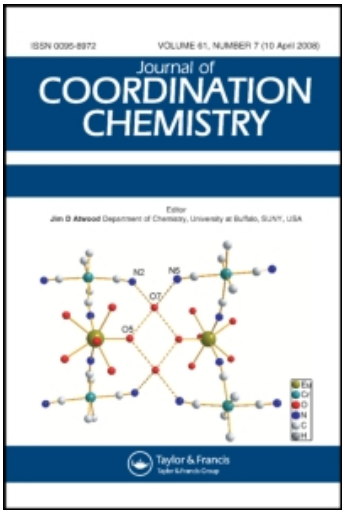

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Synthesis, crystal structure and electrochemical behavior of di-μ-{salicylidene-[1-(t-butyl)-5-methyl-1H-pyrazole]-formohydra-zino-κ⁴ O,N,O':O'}-nitratocopper(II)

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Synthesis, crystal structure and electrochemical behavior of di-μ-{salicylidene-[1-(*t*-butyl)-5-methyl-1H-pyrazole]-formohydra-zino-κ^4 O,N,O′:O′}-nitratocopper(II)

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The reaction of $Cu(NO_3)_2$ with salicylidene-[1-(*t*-butyl)-5-methyl-1H-pyrazole]-formohydrazine (Hsal-pfh, **1**) gives a binuclear Cu(II) complex $[Cu_2(sal\text{-}pfh)_2(NO_3)_2]$ (**2**). The structure of the ligand was characterized by IR, EA, ^{1}H NMR spectroscopy. The binuclear Cu complex was determined by X-ray crystallography and thermal analysis. The two Cu(II) ions are bridged by two O atoms and each copper ion is surrounded by an asymmetric sal-pfh chromophore and a NO_3^- group. The coordination around each copper can be best described as a distorted square-pyramidal geometry. The electrochemical experimental results indicate that **2** can bind to DNA with good stability.

Keywords: Binuclear copper complex; Crystal structure; Thermal analysis; Electrochemical behavior

1. Introduction

Azoles are a common component of a large number of natural products and pharmacologically active molecules [1, 2]. The azole ring functions as a ligand towards transition metal ions in a number of biologically important systems [3–5]. Copper(II) complexes are known to play a significant role either in naturally occurring biological systems or as pharmacological agents [6–9]. A large number of copper(II) complexes have been shown to exhibit superoxide dismutase activity [10, 11]. It was reported that metal coordination compounds of Schiff-base ligands could inhibit tumor and bacteria growth by interacting with DNA [12–15]. In the present work, a novel salicylidene-[1-(*t*-butyl)-5-methyl-1H-pyrazole]-formohydrazine compound and its binuclear Cu(II) complex were synthesized, and their structures were characterized by X-ray crystallography. In order to investigate the biological activities of this Schiff-base metal complex containing pyrazole group, the interaction between **2** and DNA has been studied by differential pulse voltammetry. The electrochemical results indicate that **2** binds strongly to DNA, bringing insight into the interaction of CuL with DNA and

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providing information for designing new and efficient drugs for disease diagnosis and as chemotherapeutic agents [16].

2. Experimental

2.1. *Materials and general methods*

IR spectra were taken on a Nicolet 510P FT-IR spectrometer (KBr). Elemental analyses were performed by Perkin-Elmer 240 elementar. An ^{1}H NMR spectrum was recorded by Bruker AC-300 with TMS as an internal standard. Voltammetric measurements were performed with a CHI832 electrochemical analyzer. The three-electrode system was composed of a glassy carbon electrode (GCE) as working electrode, a Ag/AgCl electrode as the reference electrode and a platinum electrode as auxiliary electrode. Salmon sperm DNA was purchased from Shanghai Huashun Biologic Engineering Company, its concentration was determined by the ultraviolet absorption at 260 nm ($\varepsilon = 6600\,\mathrm{L\,mol^{-1}\,cm^{-1}}$), and used without further purification. $[Cu_2(sal\text{-}pfh)_2(NO_3)_2]$ solution was prepared by dissolving **2** in DMF. 0.2 mol L^{-1} pH 2.3 Britton-Robinson was used as buffer solution. The other reagents were all analytical reagents prepared with doubly deionized water.

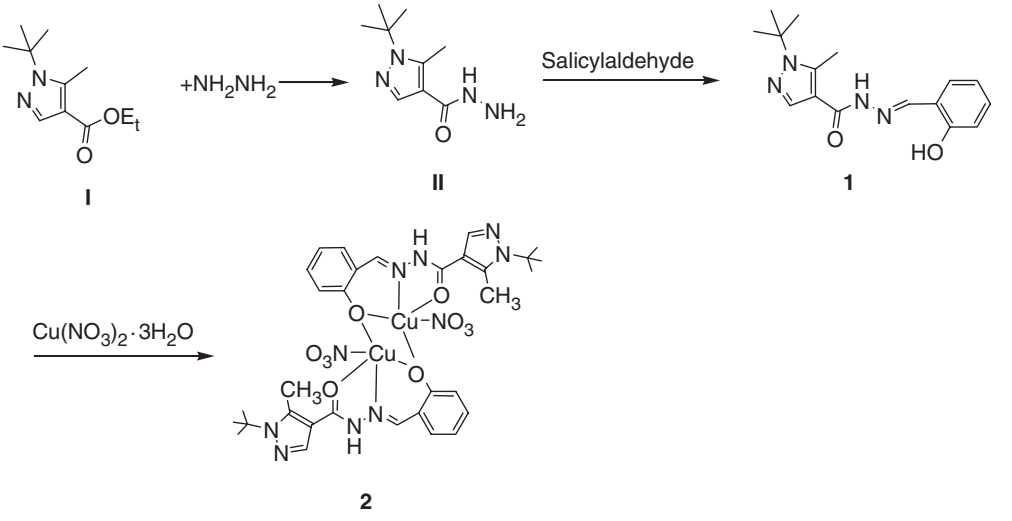
2.2. *Synthesis of $[Cu_2(sal\text{-}pfh)_2(NO_3)_2]$ (2)*

A solution containing 1 g ethyl 1-*t*-butyl-5-methyl-1H-pyrazole-4-carboxylate (**I**) and 1.5 g 85% hydrazine hydrate in 5 mL ethanol was stirred and refluxed for 12 h. The solvent was removed *in vacuo*. The separated solid was collected by filtration after cooling, and recrystallized from ethanol–petroleum ether. The product is 1-(*t*-butyl)-5-methyl-1H-pyrazole-4-formhydrazide (**II**). To a warm solution of 3 mmol of (**II**) and a catalytic amount of acetic acid in EtOH, 3 mmol salicylaldehyde was added dropwise and refluxed for 8 h with stirring. The desired product was obtained by filtration, drying and recrystallization from DMF. Yield: 73%. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the filtrate in air at room temperature.

IR: 3427 (m, N–H); 3217 (s, OH); 1640 (s, C=O); 1608 (s, C=N) cm^{-1}. Anal.: Calcd for $C_{16}H_{20}N_4O_2$ (%): C, 63.98; H, 6.71; N, 18.65; found: C, 63.64; H, 6.25; N, 18.64. ^{1}H NMR: *pz* = pyrazole ring, δ 1.61 (s, 9H, *t*-butyl), 2.73 (s, 3H, CH_3), 6.92 ~ 7.52 (m, 4H, Ar–H), 7.92 (s, 1H, *pz*-CH=C), 8.26 (s, 1H, CH=N), 8.52 (s, 1H, *pz*-CH=N), 11.32 (s, 1H, N–H), 11.52 (s, 1H, OH).

0.5 mmol of **1** and 0.5 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in ethanol, refluxed for 4 h. Dark brown products were obtained by filtration and the filtrate was left to stand undisturbed. Two weeks later, single crystals of **2** suitable for X-ray analysis appeared. IR: 3437 (m, N–H); 1640 (s, C=O); 1605 (s, C=N); 609, 468 (w, Cu–O, Cu–N) cm^{-1}. Anal.: Calcd for $C_{32}H_{40}Cu_2N_8O_4.2NO_3$ (%): C, 45.12; H, 4.73; N, 16.44; found: C, 45.34; H, 4.66; N, 16.64. The reaction equation for the synthesis of the title

compound is as follows:



Scheme 1. Synthesis of **2**.

2.3. *X-Ray crystallographic analysis*

A single crystal of **2** was mounted on a SMART 1000 CCD diffractometer. Reflection data were measured at 293(2) K using Mo-Kα radiation ($\lambda = 0.71073$ Å) with a graphite monochromator. The technique used was ω-scan with θ limit $1.35^\circ < \theta < 26.09^\circ$. An empirical absorption correction was carried out by using the SADABS [17] program. The structures were solved by direct methods and refined by least squares on F^2 using the SHELXTL [18] software package. All non-H atoms were anisotropically refined. Hydrogen atoms were located by difference synthesis and refined isotropically. Atomic scattering factors and anomalous dispersion corrections were taken from International tables for X-ray crystallography [19].

2.4. *Electrochemical studies of the interaction between* **2** *and DNA*

A certain volume of solution of 2 was added to 5 mL of 0.2 mol L^{-1} pH 7.0 BR buffer solution. The cyclic voltammetry and differential pulse voltammograms of the solutions were recorded on a CHI832 electrochemical analyzer with glassy carbon electrode as working electrode. Then 20 L of 4.68×10^{-2} mol L^{-1} DNA was added to the solution followed by recording the data. The potential scanning range is from -0.85 to -0.40 V, the pulse width 0.05 s and the quiet time 2 s.

3. Results and discussions

3.1. *X-ray crystal structure*

A summary of the crystal data, experimental details and structure refinement for **2** are listed in table 1. Selected bond lengths and angles are given in table 2. The molecular structures of **2** with atomic numbering scheme are shown in figure 1. Figure 2 depicts the molecular packing in the unit cell for **2**.

The structure of **2** consists of binuclear $[Cu_2(sal\text{-}pfh)_2(NO_3)_2]$ molecules with a crystallographically imposed inversion center at the midpoint of the line between the two copper atoms. The two Cu(II) ions are bridged by two O atoms and each copper ion is surrounded by an asymmetric sal-pfh chromophore and a NO_3^- group. The coordination around each copper atom can best be described as distorted square-pyramid. The basal plane is formed by O1, O1A, O2 and N1 atoms with O3 in the axial direction. The Cu atom is displaced out of the basal plane by 0.721(7) Å in the direction of the axial atom, which is normally observed for five-coordinate square-pyramidal geometry [20, 21]. The Cu–Cu distance is 3.03 Å, larger than the sum of the van der Waals radii of copper atoms ($r_{vdw}(Cu) = 1.40$ Å [18]), implying there are no formal Cu–Cu bonds; weak Cu···Cu interactions cannot be totally excluded. The bond lengths of the ligands in the molecule are between single and double bonds, showing high π-electron delocalization and a large conjugated system formed. The Cu1–O1, Cu1–O1A, Cu1–O2A, Cu1–O3 and Cu1–N1A distances are of 2.014(2), 1.928(2), 1.958(2), 2.217(3) and 1.933(3) Å, respectively.

Tridentate ligands in one molecule of **2** are planar except for the *t*-butyl group, while the two planes are parallel to each other. The two NO_3^- anions occupy two axial position above and below the two paralleled planes due to steric effects. The ketonic oxygen atoms are involved in intramolecular hydrogen bonds of the type C–H···O. There exists one intermolecular C4–H4···O5 interaction connecting the molecules into one-dimensional ribbons along the *b* axis. The packing is further stabilized by other intermolecular interactions.

3.2. *Thermal analysis*

Thermogravimetric (TG) and differential thermogravimetric analysis (DTA) for complex **2** are presented in figure 3, showing no decomposition below 220°C. Above 220°C, the thermal decomposition includes two transitions corresponding to exothermal processes— that is, a weight loss corresponding to *tert*-butyl group at 249.7°C, immediately followed by another weight loss corresponding to the 5-methyl-1H-pyrazol-4-yl-formyl moiety at 303.6°C.

3.3. *Electrochemical studies*

Electrochemical study on **2** and its interaction with DNA were performed at 25°C. CVs of **2** in the absence and presence of DNA were investigated. With the addition of DNA, both the cathodic and anodic peak currents (I_{pc} and I_{pa}) of **2** decreased and its formal potential ($E^{\circ\prime}$) shifted to positive potentials. The phenomena indicated a new association complex. According to research conducted by Bard [22], intercalative

Table 1. Crystal data and structure refinement parameters for complex **2**.

	2
Formula	$C_{16}H_{19}CuN_4O_2NO_3$
Formula weight	424.90
Temerature (K)	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	6.723 (4)
b	8.870 (5)
c	15.739 (9)
α	100.858(9)
β	100.942 (10)
γ	95.576(9)
V (Å^3)	896.4 (9)
Z	2
D_{calcd} (g cm^{-3})	1.574
μ (mm^{-1})	1.258
$F(000)$	438
θ ranges (°)	1.35–26.09
Number of reflections measured	4843
Number of reflections unique [$I>2\sigma(I)$]	2810
Max. and min. transmission	0.9284/0.6202
Goodness-of-fit on F^2	1.051
Final R indices [$I>2\sigma(I)$]	0.0456
wR	0.1168

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

Cu1–O1	2.014(3)	O4–N5	1.222(5)
Cu1–O3	2.217(3)	O5–N5	1.213(5)
Cu1–O1A	1.928(3)	N1–N2	1.379(4)
Cu1–O2A	1.958(3)	N1–C7	1.289(4)
Cu1–N1A	1.933(3)	N2–C8	1.348(5)
O1–C1	1.355(4)	N3–N4	1.363(4)
O2–C8	1.265(4)	N3–C10	1.311(6)
O3–N5	1.280(4)	N4–C11	1.352(4)
O1–Cu1–O3	88.97(10)	O2A–Cu1–N1A	81.20(12)
O1–Cu1–O1A	79.48(11)	N2–N1–C7	119.6(3)
O1–Cu1–O2A	103.34(11)	Cu1A–N1–N2	111.7(2)
O1–Cu1–N1A	154.11(11)	Cu1A–N1–C7	128.6(2)
O1A–Cu1–O3	98.09(11)	N1–N2–C8	114.9(3)
O2A–Cu1–O3	91.39(10)	N1–C7–C6	123.7(3)
O3–Cu1–N1A	116.62(11)	O2–C8–N2	118.3(3)
O1–Cu1–O2A	170.19(12)	N2–C8–C9	118.3(3)
O1A–Cu1–N1A	92.23(12)	O2–C8–C9	123.4(3)

binding of small molecules to DNA might make $E^{\circ\prime}$ shift to more positive value, while electrostatic binding might make $E^{\circ\prime}$ shift to more negative value.

The differential pulse voltammograms (DPV) before and after adding DNA were recorded to test whether **2** interacts with DNA. The DPVs of **2** at the glass carbon electrode in 0.2 mol L^{-1} pH 7.0 BR buffer solution are shown in figure 4. The curve 1 is the DPV of **2** solution in the absence of DNA, in which the observed cathodic peak potential (E_{pc}) of **2** is −0.740 V, the cathodic peak current (I_{pc}) is 2.515 μA. The larger

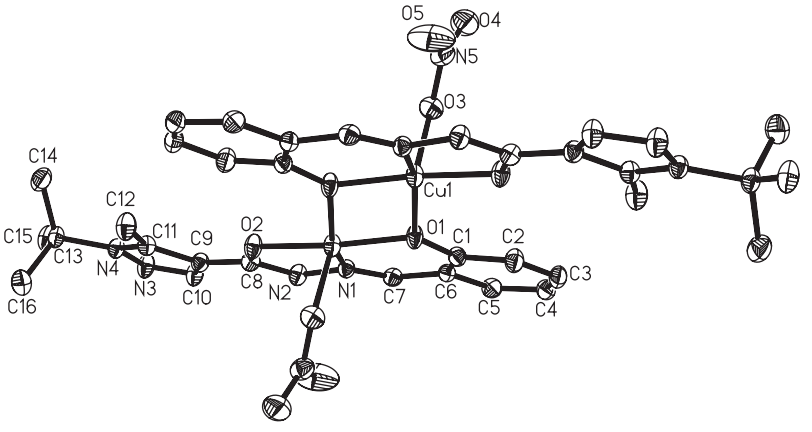


Figure 1. The structure of **2** with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are omitted for clarity.

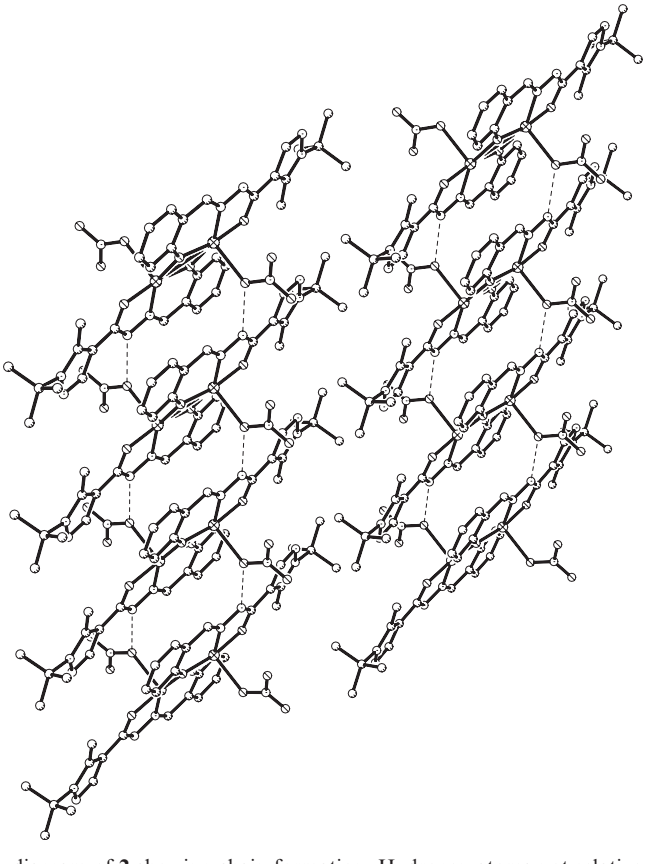


Figure 2. Packing diagram of **2** showing chain formation. Hydrogen atoms not relative to H-bondings are omitted for clarity.

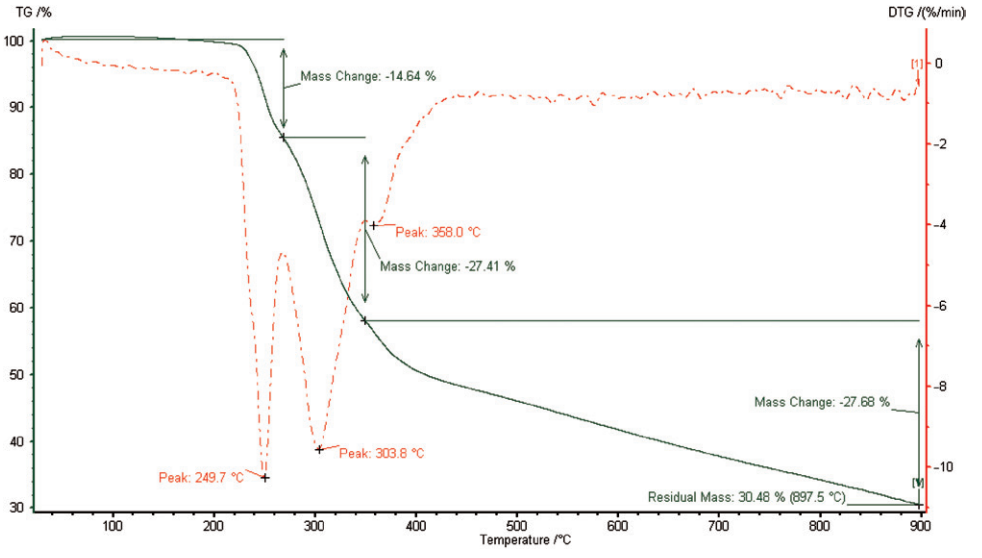


Figure 3. Thermal anaylsis curves of **2**.

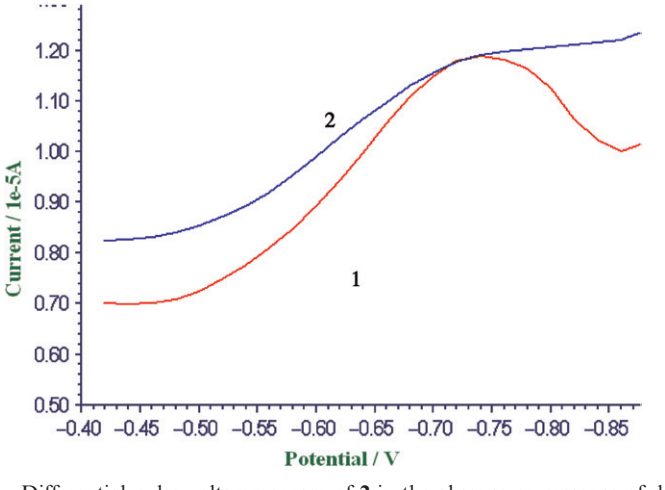


Figure 4. Differential pulse voltammogram of **2** in the absence or presence of dsDNA.

peak width at half height indicates the slower electron transition and non-reversibility. The curve 2 is the DPV of **2** in the presence of 1.0 g L^{-1} DNA showing that the cathodic peak disappeared with addition of DNA. No new oxidation-reduction peaks appear after adding DNA. So **2** interacting with DNA forms an electrochemically non-active complex, which results in a decrease of the equilibrium concentration as well as the peak current of **2**. The complete disappearance of the peak current signal implied high bonding stability between **2** and DNA.

Supplementary material

Crystallographic data for **2** reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 257711. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union road, Cambridge CB21EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

[1] Y. Zhang, R. Yang, F. Liu, K. Li. *Anal. Chem.*, **76**, 7336 (2004).
[2] J. Sisko, A.J. Kassick, M. Mellinger, J.J. Filan, A. Allen, M.A. Olsen. *J. Org. Chem.*, **65**, 1516 (2000).
[3] G.W. Yang, X.P. Xia, H. Xu, C.X. Zhao. *Chem. Res. Appl.*, **7**, 41 (1995).
[4] T. Bando, H. Iida, Z.F. Tao, A. Narita, N. Fukuda, T. Yamori, H. Sugiyama. *Chem. Bio.*, **10**, 751 (2003).
[5] W.Y. Wang, W.G. Zhao, Z.M. Li. *Chem. Res. Chinese U.*, **20**, 543 (2004).
[6] T. Miura, H. Mototani, H. Takeuchi, I.A. Hori. *Biochemistry*, **38**, 11560 (1999).
[7] H. Tamura, H. Imai, J. Kuwahara. *J. Am. Chem. Soc.*, **109**, 6870 (1987).
[8] R.N. Patel, N. Singh, K.K. Shukla, V.L.N. Gundla, U.K. Chauhan. *Spectrochim. Acta Part A*, **63**, 21 (2006).
[9] H.R. Ma, Y.Y. Wang, P. Liu, D.S. Li, Q.Z. Shi, G.H. Lee, S.M. Peng. *Chem. Res. Chinese U.*, **21**, 365 (2005).
[10] A.L. Abuhijleh. *J. Inorg. Biochem.*, **68**, 167 (1997).
[11] R.N. Patel, N. Singh, K.K. Shukla, U.K. Chauhan, J. Niclós-Gutiérrez, A. Castiñeiras. *Inorg. Chim. Acta*, **357**, 2469 (2004).
[12] H. Öner, M. Karatepe, F. Karatas, J. Öner, I. Yilmaz, A. Cukurovali. *Cell Biochem. Funct.*, **23**, 427 (2005).
[13] M. Nath, R. Yadav, M. Gielen, H. Dalil, D. de Vos, G. Eng. *Appl. Organomet. Chem.*, **11**, 727 (1997).
[14] S.B.B. Tushar, D. Sushmita, R. Eleonora, S. Michelangelo, C. Soumitra. *Appl. Organomet. Chem.*, **15**, 947 (2001).
[15] Y. Ye, J.M. Hu, Y.E. Zeng. *Chin. J. Anal. Chem.*, **28**, 798 (2000).
[16] S.Y. Niu, G.F. Jie, S.S. Zhang, Y. Li, F. Yang. *Chem. Res. Chinese U*, **21**, 149 (2005).
[17] SADABS. *Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany (1996).
[18] G.M. Sheldrick. *SHELXTL, v5 Reference Manual*, Siemens Analytical X-ray Sysytems, Inc., Madison, Wisconsin, USA (1996).
[19] A.J.C. Wilson. *International Table for X−ray Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht (1992); Tables 6.1.1.4 (pp. 500−502) and 4.2.6.8 (pp. 219−222) respectively.
[20] B.J. Hathaway. *Struct. Bonding*, **14**, 49 (1973) (Berlin).
[21] B.J. Hathaway, G. Wilkinso, R.D. Gillard, J.A. McCleverty (Eds), *Comprehensive Coordination Chemistry, the synthesis, Reactions, Properties and Applications of Coordination Compounds*, Vol. 5, pp. 533–774, Pergamon, Oxford (1987).
[22] M.T. Carter, A.J. Bard. *J. Am. Chem. Soc.*, **111**, 8901 (1989).