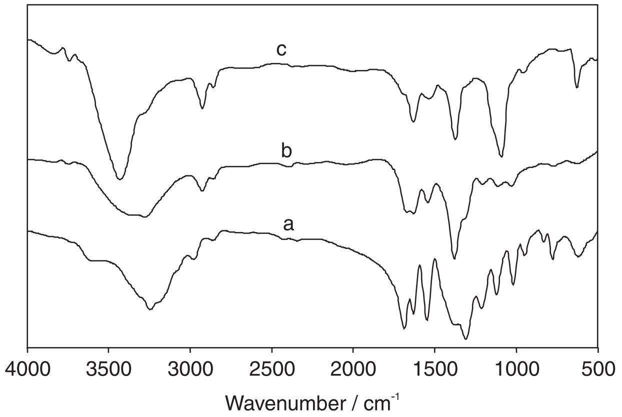

Figure 5. FT-IR spectra of: (a) $[Zn(MCZ)_3](NO_3)_2 \cdot H_2O$; (b) Residue after heating $[Zn(MCZ)_3](NO_3)_2 \cdot H_2O$ at 200 °C; (c) Residue after heating $[Zn(MCZ)_3](NO_3)_2 \cdot H_2O$ at 300 °C.

heating rate under N_2 atmosphere, the complex is stable up to 181.9 °C, when the first endothermic process starts, with a change of enthalpy of 67.75 kJ mol^{-1}, and peak temperature of 185.8 °C. Corresponding to this endothermic process, there is a weight loss of 46.09% of the initial weight in the temperature range of 153.9-199.4 °C on the TG curve (see Figure 4). The dehydration process and the cleavage of the chelating rings and NO_3^- are confirmed from the disappearance of the absorbance bands at 3323, 2979, 2860, 1547, 1309, 1213 and 1018 cm^{-1} in the FT-IR spectrum of the residue at 210 °C. New bands at 3277, 1671, 1628, 1541, 1379, 1112 and 1029 cm^{-1} prove the existence of [-CO-NH-] polymer and $Zn(RCO_2)_2$ in the solid residue.[11] The nature of the gases formed was not established, however, the studies showed clearly that dehydration and decomposition of the chelating rings occur in one weight loss process, which is a peculiar decomposition mechanism compared with other lattice water containing complexes.[10]

The further decomposition occurs in the range of 263.5-278.6 °C, and two intense and separate exothermic peaks can be seen on the DSC curve. The peak temperature of the first exothermic process is 265.3 °C with a change of enthalpy of 82.07 kJ mol^{-1}, and that for the second one is 273.4 °C with 101.31 kJ mol^{-1}. These two exothermic processes are accompanied by a weight loss of 37.32% on the TG curve. The [-CO-NH-] polymer and $Zn(RCO_2)_2$ decomposed completely in the process. The weight of the final residue is 16.59% of the initial weight, coinciding with the calculating value of ZnO, 16.75%. The bands at 1375, 1093 and 626 cm^{-1} in the FT-IR spectrum of the final residue at 300 °C also prove the final residue is ZnO.[18]

Based on the experimental and calculated results, the thermal decomposition mechanism of $[Zn(MCZ)_3](NO_3)_2 \cdot H_2O$ is proposed as follows:

$$[Zn(MCZ)_3](NO_3)_2 \cdot H_2O \rightarrow \text{[-CO-NH-] polymer} + Zn(RCO_2)_2 + \text{gas products} \rightarrow ZnO + \text{gas products}$$

Experimental

Materials

The zinc(II) nitrate of analytical grade was commercially available and used as received. Methyl carbazate (MCZ) was prepared according to literature methods.[1, 2]

Preparation of $[Zn(MCZ)_3](NO_3)_2 \cdot H_2O$

$Zn(NO_3)_2 \cdot 6H_2O$ (0.02 mol) in distilled water (15 mL) was added dropwise to the stirred aqueous solution of MCZ (0.08 mol) in distilled water (30 mL) at 70 °C within 20 minutes. Stirring was continued for more 10 minutes at 70 ^{0}C, and the resulting bright colorless solution was cooled to room temperature naturally. On slow evaporation at room temperature, colorless crystals of $[Zn(MCZ)_3](NO_3)_2 \cdot H_2O$ (9.6 g, 72%) were obtained after about two weeks; Element analysis Found: C, 14.98; N, 23.51; H, 4.18. Calc. for $C_6H_{20}N_8O_{13}Zn$: C, 15.09; N 23.46; H 4.22%; IR ν_{max}/cm^{-1}: 3323, 3245, 3194, 2979, 2861, 1686, 1630, 1547, 1375, 1309, 1213, 1120, 1018, 830, 619 (film).

Physical techniques

C, H, N were determined using a Flash EA 1112 full-automatic microanalyser. Infrared spectra were recorded on a Bruker Equinox 55 infrared spectrometer as KBr microdiscs in the range of 4000-500 cm^{-1} with the resolution of 4 cm^{-1}. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) were carried out on Pyris-1 differential scanning calorimeter and thermogravimeter, respectively, using dry nitrogen as atmosphere with flowing speed of 20 mL min^{-1}. The solid sample was sealed in aluminum pans for DSC and held in platinum pans for TG with heat rate of 10 °C min^{-1}. Indium and zinc were used for temperature and heat flow calibrations for the DSC instrument. For the TG instrument, Nickel and Iron were used for temperature calibration, and a 100 mg poise was used for weight calibration.

X-ray data collection and structure refinement

X-ray diffraction data were collected with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on a Siemens P4 full automatic four-circle diffractometer using ω scans at 295(2) K. Details of data collection, refinement and crystal data are summarized in Table 1. Lorentz-polarisation and empirical absorption corrections were applied to the data of both crystal data and structure refinement parameters. The structure was solved by the direct methods routine of SHELXS-97 in the space group $P2_1/n$, and subsequent difference-Fourier map revealed the positions of the remaining non-hydrogen atoms.[19] All hydrogen atoms were located at their geometrical idealized positions and their positions were refined with bond distances restraints. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes. All non-hydrogen atoms were refined anisotropically using a full-matrix least-squares procedure on F^2 using SHELXL 97.[20] Final R_1 and wR_2 are 0.0360 and 0.1014 with goodness-of-fit on F^2 of 1.058. The maximum and minimum residual peaks in the final difference-Fourier map are 0.492 and –0.441 e·Å^{-3}. The selected bond distances and angles are listed in Table 2.

Acknowledgement

The authors acknowledge Beijing Institute of Technology for the foundamental research financial support. The No. is BIT-UBF-200302B01.

Supplementary Information

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC nº 225007. Copies of the data can be obtained, free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

References

1. Li, G. X.; *Chin. J. Fine Chem.* **2002**, *19,* 336.
2. Dong, G. J.; Wang, Z. P.; Zhang, M. L.; *Chin. J. Applied Sci. Tech.* **2002**, *29*, 54.
3. Pan, H. L.; Tian, H. S.; Song, X. J.; *Chin. J. Synth. Chem.* **1999**, *7*, 138.
4. Shi, Z. D.; Guan, Q.; *J. Chin. Three Gorges Univ. (Natural Sci.)* **2002**, *24*, 191.
5. Zhang, G. Y.; Tian, H. S.; Wang, L.; *Chin. J. Chem. World* **1995**, *6***,** 283.
6. Jiang, Q.; *Chin. J. Petroleum Chem.* **2000**, *29*, 144.
7. Ivanov, M. G.; Kaiinichenko, I. I.; Savitskiia, A. M.; *Russ. J. Coord. Chem.* **1985**, *11*, 45.
8. Ivanov, M. G.; Kaiinichenko, I. I.; *Russ. J. Inorg. Chem.* **1981**, *26*, 2134.
9. Ivanov, M. G.; Kaiinichenko, I. I.; *Russ. J. Inorg. Chem.* **1984**, *29*, 926.
10. Song, J. C.; Zhang, T. L.; Zhang, J. G.; Ma, G. X.; Li, Y. F.; Yu, K. B.; *Acta Chimica Sinica* **2003**, *61*, 1444.
11. Tang, H. T.; *Spectroscopic Identification of Organic Compounds*, Peking University Press: Beijing, 1994.
12. Lu, C. H.; Zhang, T. L.; Wei, Z. R.; Cai, R. J.; *Chin. J. Inorg. Chem.* **1999**, *15*, 377.
13. Zhang, J. G.; Zhang, T. L.; Wei, Z. R.; Yu, K. B.; *Chem. J. Chin. Univ.* **2001**, *22,* 895.
14. Kong, D.; Martell, A.E.; Reibenspies, J.; *Inorg. Chim. Acta* **2002**, *333*, 7.
15. Zvargulis, E. S.; Buys, I. E.; Hambley, T. W.; *Polyhedron* **1995**, *14*, 2267.
16. Marcus, R. A.; *Chem. Rev.* **1988**, *88,* 1492.
17. Xu, S. C.; *Organic Chemistry,* People Education Press: Beijing, 1982.
18. Nyquist, R. A.; Kagel, R. O.; *Infrared Spectra of Inorganic Compounds*, Academic Press: New York& Lodon, 1971.
19. Sheldrick, G. M.; *SHELXS 97*, *Acta Crystallogr.* **1990**, *46*, 467.
20. Sheldrick, G. M.; *SHELXL 97*; *Program for Crystal Structure Refinement from Diffraction Data*, University of Göttingen: Germany, 1997.

Received: April 21, 2004
Published on the web: May 25, 2005