Synthesis, Characterization and Antibacterial Activity of Co(II), Cu(II) and Zn(II) Complexes Derived from 4-Methylthiosemicarbazide and 5-Nitrosalicylaldehyde

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The reaction of cobalt(II), copper(II) and zinc(II) with NS donor ligand derived by condensing 5-nitrosalicylaldehyde with 4-methylthiosemicarbazide have been carried out. The structure of the NS donor ligand was determined by single-crystal X-ray diffraction analysis. The crystal belongs to monoclinic system, space group C2/c, with cell parameters: $a = 1.31165(5)$, $b = 0.71876(3)$, $c = 2.38370(7)$ nm, $\alpha = 90^\circ$, $\beta = 90.855^\circ(3)$, $\gamma = 90^\circ$, $V = 2.24701(14)$ nm³, $Z = 8$, $F_{(000)} = 1056$, $M_r = 254.27$, $D_c = 1.503$ g/cm³, $\mu(\text{MoK}\alpha) = 0.291$ mm⁻¹, $R_1 = 0.0462$, $wR_2 = 0.1202$. The analysis of the crystal structure indicates that the complex has a three-dimensional network structure, which is formed by hydrogen bonds and electrostatic interaction. The ligand and its metal complexes are determined by elemental analysis, infrared spectra, UV spectra and the antibacterial activity. It is concluded that the thionic sulphur and Schiff base nitrogen atom of ligand are bonded to the metal ion. The results of antibacterial activity show that all of the ligand and the complexes can restrain the activity of bacteria.

Key Words: Sulf-schiff base complexes, NS Donor ligand, Crystal structure, Antibacterial activity.

INTRODUCTION

Because of their biological activity, thiosemicarbazides and thiosemicarbazones, as well as their metal complexes have been the subject of many studies¹. Numerous metal complexes have been synthesized with S-alkylisothiosemicarbazide based ligands and one of the most extensively used ligands is salicylaldehyde S-alkylisothiosemicarbazone^{2,3}. This ligand can coordinate to the metal in the monoanionic or dianionic form. The coordination chemistry of thiosemicarbazones with transition metals⁴⁻⁷ has been more intensively investigated as compared to that of main group elements^{8,9}. Thiosemicarbazones are an important group of multidentate ligands with potential binding sites available for a wide variety of metal ions¹⁰⁻¹². The thiosemicarbazone ligand usually coordinates with the metal through the imine nitrogen and sulphur atom. The ligands feature more than two covalent sites, the number of which depends on the aldehyde and on the tautomeric equilibrium of the thiosemicarbazone. The most common way to coordinate is through the thiolate form¹³. Thiosemicarbazones, in their neutral or deprotonated form, behave as a ONS/NNS tridentate or tetradentate chelate towards metal ions essential for life¹³. Thiosemicarbazone derivatives have raised considerable interest in chemistry and biology due to their antibacterial^{14,15}, antimalarial¹⁵⁻¹⁷, antineoplastic^{18,19} antiviral^{20,21}, enzymatic

catalyzation and oxygen-carrier²²⁻²⁷ activities. On the other hand, 5-nitrosalicylaldehyde is being as intermediate for manufacturing pesticide, medicine, dye and spicery^{28,29}. Recently, the extensive research on the ligands and complexes of Schiff base show that the copper(II) zinc(II), cobalt(II) complexes which are derived from 5-nitrosalicylaldehyde not only could restrain diversiform cancer and bacteria but also enhance the effect because of the nitril group³⁰. In this paper, a new sulf-schiff base and three new complexes were synthesized. The structure of the sulf-schiff base was determined by single-crystal X-ray diffraction analysis. The results of antibacterial activity show that all of the ligand and the complexes can restrain the activity of bacteria.

EXPERIMENTAL

Elemental analysis was performed on a Germany VarioEL III CHNOS analyzer. IR spectra were measured with KBr pellets on an EQUINOX55 spectrometer. X-Ray intensity data were measured on a Bruker Smart-1000CCD diffractometer. All reagents were of A.R. grade.

Preparation of ligand: A solution of (0.167 g, 1 mmol) 5-nitrosalicylaldehyde in 10 mL of ethanol was dropped into a solution 4-methylthiosemicarbazide (0.133 g, 1 mmol) in 10 mL of ethanol under stirring at room temperature. After

mixing for 1 min, the yellow deposition was formed. The solution was stirring for a further 1 h and filter. The yellow deposition was washed by ethanol. 0.081 g, yield, 42.8 %. The crude product was recrystallized from THF. Pure yellow chip-like crystals suitable for X-ray diffraction were formed. m.p. 230-232 °C. Anal. calcd. (%) for $C_9H_{10}N_4O_3S$ C 42.55, H 3.96, N 22.02; found (%): C 43.18; H 3.672; N 22.40, IR (KBr, $\nu_{\max}$, cm^{-1}): 3380, 2996, 3130, 1621, 1565, 1516, 1484, 1339, 1258, 1180, 1098, 1042, 942, 843, 632, 550.

Preparation of complex 1: A solution of 0.170 g (1 mmol) copper(II) chloride in 5 mL of ethanol was mixed with a solution of ligand 0.254 g (1 mmol) in 10 mL of THF under stirring at room temperature. After mixing, a green deposition was formed. The solution was stirring for a further 1 h and filter. The green deposition was washed by ethanol. 0.190 g, yield: 58.5 %, m.p. > 300 °C. Anal. calcd. (%) for complex **1** ($C_{18}H_{20}N_8O_6S_2Cl_2Cu$): C 33.62, H 4.19; N 12.89; Found (%): C 33.18; H 3.872; N 12.40. IR (KBr, $\nu_{\max}$, cm^{-1}): 3420, 3128, 2924, 1608, 1549, 1470, 1360, 1330, 1246, 1194, 1131, 1099, 1034, 953, 823, 754, 731, 699, 654, 475.

Preparation of complex 2: A solution of 0.136 g (1 mmol) zinc(II) chloride in 5 mL of ethanol was mixed with a solution of ligand 0.254 g (1 mmol) in 10 mL of THF of under stirring at room temperature. After mixing, a yellow deposition was formed. The solution was stirring for a further 1 h and filter. The yellow deposition was washed by ethanol. 0.131 g, yield: 40.2 %, m.p. > 300 °C. Anal. calcd. (%) for complex **2** ($C_{18}H_{20}N_8O_6S_2Cl_2Zn$): C 33.52; H 4.17; N 12.86; Found (%): C 33.19; H 4.381; N 12.65. IR (KBr, $\nu_{\max}$, cm^{-1}): 3426, 2930, 3127, 1610, 1580, 1524, 1474, 1349, 1315, 1247, 1195, 1105, 946, 832, 752, 649.

Preparation of complex 3: A solution of 0.237 g (1 mmol) cobalt(II) chloride in 5 mL of ethanol was mixed with a solution of ligand 0.254 g (1 mmol) in 10 mL of THF of under stirring at room temperature. After mixing, a brown deposition was formed. The solution was stirring for a further 1 h and filter. The brown deposition was washed by ethanol. 0.194 g, yield: 60.5 %, m.p. > 300 °C. Anal. calcd. (%) for complex **3** ($C_{18}H_{22}N_8O_7S_2Cl_2Co$): C 32.93; H 4.24; N 13.05; Found (%): C 32.86; H 4.128; N 12.86. IR (KBr, $\nu_{\max}$, cm^{-1}): 3422, 3124, 2928, 1602, 1550, 1467, 1357, 1321, 1252, 1209, 1148, 1103, 956, 832, 753, 739, 654.

RESULTS AND DISCUSSION

Ligand crystal structure: A single crystal with dimensions 0.39 mm $\times$ 0.23 mm $\times$ 0.11 mm was selected for data collection, using a Bruker Smart-1000CCD diffractometer with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.071073$ nm). Data were collected by ω -2 θ scan technique. The total reflections of 13094 were collected, of which unique 4282 reflections could be observed and used in the structure analysis. The structure was solved by direct methods. The positions of all remaining non-H atoms were obtained from successive Fourier syntheses. The positions of all non-H atoms were

refined anisotropically with full-matrix least-squares on F^2 . In the final difference map, the residual densities are 288 and -288 e/nm^3 , respectively. The crystallographic data and analysis parameters are shown in Table-1. The crystal belongs to monoclinic system, space group $C2/c$, with cell parameters: $a = 1.31165(5)$, $b = 0.71876(3)$, $c = 2.38370(7)$ nm, $\alpha = 90^\circ$, $\beta = 90.855^\circ(3)$, $\gamma = 90^\circ$, $V = 2.24701(14)$ nm^3 , $Z = 8$, $F_{(000)} = 1056$, $M_r = 254.27$, $D_c = 1.503$ g/cm^3 , $\mu(\text{MoK}\alpha) = 0.291$ mm^{-1} , $R_1 = 0.0462$, $wR_2 = 0.1202$.

TABLE-1
CRYSTAL DATA AND STRUCTURE
ANALYSIS PARAMETERS OF COMPOUND

Empirical formula	$C_9H_{10}N_4O_3S$
Crystal size (mm^3)	$0.39 \times 0.23 \times 0.11$
Temperature (K)	273(2)
Wavelength (nm)	0.071073
Formula weight	254.27
Crystal system	Monoclinic
Space group	$C2/c$
a (nm)	1.31165(5)
b (nm)	0.71876(6)
c (nm)	2.38370(3)
β ($^\circ$)	90.855(3)
V (nm^3)	2.24701(14)
Z	8
D_c (g cm^{-3})	1.503
$F_{(000)}$	1056
h (nm)	$-20 \leq h \leq 20$
k (nm)	$-10 \leq k \leq 8$
l (nm)	$-32 \leq l \leq 37$
Scan mode	ω -2 θ
θ range for data collection ($^\circ$)	3.23-34.25
Scan speed (min)	16 $^\circ$
Reflection collected	13094
Reflections unique	4282 ($R_{\text{int}} = 0.0365$)
Refinement method	Full-matrix least-squares on F^2
$R[I > 2.00\sigma(I)]$	0.0462
R indices(all data)	0.1202
Largest diff. Peak and hole (e nm^{-3})	288 and -288

The selected bond lengths and angles are listed in Table-2. All the data in brackets are standard deviation. Figs. 1 and 3 are the crystal structure and packing diagram of the compound, respectively. The bond lengths of the $\text{C}=\text{N}$ double bond is $\text{N}(3)-\text{C}(3)$ 0.1281(2) nm. However, the length of the typical double bond is between the 0.1279(5)-0.1293(5) nm. It suggests that the double bond exists in the compound. That is to say, there is the new characteristic Schiff base bond in the compound. There are two types of hydrogen bonds (Fig. 2): the intramolecular hydrogen bonds $\text{N}(3)-\text{H}(3)-\text{O}(3)$ composed of $\text{O}(3)$ from hydroxyl of hydroxybenzene and $\text{N}(3)$ from imine, the bond lengths data: $\text{N}(3)---\text{H}(3)-\text{O}(3)$ 0.2731 nm, $\text{N}(1)---\text{H}(1)-\text{O}(1)$ 0.2305 nm, $\text{H}(1)-\text{O}(1)$ 0.0620 nm; the bond angle data: $\text{N}(1)-\text{H}(1)-\text{O}(1)$ 142.40° and the intermolecular hydrogen bonds $\text{N}(2)-\text{H}(2) \dots \text{S}(1)$ consisting of $\text{N}(2)$ from imide and $\text{S}(1)$ from another molecular: the bond lengths data: $\text{N}(2)-\text{H}(2) \dots \text{S}(1)$ 0.3338 nm, $\text{H}(2) \dots \text{S}(1)$ 0.2494, $\text{N}(2)-\text{H}(2)$ 0.0860, the bond angle data: $\text{N}(2)-\text{H}(2) \dots \text{S}(1)$ 166.96° . The hydrogen bond lengths and bond angles (Table-3) are in the ranges described by Jeffrey³¹. In the theory of Jeffrey: The bond length data is between 0.25-0.32 nm and the bond angles relation is $\text{H}-\text{X} <$

TABLE-2

SELECTED BOND LENGTHS (nm) AND BOND ANGLES (°)

S(1)-C(2)	1.6895(15)	N(1)-C(2)	1.312(2)
N(1)-C(1)	1.459(2)	N(1)-H(1)	0.8600
N(2)-C(2)	1.350(2)	N(2)-N(3)	1.3774(17)
N(2)-H(2)	0.8600	N(3)-C(3)	1.281(2)
N(4)-O(2)	1.217(2)	N(4)-O(1)	1.2217(18)
N(4)-C(8)	1.460(2)	O(3)-C(5)	1.3451(19)
O(3)-H(3)	0.8200	C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600	C(1)-H(1C)	0.9600
C(3)-C(4)	1.4556(19)	C(3)-H(3A)	0.9300
C(4)-C(9)	1.389(2)	C(4)-C(5)	1.415(2)
C(5)-C(6)	1.3935(19)	C(6)-C(7)	1.374(2)
C(6)-H(6)	0.9300	C(7)-C(8)	1.386(2)
C(7)-H(7)	0.9300	C(8)-C(9)	1.379(2)
C(9)-H(9)	0.9300	—	—
C(2)-N(1)-C(1)	125.06(15)	C(2)-N(1)-H(1)	117.5
C(1)-N(1)-H(1)	117.5	C(2)-N(2)-N(3)	121.30(13)
C(2)-N(2)-H(2)	119.3	N(3)-N(2)-H(2)	119.3
C(3)-N(3)-N(2)	115.35(13)	O(2)-N(4)-O(1)	122.91(16)
O(2)-N(4)-C(8)	118.90(13)	O(1)-N(4)-C(8)	118.19(15)
C(5)-O(3)-H(3)	109.5	N(1)-C(1)-H(1A)	109.5
N(1)-C(1)-H(1B)	109.5	H(1A)-C(1)-H(1B)	109.5
N(1)-C(1)-H(1C)	109.5	H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5	N(1)-C(2)-N(2)	117.50(13)
N(1)-C(2)-S(1)	123.93(12)	N(2)-C(2)-S(1)	118.56(12)
N(3)-C(3)-C(4)	121.97(14)	N(3)-C(3)-H(3A)	119.0
C(4)-C(3)-H(3A)	119.0	C(9)-C(4)-C(5)	118.83(13)
C(9)-C(4)-C(3)	118.08(14)	C(5)-C(4)-C(3)	123.08(14)
O(3)-C(5)-C(6)	116.82(14)	O(3)-C(5)-C(4)	123.19(13)
C(6)-C(5)-C(4)	119.99(14)	C(7)-C(6)-C(5)	120.64(15)
C(7)-C(6)-H(6)	119.7	C(5)-C(6)-H(6)	119.7
C(6)-C(7)-C(8)	118.82(13)	C(6)-C(7)-H(7)	120.6
C(8)-C(7)-H(7)	120.6	C(9)-C(8)-C(7)	122.05(15)
C(9)-C(8)-N(4)	118.73(15)	C(7)-C(8)-N(4)	119.20(13)
C(8)-C(9)-C(4)	119.60(15)	C(8)-C(9)-H(9)	120.2
C(4)-C(9)-H(9)	120.2	—	—

TABLE-3

HYDROGEN BONDS FOR (nm AND °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3)...N(2)	0.0620	0.2305	0.2731	142.40
N(2)-H(2)...S(1)	0.0860	0.2494	0.3338	166.96

Fig. 1. Crystal structure of ligand L

A---H for the moderate hydrogen bond A---H-X. And that all of the bonds angle bigger than 130° , electrostatic interaction is the dominant effect. The bond length data is $A\cdots X > 0.32$ nm and the bond angles relation is $H-X < A\cdots H$ for the weak hydrogen bond A---H-X. And that all of the bonds angle bigger than 90° , electrostatic interaction and dispersive interaction is the dominant effect. In the compound, the inter-

Fig. 2. Hydrogen bonds of ligand L molecular in the crystal cell

Fig. 3. Space filling model of ligand L molecular in the crystal cell

molecular hydrogen bonds $N(3)\cdots H(3)-O(3)$ is a typical moderate hydrogen bond and the intramolecular hydrogen bond is a typical weak hydrogen bond. Thus, there are not only intramolecular hydrogen bonds which are moderate but also intermolecular hydrogen bonds which are weak in the compound. The intramolecular hydrogen bonds make the structure extend along the line and the intramolecular short interaction make the structure extend along space. Because of the hydrogen bonds and short interaction, the compound forms three-dimensional cavity structure. In the structure, there are two type cavities: square cavity and elliptical cavity.

IR photoemission spectroscopy and ultraviolet photoemission spectroscopy: The UV spectra of ligand and complexes were determined in DMF. Their absorption peaks are strong in ultraviolet. Ligand shows three absorbed peaks in DMF: 242, 263 and 340 nm. The complexes come forth the $d\text{-}\pi^*$ absorption peaks about the 390 nm in DMF. At the same time, the absorption peaks of ligand changed. So the ligand bonded to the metals.

The IR spectra of complex and ligand (L) were obtained as KBr discs in the rang of $4000\text{--}400\text{ cm}^{-1}$ (Table-4). The IR spectra of the ligand show $\nu(-NH + NH_2)$ ca. 3380 and 2996 cm^{-1} , which is blue-shifted $60\text{--}70\text{ cm}^{-1}$ compared with the corresponding value of the complex. The absorbed peak of $\nu(C=N)$ in ligand is 1621 cm^{-1} . In the complexes, the absorbed peaks of $\nu(C=N)$ red-shift $10\text{--}20\text{ cm}^{-1}$, which show that the bond formed between nitrogen atom of imine and the metal ion. The absorbed peaks of $\nu(N-C=S)$ in ligand is $1258, 1098, 1042\text{ cm}^{-1}$, which red-shift $10\text{--}50\text{ cm}^{-1}$ in the complexes. The shifting of peaks due to the formation of coordinate bond between the sulphur atom and metal atom in the complex.

TABLE-4
 IR PHOTOEMISSION SPECTROSCOPY OF THE LIGAND AND THE COMPLEXES (cm⁻¹)

	$\nu(-\text{NH}+\text{NH}_2)$	$\nu(\text{Ar}-\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{Benzene ring})$	$\nu(-\text{NO}_2)$	$\nu(-\text{CSNH})$	$\nu(\text{C}=\text{S})$
L ₂	3380, 2996	3130	1621	1565, 1484	1516, 1339	1258, 1042	1098
Cu(L ₂)Cl ₂	3420, 2924	3128	1608	1549, 1470	1360, 1330	1246, 1099	1194
Zn(L ₂)Cl ₂	3426, 2930	3127	1610	1524, 1474	1349, 1315	1247, 1105	1209
Co(L ₂)Cl ₂	3422, 2928	3124	1602	1550, 1467	1357, 1321	1252, 1103	1195

Based on the composition of these complexes, as well as the +2 oxidation state of metal in them, the thiosemicarbazones are believed to coordinate the metal center in the expected dianionic N,S,O-fashion. It has been observed that salicylaldehyde thiosemicarbazone, in spite of having the phenolic oxygen as a potential third donor site, coordinates as a bidentate N, S donor forming a rather unusual four-membered chelating. This mode of binding has also been displayed by some other thiosemicarbazones. Formation of such a chelate ring by salicylaldehyde thiosemicarbazone, leaving some potential donor sites unused, has been successfully utilized for the synthesis of interesting polynuclear complexes³².

Determination of antibacterial activity: "-" shows no antibacterial activity; "*" shows that the time of the antibacterial activity is 12 h, the antibacterial activity lost 24 h later. The character is white velum appear again on the quondam lucency cirque. The determination mass concentration is 0.01 %. The bacteria are *Staphylococcus* (Sa.), *Bacillus subtilis* and *Enterobacteriaceae* (*E. coli*).

Table-5 shows that the antibacterial activity of the complexes almost stronger than the ligand. The cobalt complex makes an exception. This results due to the increasing of the field of the electronic moving in the complex. The transformation is distinction the copper complex. On the other hand, all of the ligand and complexes have antibacterial activity which is selective. It is easier for the compound to restrain the propagating of the *Staphylococcus* than to pollenosis bacteria. The acting direction for the pollenosis bacteria show as flowing: [Cu(L₂)Cl₂] > L > CuSO₄ > [Zn(L₂)Cl₂] > [Co(L₂)Cl₂·H₂O]; the acting direction for the *Staphylococcus* show as flowing: [Cu(L₂)Cl₂] > [Zn(L₂)Cl₂] = L > CuSO₄ > [Co(L₂)Cl₂·H₂O]. The whole direction is the copper complex is the most strongest and the cobalt complex is the most weakest in all of the compound.

 TABLE-5
 ANTIBACTERIAL ACTIVITY OF LIGAND
 AND THE COMPLEXES (DIAMETER/mm)

No.	Compound	Bacteria		
		<i>Staphylococcus</i> (Sa.)	<i>Bacillus subtilis</i>	<i>Enterobacteriaceae</i> (<i>E. coli</i>)
1	CuSO ₄	9.5	8.0	6.5
2	L	11.5*	9.5*	10.5
3	[Cu(L ₂)Cl ₂]	12.5	10.5	8.5*

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REFERENCES

1. T.I. Malinovskii, Yu.A. Simonov, N.V. Gerbeleu, M.A. Yampolskaya, M.D. Revenko and S.G. Shova, *Problemi Kristallokhimii*, Nauka, Moskva, p. 39 (1985).
2. V. Divjakovic, V.M. Leovac, B. Ribar, G. Argay and A. Kalman, *Acta Crystallogr., B*, **38**, 1738 (1982).
3. A.B. Ilyukhin, V.S. Sergienko and V.L. Abramenko, *Kristallografiya*, **41**, 678 (1996).
4. M.J.M. Campbell, *Coord. Chem. Rev.*, **15**, 279 (1975).
5. S. Padhye and G.B. Kauffman, *Coord. Chem. Rev.*, **63**, 127 (1985).
6. D.X. West, S.B. Padhye and P.B. Sonawane, *Struct. Bonding*, **76**, 4 (1991).
7. D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, P.B. Sonawane, A.S. Kumbhar and R.G. Yerande, *Coord. Chem. Rev.*, **123**, 49 (1993).
8. C.E. Holloway and M. Melnik, *J. Organomet. Chem.*, **495**, 1 (1995).
9. C.E. Holloway and M. Melnik, *Main Group Met. Chem.*, **17**, 799 (1994).
10. J.S. Casas, M.S. Garcia-Tasende and J. Sordo, *Coord. Chem. Rev.*, **209**, 197 (2000).
11. A. Sreekanth, S. Sivakumar and M.R.P. Kurup, *J. Mol. Struct.*, **655**, 47 (2003).
12. R.P. John, A. Sreekanth, M.R.P. Kurup, A. Usman, I.A. Razak and H.K. Fun, *Spectrochim. Acta A*, **59**, 1349 (2003).
13. A.G. Quiroga and C.N. Ranninger, *Coord. Chem. Rev.*, **248**, 119 (2004).
14. D.X. West, S.B. Padhye and P.S. Sonawane, *Struct. Bonding*, **76**, 1 (1991).
15. A.S. Dobek, D.L. Klayman, E.T. Dickson, J.P. Scovill and C.N. Oster, *Arzneim.-Forsch./Drug Res.*, **33**, 1583 (1983).
16. O.E. Offiong and S. Martelli, *Farmaco*, **49**, 513 (1994).
17. D.L. Klayman, J.P. Scovill, J.F. Bartosevich and C.J. Mason, *J. Med. Chem.*, **22**, 1367 (1979).
18. P.M. Loiseau and D.X. Nguyen, *Trop. Med. Int. Health*, **1**, 379 (1996).
19. D.L. Klayman, J.P. Scovill, C.J. Mason, J.F. Bartosevich, J. Bruce and A. Lin, *Arzneim.-Forsch./Drug Res.*, **33**, 909 (1983).
20. A.G. Quiroga, J.M. Perez, I. Lopez-Solera, J.R. Masaguer, A. Luque, P. Roman, A. Edwards, C. Alonso and C. Navarro-Ranninger, *J. Med. Chem.*, **41**, 1399 (1998).
21. C. Shipman, S.H. Smith, J.C. Drach and D.L. Klayman, *Antiviral Res.*, **6**, 197 (1986).
22. D. Hadjipavlou-Litina, *Pharmazie*, **51**, 468 (1996).
23. Y.M. Jiang, S.H. Zhang and Q. Xu, *Acta Chim. Sin.*, **61**, 578 (2003).
24. J.C. Xian and C. Li, *Chin. J. Inorg. Chem.*, **12**, 12 (2000).
25. J.C. Xian, R.Y. Li and G.W. Cao, *Chin. J. Inorg. Chem.*, **16**, 833 (2000).
26. T.B. Wei and J.C. Chen, *Chem. J. Chin. Univ.*, **13**, 217 (1992).
27. X.C. Wang and T.Z. Yu, *Chem. J. Chin. Univ.*, **20**, 581 (1999).
28. J.H. Xu, Y.L. Li and D. Zhu, *Synth. Commun.*, **31**, 1647 (2002).
29. Z.J. Li, Y.S. Tan and Y.M. Ma, *Chemistry*, **10**, 41 (1991).
30. S. Goyal, *J. Indian Chem. Soc.*, **66**, 477 (1989).
31. G.A. Jeffrey, *An Introduction to Hydrogen Bonding*. Oxford University Press, Oxford (1997).
32. S. Halder, R.J. Butcher and S. Bhattacharya, *Polyhedron*, **26**, 2741 (2007).