

奇异顺式双二茂铁三核镍配合物的合成、 电化学和晶体结构

刘永江* 刘泽华 吴德洪

0614.813

(南京大学配位化学研究所, 配位化学国家重点实验室, 南京 210093)

本文报道了希夫碱配体, N-(二茂铁基-1-甲基-甲叉)胍基硫代甲酸甲酯(简称为 HL)的双二茂铁三核镍配合物的合成和表征。单晶 X 射线结构分析表明镍原子的配位构型为奇异的顺式正方形, 两个二茂铁基团在镍原子的同一边。电化学测定表明正方形的镍配合物能有效地传递两个二铁基团间的电子转移。

关键词: 双二茂铁 电化学 晶体结构 电子转移

三核
镍配合物

SYNTHESIS, ELECTROCHEMISTRY AND CRYSTAL STRUCTURE OF A NOVEL CIS-CONFIGURATION BIFERROCENE TRINUCLEAR NICKEL (II) COMPLEX

Liu Yongjiang* Liu Zehua Wu Dehong

(Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing 210093)

The Synthesis and characterization of a novel biferoocene trinuclear nickel (II) complex with Schiff base ligand, S-methyl-N(ferrocenyl-1-methyl-methylidene) dithiocarbazate (hereafter abbreviate as HL), are described, X-ray diffraction studies established that the coordinated geometry of Ni(II) is close to square planar and in novel cis-configuration with two ferrocene moieties in the same side. Electrochemical measurements suggest that the square planar configuration of the Ni(II) can effectively transmit the redox effects of the ferrocene moieties.

Keywords: biferoocene electrochemistry crystal structure electron transfer

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* 通讯联系人。

第一作者: 刘永江, 男, 50 岁; 研究方向: 无机化合物的晶体结构解析。

0 Introduction

Bridged biferrocenes have been proven to be good candidates for mixed-valence compounds owing to their variability in structure and suitability for study with several physical techniques such as ^{57}Fe Mössbauer spectra, EPR, Near-IR and IR spectra^[1,2]. It has been postulated that the intervalence transfer may be accomplished in two different ways, through ligand and through space^[3]. The first takes place through a bridge or a single bond between the ligands of two ferrocene units. The second occurs via direct metal-metal interaction. It is often difficult to determine which mechanism is dominant in a particular case. By the proper choice of model system, one should be able to distinguish qualitatively as to which is more important mechanism for electron transfer in the ferrocene-ferricenium system.

It is the purpose of this paper to report the design, synthesis and structural characterization of metal bridged biferrocene trinuclear nickel (II) complex derived from the schiff-base ligand, HL, S-methyl-N-(ferrocenyl-1-methyl-methylidene)-dithiocarbamate, the relative long iron-iron distance could minimize the through space interaction, the extensive electron delocalization of the whole molecule might maximize the through ligand interaction, and the variety coordination configuration of different bridging metal moieties can also help us to determine the possible mechanism of the electron transfer.

1 Experimental

1.1 General comments

All chemicals are reagent grade and used without further purification. S-methyl-dithiocarbamate was synthesized according to the literature method^[4]. Electronic absorption spectra were obtained on a Shimadzu 3100 spectrophotometer in dichloromethane solution. Solid state electronic spectra were obtained by reflectance technique on a Shimadzu UV-240 spectrophotometer using MgO as reference material. IR spectra were recorded on a Nicolet FT-IR 170SX instrument (KBr discs) in the 400-400 cm^{-1} region, The far-IR spectra (500-100 cm^{-1}) were recorded in Njuol mills between polyethylene sheets. Elemental analyses of carbon, nitrogen, and hydrogen were performed on a Perkin-Elmer 240 analytical instrument.

1.2 Synthesis of the free liand $[\text{Cp}_2\text{Fe}]\text{C}(\text{CH}_3)\text{NNHCSSCH}_3$, HL

Five drops of acetic acid were added to a mixture of S-methyl-dithiocarbamate (1.22 g, 10 mmol) and acetylferrocene (2.28 g, 10 mmol) in refluxing ethanol (50 mL). The solution was further refluxed for 2 h and on cooling a red-brown solid was formed. The solid was collected by filtration and washed with ethanol and dried under vacuum. Yield, 2.80 g (85%). Anal. Found: C, 50.8; H, 4.8; N, 7.9. $\text{C}_{14}\text{H}_{16}\text{N}_2\text{S}_2\text{Fe}$ Calc. :C, 50.6; H, 4.8; N, 8.4%.

1.3 Synthesis of the metal complex, NiL_2

Ethanol solutions (25 mL) of the ligand (0.66 g, 2 mmol) and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.24 g, 1 mmol) were mixed. The brown crystalline solid formed after refluxing for 4 h was collected by filtra-

tion, washed with ethanol and dried under vacuum. Yield 0.50 g (69%). Anal. Found: C, 46.7; H, 4.5; N, 7.5. $C_{28}H_{30}N_4S_2Fe_2Ni$ Calc.: C, 46.6; H, 4.2; N, 7.8%.

1.4 Electrochemistry measurements

Differential-pulse voltammetry was done with an EG and GPAR model 273 instrument, which has a 50ms pulse width, with current sampled 40ms after the pulse was applied. A sweep rate of 2 mV/s was used in all pulse experiments with a drop time of 0.5s. Cyclic voltammetry were also performed using EG and GPAR model 273 potentiostats, in conjunction with a three-electrodes cell fits with a purged dinitrogen gas inlet and outlet, a platinum-wire working electrode. The potentials quoted in this work are relative a Ag/AgCl electrode at 25°C and a platinum auxiliary electrode. Current-potential curves were displayed on an IBM computer using model 270 electrochemical analysis software. Data were recorded on a Hewlett-Packard recorder. The voltammograms of the complexes were obtained in dichloromethane with $n\text{-Bu}_4\text{NClO}_4$ ($0.1 \text{ mol} \cdot \text{dm}^{-3}$) as the electrolyte and ferrocene ($2.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) as internal standard.

1.5 X-ray data collection and solution

The relevant crystal data and structural parameters are summarized in Table 1. The intensities were collected at 294K on a Rigaku RAXIS-IIC imaging-plate diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{\text{max}} = 55.0^\circ$), 60 oscillation frames and in the range of $0 \sim 180^\circ$, exposure 8 min per frame for the complex^[5,6].

The structure of title compound was solved by the direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Hydrogen atoms were placed in calculated positions (C-H 0.96 \AA), assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were include in the structure-factor calculations.

All computation were carried out on a PC-486 computer using the SHELXL-PC program^[7] package. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated^[8]. Table 2 give the atomic coordinates and equivalent isotropic displacement parameters.

Table 1 Crystal data and the refine parameters of the nickel complex

formula	$C_{28}H_{30}N_4S_2Fe_2Ni$	$\mu(\text{cm}^{-1})$	18.6
formula weight	721.21	$d(\text{calcd.}) (\text{g} \cdot \text{cm}^{-3})$	1.577
colour/habit	dark-brown prism	$F(000)$	2960
size(mm)	$0.34 \times 0.32 \times 0.25$	temp. (K)	294
crystal system	orthorhombic	$\lambda(\text{ \AA})$	0.71073
space group	$Pbca$	reflections collected	5668
$a(\text{ \AA})$	19.850(1)	reflections unique	5457 ($R_{\text{int}} = 12\%$)
$b(\text{ \AA})$	19.982(1)	reflections observed	2862 ($F_o > 4.0\sigma(F)$)
$c(\text{ \AA})$	15.314(1)	R	0.07
$V(\text{ \AA}^3)$	6074.2(6)	R_w	0.12 ($w^{-1} = \sigma^2(F)$)
Z	8	$(\Delta\rho)_{\text{max, min}} (\text{e} \cdot \text{ \AA}^{-3})$	0.31, -0.31

Table 2 Atomic Coordinates and Thermal Parameters

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> eq(B)
Ni(1)	0.0015(1)	0.1690(1)	0.4828(1)	5.9(1)
Fe(1)	0.1896(1)	0.3024(1)	0.6001(1)	6.2(1)
Fe(2)	0.0914(1)	0.1184(1)	0.1903(1)	6.4(1)
S(1)	-0.1009(1)	0.2023(1)	0.4690(1)	8.0(1)
S(2)	-0.1480(1)	0.3167(1)	0.3631(1)	9.9(1)
S(3)	-0.0241(1)	0.0927(1)	0.5767(1)	9.3(1)
S(4)	0.0704(1)	-0.0081(1)	0.6475(1)	10.8(1)
N(1)	-0.0220(1)	0.2876(2)	0.3779(3)	11.2(2)
N(2)	0.0279(2)	0.2520(2)	0.4414(3)	5.1(1)
N(3)	0.1055(1)	0.0732(2)	0.5299(2)	12.6(1)
N(4)	0.0833(2)	0.1142(2)	0.4580(3)	4.7(1)
C(1)	-0.0811(1)	0.2680(2)	0.3988(2)	6.7(1)
C(2)	0.0887(3)	0.2814(3)	0.4460(4)	6.3(2)
C(3)	0.0999(2)	0.3454(2)	0.3934(4)	6.1(2)
C(4)	0.1306(2)	0.2219(2)	0.5815(3)	4.9(2)
C(5)	0.1939(2)	0.2019(2)	0.6129(4)	6.2(2)
C(6)	0.2423(2)	0.2236(2)	0.5528(3)	6.5(2)
C(7)	0.2102(2)	0.2595(3)	0.4864(3)	6.5(2)
C(8)	0.1404(2)	0.2562(3)	0.5022(3)	6.1(2)
C(9)	0.2232(2)	0.3534(3)	0.7097(4)	12.1(3)
C(10)	0.2566(3)	0.3750(4)	0.6399(4)	20.0(5)
C(11)	0.2110(2)	0.4043(3)	0.5872(5)	13.3(3)
C(12)	0.1481(3)	0.3972(3)	0.6239(4)	12.6(3)
C(13)	0.1557(3)	0.3649(4)	0.6991(4)	14.5(4)
C(14)	-0.1100(2)	0.3825(2)	0.3046(3)	12.8(2)
C(15)	0.0563(2)	0.0571(2)	0.5786(2)	8.5(1)
C(16)	0.1223(2)	0.1176(3)	0.3916(3)	4.7(2)
C(17)	0.1894(2)	0.0803(3)	0.3918(4)	6.7(2)
C(18)	0.1452(2)	0.1878(2)	0.2577(3)	6.3(2)
C(19)	0.1070(2)	0.2181(3)	0.1848(4)	7.7(2)
C(20)	0.0348(2)	0.2024(3)	0.2043(4)	8.0(2)
C(21)	0.0330(2)	0.1615(2)	0.2826(3)	5.4(2)
C(22)	0.1015(2)	0.1480(3)	0.3166(3)	6.6(2)
C(23)	0.1504(2)	0.0364(3)	0.1584(4)	9.4(2)
C(24)	0.1361(3)	0.0718(3)	0.0859(4)	9.8(2)
C(25)	0.0686(3)	0.0699(3)	0.0755(4)	13.5(3)
C(26)	0.0433(3)	0.0346(3)	0.1409(3)	11.0(2)
C(27)	0.0932(3)	0.0145(3)	0.1954(4)	11.7(3)
C(28)	0.1550(2)	-0.0295(2)	0.6221(3)	13.4(2)

2 Results and discussion

2.1 Synthesis and characterization

The title complex can easily form by refluxing the mixture of the ligand HL and the metal salt in ethanol solution. The IR spectra of HL exhibit strong bands at ca 3164 and 3092 cm^{-1} , which can be

assignes as the ν (N-H). These bands disappear in the IR spectra of the metal complex which suggest that the proton on the α -nitrogen atom is lost upon complex formation with a metal ion. A strong band at 1060 cm^{-1} in the IR spectrum of HL is assigned to ν (C=S). The band is red shift ca 60 cm^{-1} in the spectra of the metal complex. This observation can be explained by the change in the nature of the C=S bond on coordination of the ligand through the sulfur atom, which is proven by crystal structure determination of the relative ligand, S-methyl-(1-ferrocenyl-methylene) dithiocarbazate and the metal complex containing dithiocarbazate as well as the relative free ligands^[4,9~11]. This tendency of HL to deprotonate may be attributed to the stabilization of the deprotonated form by conjugation of the -C=N-N=C- group^[12]. The far-IR spectra ($500\text{-}100\text{ cm}^{-1}$) of the complex display a medium to strong band in the region 365 cm^{-1} which can be assigned to the metal-nitrogen stretching vibrations^[13,14], and in most case, another band in the range 334 cm^{-1} , may be assigned to the metal-sulphur band^[15].

The visible spectra are consistent with the structural formula, the broad band at ca $450\text{-}470\text{ nm}$ is assigned to the MLCT band of ferrocene and the bridging metal moiety which coupled each other^[9~11]. Three bands corresponding to the transition ${}^1A_{1g} \leftarrow {}^1A_{2g}$, ${}^1A_{1g} \leftarrow {}^1B_{1g}$ and ${}^1A_{1g} \leftarrow {}^1E_g$ are expected in the electronic spectrum of a square-planar d^8 complex. However, in many instances, especially with sulphur ligands, the bands corresponding to the transitions ${}^1A_{1g} \leftarrow {}^1A_{2g}$, ${}^1A_{1g} \leftarrow {}^1B_{1g}$ and ${}^1A_{1g} \leftarrow {}^1E_g$ are submerged under very intense inter-ligand and charge transfer band, and only one band in the range $620\text{-}500\text{ nm}$ is observed. The shoulder is around 660 nm in the solid electronic reflectance therefor may be assigned to the ${}^1A_{1g} \leftarrow {}^1A_{2g}$ transition^[16].

2.2 Structure of the nickel (I) complex

Figure 1 shows and ORTEP drawing of the molecule with the atomic numbering scheme. The Ni(I) atom is coordinated in slight distorted square-planar configuration with two Ni-N bonds [$1.851(4)$ and $1.996(4)\text{ \AA}$] and Ni-S bonds [$2.149(1)$ and $2.158(1)\text{ \AA}$]. The dihedral angle between the two coordination plane [Ni(1)-S(1)-C(1)-N(1)-N(2), and Ni(1)-S(3)-C(15)-N(3)-N(4)] is 26.4° . The ligand, as expected, losses a proton from the tautomeric thiol form and act as a single negatively charge bidentate ligand coordinating to nickel ion via the mercapto sulphur and β -nitrogen atoms^[9~11], forming an delocalized coordination plane. The complex has a quite surprising cis-configuration [N(2)-Ni(1)-N(4), $101.3(2)^\circ$, S(1)-Ni(1)-S(3), $93.5(1)^\circ$, N(2)-Ni(1)-S(3), 158.2° , N(4)-Ni(1)-S(1), $157.1(1)^\circ$] with two ferrocene moieties on the same side. The structure is much rare, to our knowledge, this might be the first example for the negatively charge bidentate thiocarbazates coordinate in cis configuration^[17,18]. It is suggesting that, the cis positioning of the two ferrocene containing ligand might be stabilized by the interactions between the substituted cyclopentadienyl planes associated with difference iron atoms. The bond distances (Table 3) in the side chain are intermediate between formal single and double bonds, pointing to electron delocalization over the entire moiety. The Ni \cdots Fe distance is ca 4.93 \AA , the Fe \cdots Fe distance is ca 7.53 \AA , which is much larger than those found in most biferrocene compounds ($3.8\sim 5.1\text{ \AA}$) and much closer to the average encounter diameter between ferrocene and ferrocenium ion in solution (7.6 \AA)^[20].

Table 3 Selected Bond Distances (Å) and Angles(°)

Ni(1)-N(2)	1.851(4)	S(4)-C(15)	1.701(4)
Ni(1)-N(4)	1.996(4)	N(1)-C(1)	1.278(4)
Ni(1)-S(1)	2.149(1)	N(1)-N(2)	1.559(5)
Ni(1)-S(3)	2.158(1)	N(3)-C(15)	1.270(4)
S(1)-C(1)	1.741(4)	N(3)-N(4)	1.442(5)
S(2)-C(1)	1.735(3)	N(2)-C(2)	1.343(6)
S(3)-C(15)	1.747(4)	N(4)-C(16)	1.278(6)
N(2)-Ni(1)-N(4)	101.3(2)	N(2)-Ni(1)-S(3)	158.2(1)
N(2)-Ni(1)-S(1)	87.5(1)	N(4)-Ni(1)-S(3)	86.0(1)
N(4)-Ni(1)-S(1)	157.1(1)	S(1)-Ni(1)-S(3)	93.6(1)

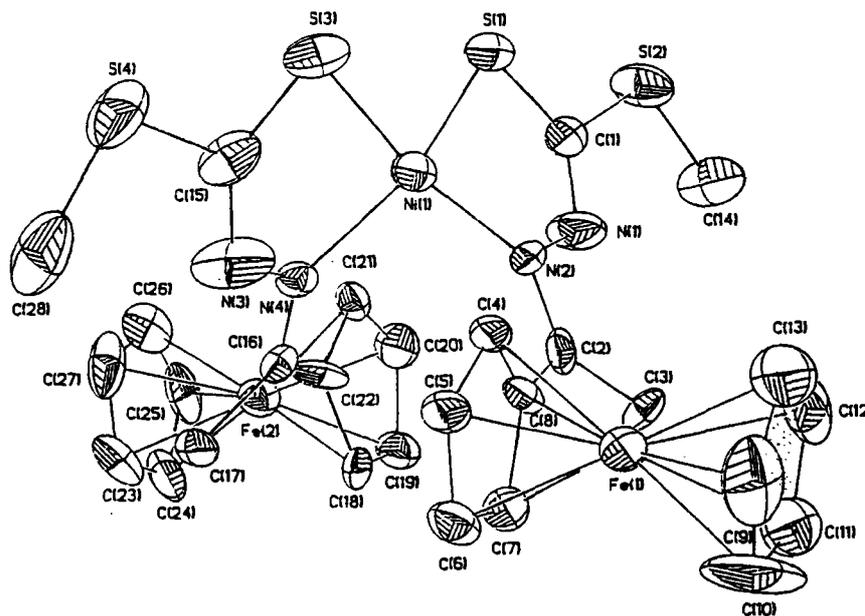
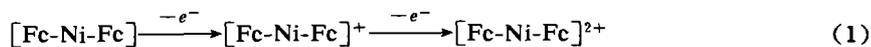


Figure 1 Molecular structure and atom numbering of the title complex.
Thermal ellipsoids are drawn at 30% probability level.

2.3 Electrochemistry studies

The internal standard, ferrocene, undergoes a reversible one-electron oxidation uncomplicated reaction as expected. ($E_{pa}=0.59$, $E_{pc}=0.65$ V vs Ag/AgCl electrode, scanning rate, $50 \text{ mV} \cdot \text{s}^{-1}$), The ligand HL ($2.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) undergoes a reversible one-electron oxidation uncomplicated reaction ($E_{pa}=0.77$ V, $E_{pc}=0.71$ V vs Ag/AgCl electrode, scanning rates, $50 \text{ mV} \cdot \text{s}^{-1}$). The metal-bridged-biferrocene complex like many homobinuclear species, show two sequential reversible one-electron oxidation E_1 and E_2 , separated by ΔE (0.13 V) (Figure 2) to yield the mono- and dications respectively and the equilibrium constants K_{con} (160) of equation (2).



can be calculated, by use of the Nernst equation from the ΔE , where Fc represents a ferrocenyl unit and M represents the metal moiety of bridging group.

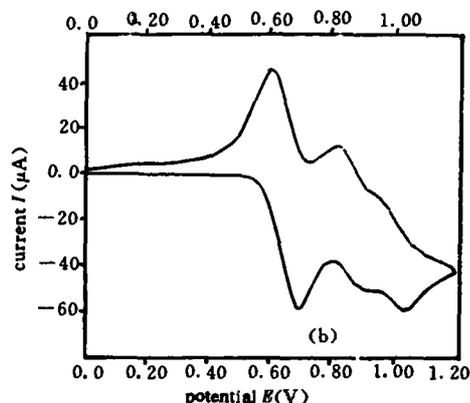


Figure 2 Cyclic voltammogram of the complex in CH_2Cl_2 containing $n\text{-Bu}_4\text{NClO}_4$ ($0.1 \text{ mol} \cdot \text{l}^{-1}$) and NiL_2 ($1.0 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$) at scanning rate of $50 \text{ mV} \cdot \text{s}^{-1}$ with ferrocene ($2.0 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$) as internal standard (vs AgCl/Ag).

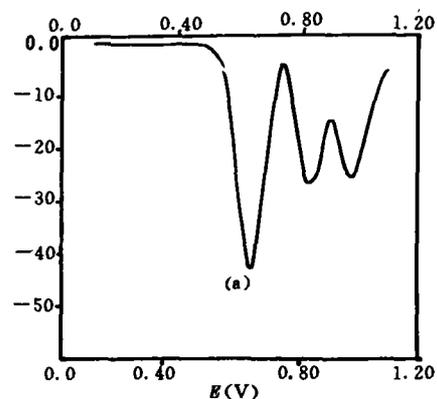


Figure 3 Current-potential curves for differential-pulse voltammetry for the complex ($1.0 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$) in CH_2Cl_2 containing $n\text{-Bu}_4\text{NClO}_4$ ($0.1 \text{ mol} \cdot \text{l}^{-1}$) and internal standard (ferrocene $2.0 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$) (vs AgCl/Ag).

As in the cyclic case, a simple sum of two n -electron responses can not be used to determine ΔE , except when the value is larger. It has been postulated that, when $\Delta E_1 > 160 \text{ mV}$, an error of $< 1 \text{ mV}$ will be introduced, if the peak separation is used to measure the value. The complexity of multistep cyclic voltammetry current-potential curves when $\Delta E_{1/2} < 250 \text{ mV}$ led us to evaluate application of pulse voltammetry to the problem. Figure 3. shows the current-potential curves for differential-pulse voltammetry. The peak at ca 0.62 V is simply assigned to redox reaction of ferrocene, the internal standard. The other two peaks might be assigned to the redox potential of the nickel (II) complex and it is easy to obtain ΔE as 0.13 for the complex. This value is accordance with the value measured in cyclic voltammogram.

It is postulated that the ΔE with K_{an} depends on a number of factors^[21-22]. (I) Major structure changes such as bond making and breaking, changes in coordination number, and severe changes in coordination geometry upon charge transfer can shift composition equilibrium. (II) If the metal ions are in close proximity, a through-space coulombic interaction may be important. (III) Electronic delocalization will enhance the stability of these mixed oxidation states species with resulting increases in ΔE .

The trinuclear complex was designed to help quantitatively define some of these effects. (I) Crystallographic data on ferrocene^[23] and its salts^[24] indicate that the oxidation state and charge of the iron atom have almost no effect on the interatomic distances. Therefore, little reorganizational energy is needed to make the mixed valence sites identical and as a result it would be expected that properly oriented ferrocene and ferrocenium molecules will undergo electron exchange quite readily. (II) Through space metal-metal coulombic contribution to the $\text{Fe(II)}/\text{Fe(III)}$ oxidation potential in Fc-M-Fc complexes are essential constant and could be canceled since the distances between iron atoms is quite close to, 7.6 \AA , the average encounter diameter between ferrocene and ferricenium ion in solu-

tion. In fact, these metal-bridged biferrocene designed is used to minimize the through space metal-metal interaction between the ferrocene moieties and then determine the possible mechanism the intervalence transfer. (Ⅱ) Crystal structure study shows that complex is almost planar, which might be suggests that the electrochemical measurement would then do a determination of electronic delocalization in the complex.

References

- [1] Hendrickson, D. N.; Oh, S. M.; Dong, T. Y.; Kambara, T.; Cohn, M. J.; Moore, M. F. *Comment. Inorg. Chem.*, **1985**, *4*, 329.
- [2] Webb, R. J.; Dong, T. Y.; Pierpont, C. G.; Boone, S. R.; Chadha R. K.; Hendrickson, D. N. *J. Am. Chem. Soc.*, **1991**, *113*, 4806.
- [3] Shu, P.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.*, **1976**, *41*, 1849.
- [4] Duan, C. Y.; Xia, X. B.; Zhu, L. G.; You, X. Z.; Yang, Y.; Wang, H. Q. *Chinese J. Chem.*, **1994**, *12*, 321.
- [5] Tanner, J.; Krause, K. *The Rigaku Journal*, **1994**, *11*, 4, *ibid.*, **1990**, *7*, 28.
- [6] Kraus, K. L.; Phillips, G. N. *J. Appl. Crystallogr.*, **1992**, *25*, 146.
- [7] Sheldrick, G. M. in *Computational Crystallography*, Sayre, D. Ed., Oxford University Press; New York, **1982**, pp 506-514.
- [8] *International Tables for X-ray Crystallography*, Kynoch Press; Birmingham (now distributed by Kluwer Academic Press, Dordrecht), **1974**, *4*, p55, 99, 149.
- [9] Tian, Y. P.; Duan, C. Y.; Lu, Z. L.; You, X. Z. *J. Coord. Chem.*, **1996**, *38*, 219.
- [10] Tian Y. P.; Duan, C. Y.; Lu, Z. L.; You, X. Z. *Polyhedron*, **1996**, *15*, 2263.
- [11] Tian, Y. P.; Duan, C. Y.; Lu, Z. L.; You, X. Z.; *Transition Met. Chem.*, **1996**, *21*, 254.
- [12] Gingras, B. A.; Sirianni, A. F. *Can. J. Chem.*, **1964**, *42*, 17.
- [13] Adams, D. M. *Metal-Ligand and Related Vibrations* (Arnold London **1967**).
- [14] Adams, D. M.; Correll, J. B. *J. Chem. Soc. (A)*, **1968**, 1299.
- [15] Tarafder, M. T. H.; Ali, M. A. *Can. J. Chem.*, **1978**, *56*, 2000.
- [16] Lathan, A. R.; Hascall, V. C.; Gray, H. B. *Inorg. Chem.*, **1965**, *4*, 783.
- [17] Podhyé, S.; Kauffman, G. B. *Coord. Chem. Revs.*, **1985**, *63*, 127.
- [18] (a) Ali, M. A.; Livingstone, S. E. *Coord. Chem. Revs.*, **1974**, *13*, 101.
(b) Campbell, M. J. M. *Coord. Chem. Revs.*, **1975**, *15*, 279.
- [19] Pauling, L. *The Nature of the Chemical Bond*, 3rd, ed Cornell University, Press; Ithaca, N. Y., **1960**, P260.
- [20] Stank, D. R. *Discuss, Faraday Soc.*, **1960**, *29*, 73.
- [21] Gagne, R. R.; Spiro, C. L.; Smith, T. I.; Hamann, C. A.; Thies, W. R.; Shiemke, A. K. *J. Am. Chem. Soc.*, **1981**, *103*, 4073.
- [22] Tom, G. M.; Creutz, C. Taube, H. *J. Am. Chem. Soc.*, **1974**, *96*, 7827.
- [23] Rosenblem *Chemistry of the Iron Group Metallocenes*, New York, **1965**.
- [24] Berstern, T.; Herbstein, F. H. *Acta Crystallogri, Sect B*, **1968**, *24*, 1546.