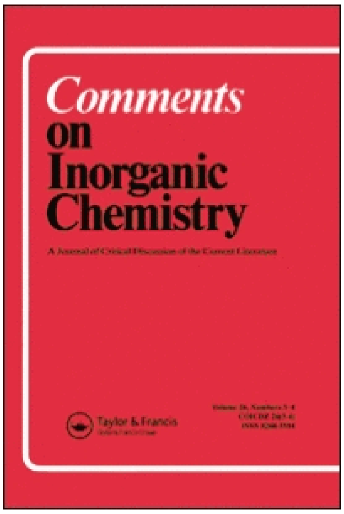

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Studies on the Mixed Trimeric Reaction of Schiff Bases and Structures of Related Metal Complexes

Xiu-Ren Bu[a]; Xiao-Zeng You[a]; Qing-Jin[a]
[a] Coordination Chemistry Institute. Nanjing University, Nanjing, People's Republic of China

To cite this Article Bu, Xiu-Ren , You, Xiao-Zeng and Qing-Jin(1990) 'Studies on the Mixed Trimeric Reaction of Schiff Bases and Structures of Related Metal Complexes', Comments on Inorganic Chemistry, 9: 3, 221 — 244

To link to this Article: DOI: 10.1080/02603599008035811

URL: http://dx.doi.org/10.1080/02603599008035811

Studies on the Mixed Trimeric Reaction of Schiff Bases and Structures of Related Metal Complexes

XIU-REN BU, XIAO-ZENG YOU*
and QING-JIN MENG
Coordination Chemistry Institute,
Nanjing University,
Nanjing, People's Republic of China

An efficient and direct method for the syntheses of new double Schiff bases by reactions of two different aldehydes and ammonia have been developed. These reactions have also been extended to obtain some novel types of ferrocene derivatives. Specific catalytic hydrolysis of double Schiff bases by metallic ion through intramolecule axial coordination was ascertained. The ESR characteristic of hydrolytic products in solution is discussed, and some crystal structures of new metal complexes are reported.

Key Words: *mixed trimeric reaction, double Schiff bases, ferrocenes, nitrile–Cu(II) complexes, pyridine adducts, catalytic hydrolysis, ESR spectra, crystal structure*

INTRODUCTION

Many mono- and bis-Schiff bases obtained from monoamine and diamine such as ethylene diamine, propylene diamine have been investigated extensively and reviewed from the point of view of

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*To whom correspondence should be addressed.

Comments Inorg. Chem.
1990, Vol. 9, No. 3 & 4, pp. 221–244
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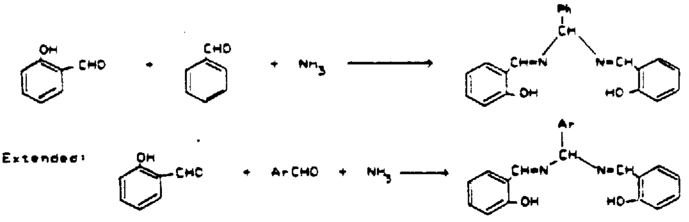
syntheses and the structures of their metal complexes.[1,2] Several interesting model structures for biological and catalysis chemistry have also been devised, making use of various ligands and metal ions.

There is little research on Schiff bases with shorter chain diamines such as methanediamine, because methanediamine is usually an active intermediate and difficult to isolate. Our studies were stimulated to investigate structural properties of complexes resulting from such a ligand. We have studied three component reactions, which give excellent yields of a series of double Schiff bases. These studies were also successfully extended to the syntheses of organometallics and some novel types of ferrocene derivatives.

SYNTHESIS OF MIXED TRIMERIC DOUBLE SCHIFF BASES

We have developed an efficient and direct method for the synthesis of a large number of new mixed double Schiff bases possessing an active alkane-1,1-diamine unit. When two kinds of aldehydes are allowed to react with ammonia, a series of N,N'-bis(2-hydroxyarylidene)aryl (or alkyl) methanediamines are obtained. One or both aldehydes must be salicylaldehyde or its analogues. The other kind of aldehyde may be aromatic or aliphatic aldehydes. The products, namely, double Schiff bases with methanediamine units, all consist of two molecules of salicylaldehydes and one molecule of aromatic or aliphatic aldehyde. The dianions of these Schiff bases present the tetradentate N_2O_2 ligand atoms in the formation of metal chelates.

(a) Reaction of salicylaldehyde and aromatic aldehydes with ammonia.[3]



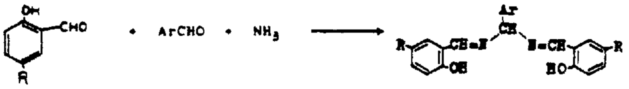
(See Table I.)

TABLE I

Synthesis of N,N′-bis(2-hydroxybenzylidene)arylmethanediamines

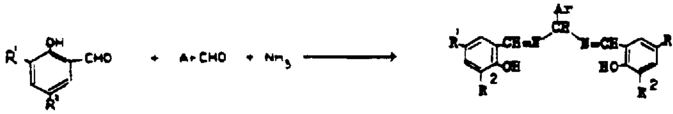
No.	Ar	Y(%)	No.	Ar	Y(%)
1	Ph	92	7	4-MeOC_6H_4	91
2	2-Cl-C_6H_4	90	8	4-Me_2N-C_6H_4	90
3	3-Cl-C_6H_4	85	9	4-F-C_6H_4	92
4	4-Cl-C_6H_4	79	10	3,4-OCH_2O-C_6H_3	87
5	2-Br-C_6H_4	93	11	1-naphthyl	82
6	4-Br-C_6H_4	94	12	3,4-Cl_2-C_6H_3	85

(b) Reaction of monosubstituted salicylaldehyde and aromatic aldehyde with ammonia.[4]



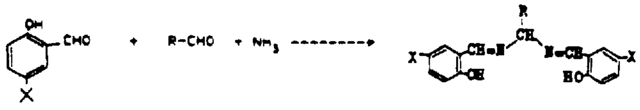
(See Table II.)

(c) Reaction of bisubstituted salicylaldehyde and aromatic aldehydes with ammonia.[5]



(See Table III.)

(d) Reaction of salicylaldehyde and aliphatic aldehydes with ammonia.[6]



Here, the aldehydes used are all aliphatic aldehydes with either short or long chain alkyl (R) groups. The isolated products are pale-yellow needles or platelets. Compared with the above reactant of aromatic aldehydes, good yields are also found for the alkyl compounds.

It should be pointed out that the reactions proceed easily at room temperature except for the reaction of 5-bromosalicylaldehyde and an aromatic aldehyde with ammonia which was carried out in refluxing methanol. Ammonia in the reactions comes either directly by the addition of aqueous ammonia or indirectly from dissociation of added ammonium acetate. The choice of ammonia depends on the system involved; in some cases, the form of ammonia presented will result in different products. (See Table IV). For example, in the case of the reaction of salicylaldehyde and anisaldehyde, when aqueous ammonia is used as ammonia mate-

TABLE II

Syntheses of N,N'-bis(2-hydroxy-5-R-benzylidene)arylmethanediamines

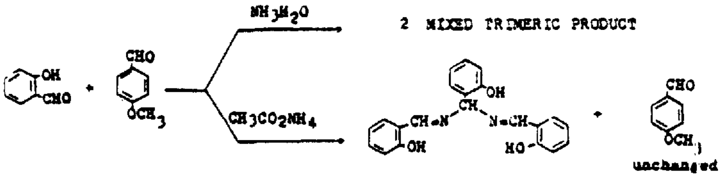
No.	R	Ar	*Y*(%)	No.	R	Ar	*Y*(%)
1	Cl	Ph	92	8	Br	Ph	92
2	Cl	2-Cl-Ph	95	9	Br	2-Cl-Ph	90
3	Cl	4-MeO-Ph	85	10	Br	2-Br-Ph	93
4	OMe	Ph	92	11	Br	3-Cl-Ph	67
5	OMe	2-Cl-Ph	78	12	Br	4-Cl-Ph	80
6	OMe	2-Br-Ph	79	13	Br	4-F-Ph	85
7	OMe	4-Cl-Ph	70	14	Br	2-NO-Ph	92
				15	Br	3,4-Cl-Ph	87

TABLE III

Syntheses of N,N′-bis(2-hydroxy-3,5-dihalobenzylidene)arylmethanediamines

No.	R^1	R^2	Ar	*Y*(%)	No.	R^1	R^2	Ar	*Y*(%)
1	Cl	Cl	Ph	92	6	Br	Br	2-Cl-Ph	95
2	Cl	Cl	2-Cl-Ph	95	7	Br	Br	2-Br-Ph	93
3	Cl	Cl	2-Br-Ph	92	8	Br	Cl	Ph	92
4	Cl	Cl	3-NO-Ph	91	9	Br	Cl	2-Br-Ph	93
5	Br	Br	Ph	92	10	Br	Cl	2-Cl-Ph	92

rial, the normal mixed trimers are formed; however, if ammonium acetate is used as ammonial material, the self-trimeric compound, N,N'-bis(2-hydroxylbenzyli-dene)-2-hydroxyphenylmethanediamine is obtained as the sole isolated product and anisaldehyde is recovered unchanged.



SYNTHESES AND STRUCTURES OF ORGANOMETALLIC ANALOGUES

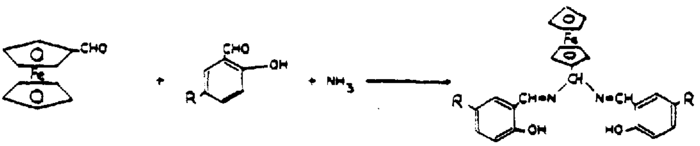
Our success with these syntheses prompted us to investigate corresponding reactions using organometallic aldehyde derivatives instead. One of our aims is to synthesize analogous organometallic compounds with the same methanediamine units; but it is difficult to realize how this might be done considering the difference between organic and organometallic compounds. For example, ferrocenealdehyde used here can not be condensed into benzoin as can benzaldehyde. Thus, many efforts have been made to extend this reaction to include organometallic compounds.

We considered the reaction of ferrocenylaldehyde and salicylaldehyde with ammonia. Two novel kinds of ferrocene derivatives were obtained. One new kind of ferrocenes are the N,N'-bis(2-hydroxybenaylidene)ferroceylmethanediamines, which consist of one molecule of ferrocenylaldehyde and two molecules of salicylaldehydes. The other novel compounds are the N,N'-bisferrocenylidene-2-hydroxyarylmethanediamines which contain two molecules of ferrocenylaldehyde and one molecule of salicylaldehyde. Which of the two types of compounds result depends on the salicylaldehyde ring. When salicylaldehyde rings have Cl, Br, Me, OMe, Ph as monosubstituents, the mononuclear ferrocenes are formed.[7]

TABLE IV

Synthesis of N,N'-bis(2-hydroxy-5-R-benzylidene)alkylmethanediamines

No.	X	R	*Y*(%)	No.	X	R	*Y*(%)
1	H	CH_2CH_3	91	8	Br	$(CH_2)_2CH_3$	90
2	H	$(CH_2)_2CH_3$	97	9	Br	$(CH_2)_3CH_3$	92
3	H	$(CH_2)_3CH_3$	93	10	Br	$(CH_2)_4CH_3$	92
4	H	$(CH_2)_4CH_3$	90	11	Br	$(CH_2)_5CH_3$	89
5	H	$(CH_2)_5CH_3$	92	12	Br	$(CH_2)_6CH_3$	91
6	H	$(CH_2)_7CH_3$	95	13	Br	$(CH_2)_7CH_3$	92
7	H	$(CH_2)_9CH_3$	95	14	Br	$(CH_2)_9CH_3$	93



R = H. OMe. Cl. Br. Ph

(See Table V).

In solution, mononuclear ferrocenes have two equivalent intramolecular hydrogen bonds (N···H–O) identified by ^{1}H and ^{13}C NMR (CH═N) and also confirmed by x-ray crystallographic study with N–O distances of 2.60 Å for compound (2) and 2.57 Å for compound (3) (Fig. 1).[8]

A large dihedral angle of 13.3° between the two Cp rings was discovered for the first time in compound (3). For nonbridged and for single "ferrocene unit" mononuclear derivatives, the dihedral angle is normally close to 0°. Usually, the large ring tilts occur only in some bridged ferrocenes due to the constraint of bridged atoms.[9,10] The present dihedral angle is smaller than in two-atom bridged ferrocenes,[9] but significantly larger than in those ferrocenes with one or two bridges of three atoms.[11,12] Thus, it suggests that both Cp rings are unusually sloped instead of being parallel. This may be caused by the extra interaction between the center iron atom and the other oxygen and nitrogen atoms. The relative distances of oxygen to iron and nitrogen to iron are 3.616 Å (N1–Fe), 3.624 Å (N2–Fe), 4.785 Å (O1–Fe), and 4.520 Å (O2–Fe), respectively. This novel structural characteristic will be further investigated based on more model compounds to be synthesized and determined.

A correlation between ^{13}C NMR chemical shifts of carbon in the Cp ring and the Hammett constants (*m*) was observed (Fig. 2). The slope of lines are negative for 1″–C, but positive for 2″–C, consistent with the distribution of electron densities on the ring.[13]

The second type of reaction to formation of binuclear ferrocenes, especially when either 5-6-butylsalicylaldehyde or other dimethylsalicylaldehydes are allowed to react with ferrocenealdehyde.

TABLE V

Reactions of ferrocenealdehyde and salicylaldehydes with ammonia

No.	R	Ammonia	Reaction Time (hr)	*Y* [%]	m.p. [C]
1	H	$AcONH_4$	0.1	80	173–174
2	OMe	$AcONH_4$	3	82	146–148
3	Me	$AcONH_4$	2	76	144–146
4	Cl	$AcONH_4$	2	81	168–169
5	Br	NH_3H_2O	3	90	158–160
6	Ph	NH_3H_2O	5	70	186–187

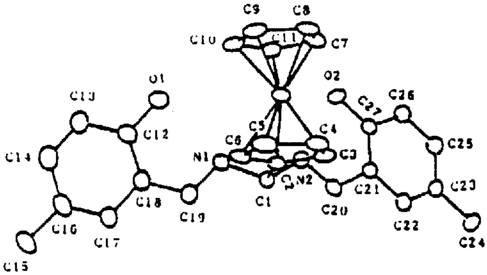
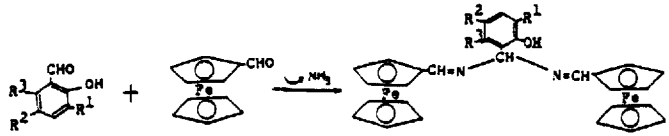


FIGURE 1 X-ray crystalograph for (3), orthorhombic, a = 10.376(2), b = 10.588(2), c = 20.943(3), R = 0.051.



1: $R^1 = R^3 = H, R^2 = C(CH_3)_3$;

2: $R^1 = R^2 = CH_3, R^3 = H$;

3: $R^1 = R^3 = CH_3, R^2 = H$.

Unlike mononuclear ferrocenes, binuclear ferrocenes have a single intramolecular hydrogen bond. This is based on the ^{1}H NMR spectrum (Fig. 3) which shows that the chemical shifts of the two CH=N appear at 8.36 and 8.71 pm, respectively. Two ferrocenyl

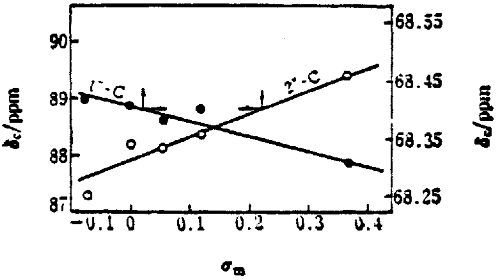


FIGURE 2 Chemical schematic shifts vs. Hammett constants for ferrocene.

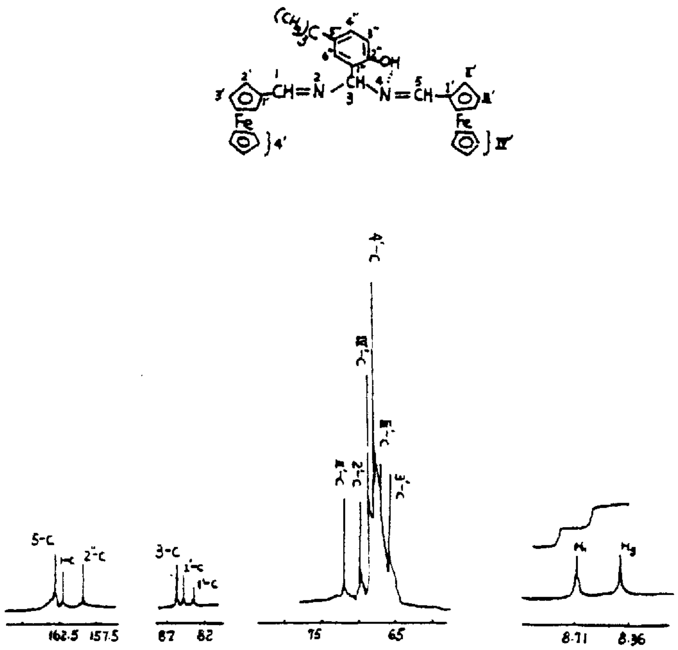


FIGURE 3 Binuclear ferrocene (1): ^{1}H and ^{13}C NMR spectra.

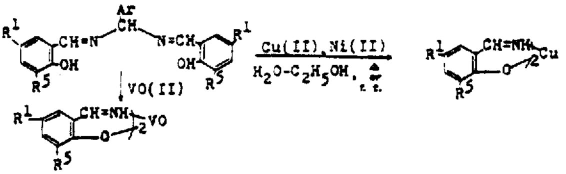
groups show two kinds of ferrocenyl rings, according to ^{13}C NMR results. These unsymmetric environments are well understood from conformation analysis due to steric and intramolecular hydrogen bond effects.

REACTIVE PROPERTIES WITH TRANSITIONAL METAL IONS

This section discusses the catalytic hydrolysis of the Schiff bases by metallic ions through intramolecular axial coordination and a C–N single bond breaking model. Such a property for these systems with a methanediamine unit is quite different from what is found for other double Schiff bases.

Generally, the Schiff bases consisting of ethylene diamine (or propylene diamine) and aldehydes react with metal ions to form normal and stable complexes; but some researchers have pointed out that in a few cases the Schiff bases are decomposed as a result of CH═N double bonds breaking when they are allowed to react with certain metal ions.[14,15] Metal ions are thought to be effective catalysts for Schiff base hydrolysis.

Such metal ion catalyzed hydrolysis provides another better method for opening the double bonds of CH═N than do either acidic or alkaline hydrolysis.[16] When our mixed double Schiff bases were allowed to react with Cu(II), Ni(II), VO(II) they also formed imine complexes and free aldehydes. All ten of the mixed Schiff base ligands chosen to react showed the same results.[17]



(82): $R^1 = R^5 = H$, M = Cu

(83): $R^1 = Cl$, $R^5 = H$, M = Cu

(84): $R^1 = Br$, $R^5 = H$, M = Cu

(85): $R^1 = Ph$, $R^5 = H$, M = Cu

(86): $R^1 = R^5 = H$, M = Ni

(87): $R^1 = Cl$, $R^5 = H$, M = Ni

(88): $R^1 = Br$, $R^5 = H$, M = Ni

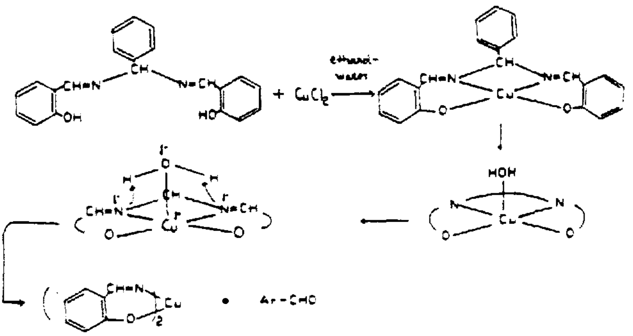
(90): $R^1 = Cl$, $R^5 = H$

(91): $R^1 = Br$, $R^5 = H$

(92): $R^1 = Ph$, $R^5 = H$

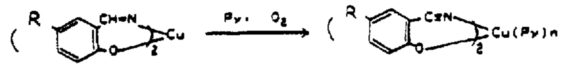
(93): $R^1 = R^5 = Br$

The reaction progress was investigated in two ways: (1) by following it with ESR and (2) by detecting the reaction intermediate using Job's method. The paramagnetic ion Cu(II) was used as a model ion to react with N,N'-bis(2-hydroxybenzylidene)phenylmethanediamine. With the help of ESR measurements at low temperature, the reaction was observed to gradually go to completion. At the beginning, a new paramagnetic particle appears which differs from the original Cu(II) salt ($CuCl_2 \cdot H_2O$). These ESR signals are slowly split into double peaks during 18 h, as the signal of the Cu(II) salt completely disappears. Much later, the spectrum of the final imine complex is obtained, following disappearance of the intermediate. Monitoring the ESR spectral changes (Fig. 4) during the complete reaction supports the appearance and disappearance of an intermediate during reaction. The double peaks above can be explained by the solvent effect.[18] In the reaction, ethanol and water are involved in the system. Both solvents are axially coordinated to copper, and this then results in coordinate catalytic hydrolysis.



Determination by Job's method shows that the intermediate consists of a complex with a 1:1 ratio of Cu(II) to (L) in solution. The strain in this four-member chelate ring, and the effect of the cordinating solvent, cause the CH–N to be more reactive and easily broken.

As mentioned above, this hydrolytic reaction is characteristic of C–N single bond cleavage by coordination catalysis in the axial direction. When the isolated imine–Cu(II) complexes are dissolved in pyridine in air, the oxidized products are interestingly obtained. It is evident from IR spectra that the original C=N and N–H peaks at 1620 cm^{-1} and at 3310 cm^{-1} are no longer present after reaction. A new peak at 2180 cm^{-1} appears as a result of the conversion of CH=N into C≡N. Then, imines–Cu(II) complexes are oxidized into nitrile–Cu(II) complexes. In fact, this reaction is efficiently catalyzed by the coordinated Cu(II). The reaction is auto-catalyzed by Cu(II) in the original complexes, instead of an external Cu(II) catalyst.



1. R = R = H, n = 2; 2. R = Cl, R = H, n = 2,

3. R = Br, R = H, n = 2; 4. R = Ph, R = H, n = 2;

5. R = Ph, R = H, n = 1.

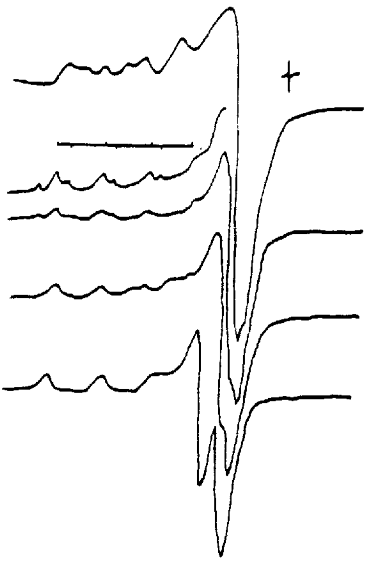


FIGURE 4 ESR change spectra for the reaction of Cu(II) and mixed trimeric ligand (L) in low temperature (−140 K), X-band.

The oxidized products were isolated as pyridine adducts. Generally, the number of pyridine molecules, n, is equal to 2; but, for R = Ph, one molecule of solvent is easily lost, then the more stable monopyridine product is formed although the adduct with two molecules of pyridine may also be obtained. Solvent molecules are directly coordinated to Cu(II) of the Schiff base chelate. In complex (1), two pyridines are in the equatorial plane. X-ray study shows that an unusual dimer is formed (Fig. 5).[19]

The environment around Cu(II) is penta-coordination: one axial nitrogen from nitrile, two equatorial oxygens and two equatorial nitrogens. The Cu atom is approximately located in the center of the plane with bond distances of Cu–N1 = 2.016 Å, Cu–N2 = 2.019 Å, Cu–O1 = 1.942 Å, Cu–O2 = 1.958 Å, Cu–N3(N–C) = 2.439 Å. Bond distances for this tetragonal pyramidal structure show that axial coordination is weaker than equatorial coordination. The structure of the other complex (4) (Fig. 7) was also determined by x-ray diffraction.[20] Unlike the above complex (1), the present complex shows a polymeric structure, where Cu(II) ions are linked by the nitrogen atom of a nitrile group forming infinite chains with a mean N–Cu bond distance of 2.476 Å.

Cu(II) is approximately located in the center of the four-atom plane: O1–Cu = 1.954 Å, O2–Cu = 1.948 Å, N1–Cu = 2.027 Å,

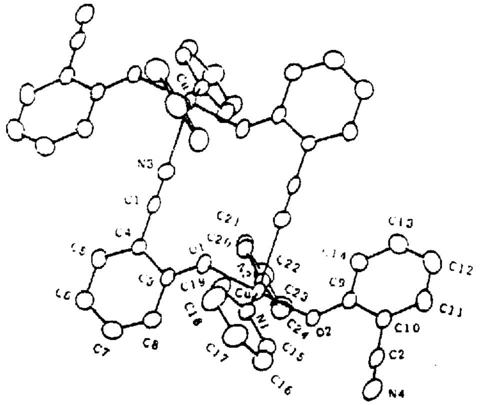


FIGURE 5 X-ray crystal structure of dimer nitrile Cu(II) complex (1) monoclinic. P2/n. a = 12.523(3). b = 8.648(2), c = 19.928(10) A, = 102.95(4). Z = 4. V = 2103.22 A.

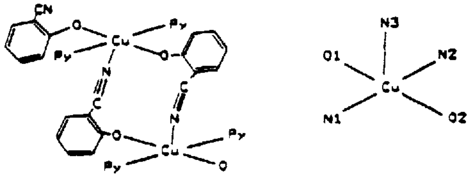


FIGURE 6 Schematic structure of compound (1).

N2–Cu = 2.027 Å. Below the plane lies one nitrogen of a nitrile with an angle of N1–Cu–N3 of 91.1°, and a slight tilt of the axial N3–Cu towards N1(Fig. 8). However, we found it interesting that the multiple bond of the other C≡N above the plane is also weakly coordinated to Cu. This is supported by the fact that the C2–Cu distance of 2.886 Å is shorter than the N4–Cu distance of 2.970 Å with the angle of C2–Cu–N4 of 22.3°. Thus, in the present complex, the environment around Cu(II) is approximately a distorted octahedral, instead of a tetragonal pyramidal considering the contribution of the multiple bond electron donor. The structural characteristics of the above complexes are summarized as

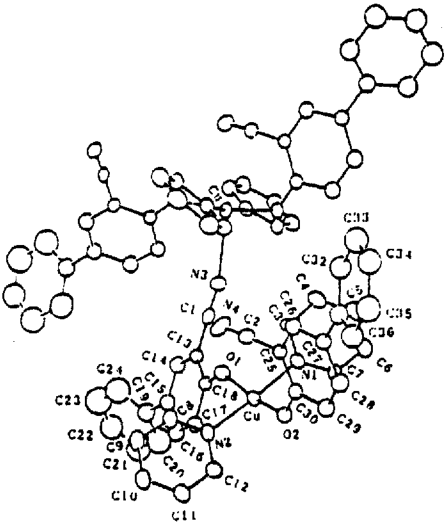


FIGURE 7 Structure of polymeric Cu(II) complex (4).

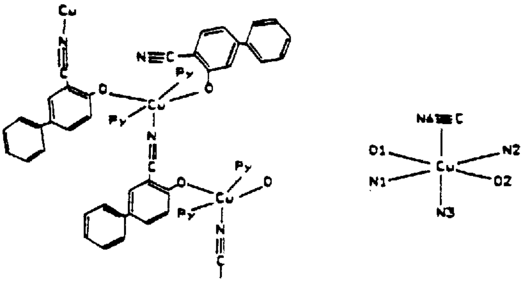
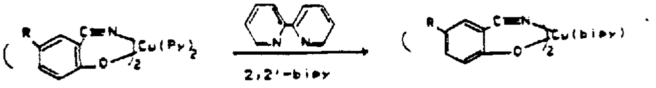


FIGURE 8 Schematic structure of polymeric complex (4).

follows: (a) dimeric or polymeric structures, (b) equatorial coordination of pyridine molecules, (c) axial addition of end-nitrogen of nitrile.

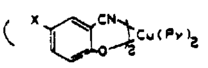
The nitrile–Cu(II) pyridine adducts can be converted into 2,2'-bipyridine adducts when mixed with bipyridine and heated in benzene solution. The original dimeric and polymeric structures, including tetragonal pyramidal and distorted octahedral coordinations, are transformed into monomeric complexes. Generally, one molecule of bipyridine with two dentates substitute for two molecules of pyridines.

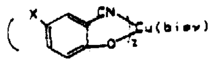


The ESR measurements on these complexes permit a detailed discussion about their structures.

ESR CHARACTERISTIC OF HYDROLYTIC PRODUCTS IN SOLUTION

As a typical example, we can focus on the discussion of Cu(II) complexes. First, for simplicity, some complicated structures are concisely expressed as follows: X–Cu–Py for nitrile–Cu(II) pyridine adducts while X–Cu–bipy for nitrile–Cu(II) bipyridine adducts.





X=H, H-Cu-Py,
X=Cl, Cl-Cu-Py,
X=Br, Br-Cu-Py,
X=Ph, Ph-Cu-Py,

X=H, H-Cu-bipy,
X=Cl, Cl-Cu-bipy,
X=Br, Br-Cu-bipy,
X=Ph, Ph-Cu-bipy.

For complexes X–Cu–Py, such as Cl–Cu–Py, an irregular ESR spectrum is revealed in DMF solvent (Fig. 9). The broad absorption shows results of magnetic interaction among copper ions.[17] The ESR behavior of Br–Cu–Py and Ph–Cu–Py is similar to the chloro complex in DMF solution at room temperature.

The results at low temperature (140 K) confirm the existence of polymeric structures. For complex Ph–Cu–Py, superhyperfine lines other than well-resonanced copper hyperfine splitting are obtained. This splitting corresponds to the contribution of three N atoms coordinated to Cu ($2nI + 1 = 2 \times 3 + 1 = 7$). Thus, besides the equatorial N atom from Py, another N atom comes from the axial nitrile.

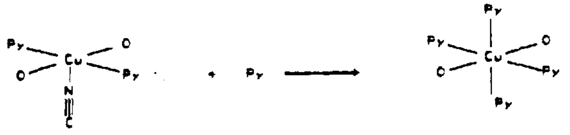
All spectra in Py solvent are discernible at room temperature. The typical mononuclear features are given. Generally, the pa-

FIGURE 9 Irregular ESR spectra for Cl–Cu–Py(2) in dmf at r.t.

rameter g(iso) is about 2.160, and a(iso) values are in the range 54–58 Å 10^{-4} cm^{-1}. These a values deviated from those derived from A(aniso) values at low temperature by this relation:

$$a(\text{iso}) - \frac{1}{3}(2A_{\parallel} + A_{\perp}) \qquad (1)$$

The sensitive structural change between room and low temperatures will result in the difference of relative parameters of ESR. Thus, the above equal a(iso) values between direct determination at room temperature and indirect derivation from Eq. (1) (at low temperature) show the change of configuration due to solvent effect and substitution. Dimeric and polymeric structures are converted into mononuclear structure, confirmed by the typical mononuclear Cu(II) signal, indicating that the present environment around Cu(II) in Py solvent differs from that of the original complexes. From ESR spectra at 140 K, nine superhyperfine lines ($2nI + 1 = 2 \times 4 + 1 = 9$) are given for X–Cu–Py, resulting from the contribution of coordination of four N atoms of four P: two equatorial N atoms and two axial N atoms.



Thus, at room temperature, polymeric structures are dissociated by solvent molecules. At low temperature, solvent molecules are tightly connected with the central ion, further forming solvent adducts with four pyridine molecules. It is interesting to compare the two sets of parameters for the DMF and Py solvents. First, g is larger in Py than in DMF for the same complex, e.g., g values are 2.2713 and 2.2658, respectively, for Cl–Cu–Py. Next, A values of 180.14×10^{-4} and 185.00×10^{-4} cm^{-1} are also larger in Py than those of 179.11×10^{-4} and 174.30×10^{-4} cm^{-1} in DMF, respectively, for Cl–Cu–Py and Br–Cu–Py. So, the solvent pyridine with its lone-pair electron always has some effect on magnetic parameters.

The ESR spectra of the type X–Cu–bipy at room temperature in DMF solution occurs with well-resonanced four hyperfine splittings due to the mononuclear copper ion. The coordination sphere includes two oxygen atoms and two nitrogen atoms, the latter confirmed by superhyperfine splittings of five lines resulting from two N nuclei in the complex H–Cu–bipy (Fig. 10). The plane structure is formed based on an N_2O_2 donor set attributable to two oxygen atoms from o-cyanophenol and one molecule of bipy with both N atoms coordinated. Five superhyperfine splittings for frozen DMF solution of the complexes X–Cu–bipy are observed other than the four parallel $A_{\parallel}(Cu)$ splittings. This further shows that two N atoms are involved in coordination. The spectra of Py solutions for X–Cu–bipy are similar to those in DMF at room temperature (Fig. 11). However, the spectra lack superhyperfine splittings due to the contribution of N atoms. Perhaps the effect of the solvated pyridine is not strongly enough attached to the central Cu(II), so the interaction between the lone-pair electron of nitrogen and the d-electron of Cu is too weak due to rapid and free tumbling in solution. The frozen (120 K) Py solution of com-

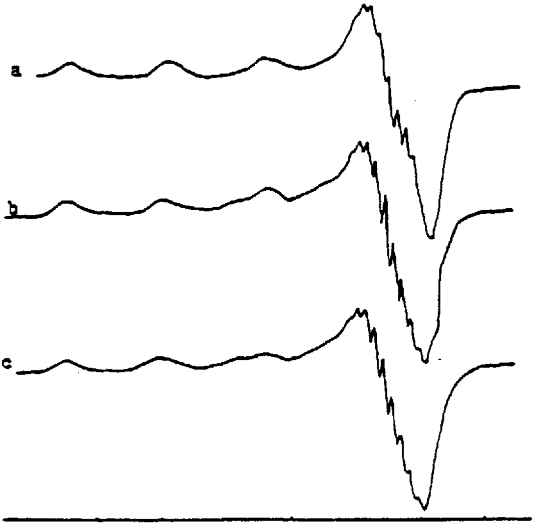


FIGURE 10 ESR spectra of 2-cyanophenylatocopper(II) pyridine adducts. a: (2) in DMF; b: (4) in Py; c: (3) in Py.

TABLE VI

Bond parameters from spin Hamiltonian parameters

Complexes	Solvents	α^2	α'^2	G	β_1^2	$k_\parallel^2$	$k_\perp^2$	ΔE_{xy} (cm^{-1})	ΔE_{xz} (cm^{-1})
Cl-Cu-Py	Py	0.83	0.26	5.15	0.72	0.60	0.75	14706	23810
Br-Cu-Py	Py	0.84	0.24	5.30	0.70	0.59	0.75	14815	25000
Ph-Cu-Py	Py	0.84	0.24	5.27	0.73	0.61	0.77	15000	25000
Cl-Cu(bipy)	DMF	0.80	0.29	5.8	0.80	0.64	0.65	15873	23191
Cl-Cu(bipy)	Py	0.81	0.28	5.2	0.81	0.55	0.69	13889	22727
Br-Cu(bipy)	DMF	0.80	0.29	5.5	0.81	0.65	0.68	15923	23148
Br-Cu(bipy)	Py	0.80	0.29	5.4	0.76	0.53	0.64	14124	22881
Ph-Cu(bipy)	DMF	0.81	0.28	5.4	0.81	0.66	0.67	16077	21739
Ph-Cu(bipy)	Py	0.80	0.29	5.2	0.66	0.53	0.62	14025	21552

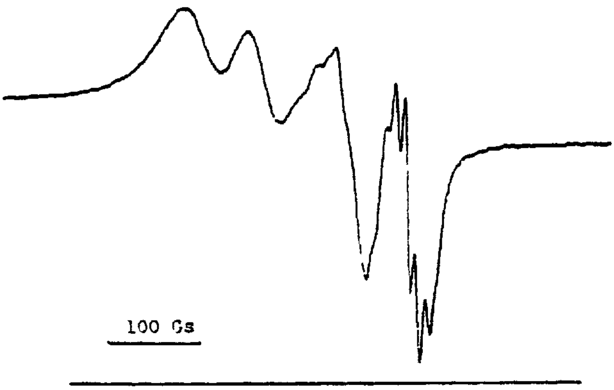


FIGURE 11 Typical ESR spectrum of H–Cu–bipy in DMF (r.t.).

plexes X–Cu–bipy provides evidence of superhyperfine splittings, indicating that more than five superhyperfine lines occur. Thus, the solvated pyridine molecules are also involved in the axial direction, in addition to the equatorial bipy.

All spectra pertinent to the monomeric structure are shown as axial symmetry, with $g_{\parallel} > g_{\perp}$. X–Cu–Py and X–Cu–bipy are considered as having $D(4h)$ symmetry, although the true symmetries of the latter for the coordination sphere are nearly $C(2h)$ in order to make some relative comparisons. From spin Hamiltonian parameters, some bond parameters are calculated based on the Kivelson and Nieman theory[21] (Table VI).

Acknowledgment

This work is supported by the National Natural Science Foundation of China as part of a major project.

References

1. E. Sinn and C. M. Harris, Coord. Chem. Rev. 4, 391 (1969).
2. S. Yamada and A. Takeuchi, Coord. Chem. Rev. 43, 187 (1982).
3. Xiu-Ren Bu, Qing-Jin Meng, Shou-Heng Sun, Xiao-Zeng You and An-Bang Dai, Acta Chim. Sinica 47, 296 (1989).

4. Xiu-Ren Bu, Qing-Jin Meng and Xiao-Zeng You, Synth. Commun. **18**, No. 18, 2289 (1988).
5. Xiu-Ren Bu, Qing-Jin Meng, Xiao-Zeng You and Shou-Heng Sun, manuscript in preparation.
6. Xiu-Ren Bu, Qing-Jin Meng, Xiao-Zeng You and Shou-Heng Sun, Synthesis, No. 4, 307 (1989).
7. Xiu-Ren Bu, Qing-Jin Meng, Rei-Xue Wang, Xiao-Zeng You and An-Bang Dai, Acta Chim. Sinica **47**, 240 (1989).
8. Xiao-Zeng You, Xiu-Ren Bu and Qing-Jin Meng, manuscript in preparation.
9. R. A. Abramovitch, J. L. Atwood, M. L. Good and B. A. Lampert, Inorg. Chem. **14**, 3085 (1975).
10. P. C. Lecomte, Y. Dusausoy, J. Portes and C. Moise, Acta Cryst. B **29**, 1127 (1973).
11. N. D. Jones, R. E. Marsh and J. H. Richards, Acta Cryst. **9**, 373 (1956).
12. M. Hillman, L. D. Spaulding and G. J. B. Williams, J. Orgnaomet. Chem. **155**, 109 (1978).
13. A. N. Nesmeyanov, P. V. Petrovskii, L. A. Fedorov, V. I. Robas and E. I. Fedin, Zh. Strukkt. Khim. **14**, 49 (1973).
14. R. K. Y. Ho and S. E. Slivingstone, Austr. J. Chem. **18**, 659 (1965).
15. E. I. Lerner and S. J. Lippard, J. Am. Chem. Soc. **98**, 5397 (1976).
16. A. Streitwieser Jr. and C. H. Heathcock, *Introduction to Organic Chemistry* (Macmillan, 1978), p. 378.
17. Xiu-Ren Bu, Qing-Jin Meng, Shou-Heng Sun and Xiao-Zeng You, J. Inorg. Chem. **5**, No. 4, 58 (1989).
18. S. Antosik, N. M. D. Bromn, A. A. McConnell and A. L. Porte, J. Chem. Soc. (A) 545 (1969).
19. Ming Wang, Po-Yi Wang, Pe-Ju Zheng, Xiu-Ren Bu, Xiao-Zeng You, Qing-Jin Meng and An-Bang Dai, to be submitted.
20. Xiu-Ren Bu, Xiao-Zeng You, Qing-Jin Men and An-Bang Dai, to be submitted.
21. D. Kivelson and R. Neiman, J. Chem. Phys. **36**, 3221 (1963).