Synthesis and Properties of Copper(II), Zinc(II), Nickel(II) and Cobalt(II) Complexes with N,N'-diaryl-β-iminoamines

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New zinc(II), copper(II), nickel(II) and cobalt(II) complexes with N,N'-diaryl-β-iminoamines were prepared, the ligands being obtained from 4-phenyl-1,2-dithiolium salt and aromatic monoamines, such as aniline, p-toluidine and p-chloroaniline. Judging from the steric consideration, the coordination geometry of the copper(II) complexes may be in between the square plane and the tetrahedron. In the absorption spectra of the copper(II) complexes, two distinct bands were observed in the ranges 6000–7000 and 13000–15000 cm^{-1}. These bands were assigned to the d–d and charge-transfer bands, respectively, on the basis of their intensities and in view of the results of other copper(II) complexes with distorted tetrahedral structures. The intensities of the bands of the copper(II) complexes are highly dependent on the ring substituents (cf. Fig. 1 in the text), however the ESR parameters suffer little effect by the ring substituents. It was concluded that the effect due to the mixing of 3d and 4p orbitals is not so important as has been claimed in distorted tetrahedral copper(II) complexes.

Introduction

It is known that there are tetrahedral and square planar coordinations for tetra-coordinated nickel(II) and cobalt(II) complexes and the diagnosis of the coordination geometry can be carried out unambiguously in terms of spectral and magnetic data [1]. In the case of copper(II) complexes, the Jahn–Teller effect is operating and intermediate structures between square planar and tetrahedral geometries are frequently recognized. However, only few studies have been reported for copper(II) complexes of such intermediate geometries.

Recently distorted tetrahedral structures have been proposed for the copper(II) ion in "Blue-copper protein", on the basis of the ESR parameters [2], giving rise to much arguments [3–6]. It seems to the authors that fundamental studies on the electronic states of distorted tetrahedral copper(II) complexes are essentially important in order to elucidate the

coordination geometry of copper ion in "Blue-copper protein".

It is known that the tetrahedral cobalt(II) and nickel(II) and distorted tetrahedral copper(II) complexes are formed with some N,N'-diaryl-β-imino-amines [7, 8]. In this study, we have prepared zinc(II), copper(II), nickel(II) and cobalt(II) complexes with various N,N'-diaryl-β-iminoamines listed in Table I, among which metal complexes with

TABLE I. Abbreviation of the Ligands (cf. Fig. 1).

R₁	R₂	R₃	Ar	Abbreviation
CH₃	H	CH₃	phenyl	H(L-a)
H	H	H	phenyl	H(L-b)
H	phenyl	H	phenyl	H(L-c)
H	phenyl	H	p-tolyl	H(L-d)
H	phenyl	H	p-chlorophenyl	H(L-e)

H(L-c), H(L-d) and H(L-e) are new complexes, and measured the ESR and optical spectra of the copper-(II) complexes, in order to elucidate the relationship among the tetrahedral distortion from the planar geometry, the position and the intensity of the d–d bands, and the ESR parameters of the distorted tetrahedral copper(II) complexes.

Experimental

Preparation of the Ligands

The ligands, H(L-c), H(L-d) and H(L-e) were obtained from the reaction mixture of the 4-phenyl-1,2-dithiolium hydrogensulfate and aromatic monoamines, such as aniline, p-toluidine and p-chloroaniline [9].

Preparation of the Metal Complexes

A chloroform solution (10 ml) containing the ligand (0.001 mol) was added to the methanol solution (10 ml) of metal acetate (0.001 mol) and the mixture was warmed for ten minutes at 60 C. After

TABLE II. Analytical Data of the New Complexes.

Complexes	C (%) Found (calcd.)	H (%) Found (calcd.)	N (%) Found (calcd.)
$[Co(L\text{-}c)_2] \cdot \frac{1}{2}C_6H_6$	77.88(78.02)	5.38(5.38)	8.04(8.09)
$[Ni(L\text{-}c)_2] \cdot \frac{1}{2}C_6H_6$	77.74(78.05)	5.34(5.39)	8.18(8.09)
$[Cu(L\text{-}c)_2] \cdot \frac{1}{2}C_6H_6$	77.41(77.51)	5.30(5.35)	8.21(8.03)
$[Zn(L\text{-}c)_2] \cdot \frac{1}{2}C_6H_6$	77.18(77.30)	5.34(5.33)	8.03(8.01)
$[Co(L\text{-}d)_2]$	77.84(77.84)	5.98(5.96)	7.69(7.89)
$[Ni(L\text{-}d)_2]$	78.02(77.86)	6.02(5.97)	7.71(7.90)
$[Cu(L\text{-}d)_2]$	77.66(77.34)	5.96(5.93)	7.77(7.84)
$[Zn(L\text{-}d)_2]$	77.14(77.14)	5.85(5.91)	7.74(7.82)
$[Co(L\text{-}e)_2]$	64.16(63.74)	3.88(3.82)	6.92(7.08)
$[Ni(L\text{-}e)_2] \cdot \frac{1}{2}C_6H_6$	64.81(65.04)	3.99(4.01)	6.81(6.75)
$[Cu(L\text{-}e)_2] \cdot C_6H_6$	66.43(65.95)	4.26(4.16)	6.27(6.40)
$[Zn(L\text{-}e)_2]$	63.22(63.20)	3.84(3.79)	6.94(7.02)

several minutes, the complexes precipitated were filtered, and recrystallized from a chloroform or a benzene solution. Analytical data of the new complexes are given in Table II.

Measurements

The absorption spectra were measured with a Shimadzu Multiporpose MPS-5000 at room temperature. ESR spectra were obtained with a JEOL ESR apparatus model JES-ME-3X using an X-band, DPPH being used as a standard marker. Since the chloroform solution of $[Cu(L\text{-}a)_2]$ was not stable (gradually changed its color from green to yellow in 24 hours), the ESR and absorption spectra were measured immediately after the solution had been prepared.

Results and Discussion

Absorption Spectra of the Complexes

In Fig. 2, the absorption spectra of the cobalt(II), nickel(II) and zinc(II) complexes obtained in this study are shown. For the cobalt(II) and nickel(II) complexes, some d–d bands were observed at 9500 and 7900 cm^{-1}, respectively, which are very similar to those reported for $[Co(L\text{-}a)_2]$ and $[Ni(L\text{-}a)_2]$ [8] (*cf.* Table III). Accordingly it is clear that these complexes have tetrahedral structures. This may be due to the steric hindrance between the aromatic groups at the nitrogen atoms. The intense bands in the region higher than 18000 cm^{-1} are assigned to the charge-
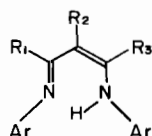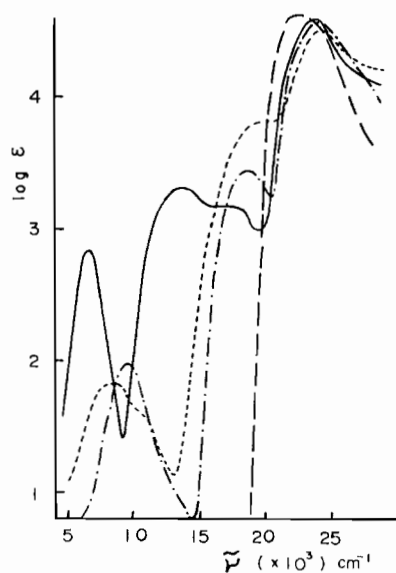

Figure 2. Absorption spectra of cobalt(II), nickel(II), copper-(II) and zinc(II) complexes with H(L-d) in chloroform. $-\cdot-\cdot-$ Co^{2+}; $\cdots\cdots$ Ni^{2+}; —— Cu^{2+}; — — Zn^{2+}.
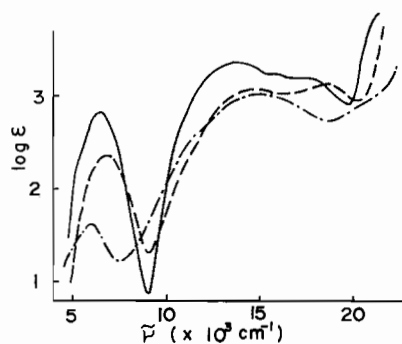
Figure 3. Absorption spectra of the copper(II) complexes in chloroform. —— $[Cu(L\text{-}c)_2]$; $----$ $[Cu(L\text{-}b)_2]$; $-\cdot-\cdot-$ $[Cu(L\text{-}a)_2]$.

Figure 1. N,N′-diaryl-β-iminoamine (*cf.* Table I).

TABLE III. Absorption Spectral Data of Cobalt(II), Nickel(II) and Zinc(II) Complexes, $\tilde{\nu}$, cm^{-1} (ϵ).

[Co(L-c)$_2$]	9500(95)	17500sh	
[Co(L-d)$_2$]	9400(95)	18500(2910)	23900(37920)
[Co(L-e)$_2$]	9500(96)	18280(3240)	
[Ni(L-c)$_2$]	7800(50)	10280sh	19000(5000)
[Ni(L-d)$_2$]	8000(64) 23980(30600)	10260sh	20000(6500)
[Ni(L-e)$_2$]	7800(50)	11360sh	19000(4100)
[Zn(L-c)$_2$]	22780(14200)		
[Zn(L-d)$_2$]	22620(14200)		

TABLE IV. ESR and Optical Spectral Data of the Copper(II) Complexes.

Complexes	$g_\parallel$ [a]	$\lvert A_\parallel \rvert$ (10^{-4} cm^{-1})	Absorption Spectra $\tilde{\nu}$ cm^{-1} (ϵ)	
[Cu(L-a)$_2$]	2.217	115	5900(41)	14800(1107)
[Cu(L-b)$_2$]	2.196	132	6990(195)	14900(1200)
[Cu(L-c)$_2$]	2.178	134	6490(655)	13900(2100)
[Cu(L-d)$_2$]	2.177	135	6580(690)	13500(2030)
[Cu(L-e)$_2$]	2.178	126	6450(640)	13700(1610)
[Cu(t-Bu-sal)$_2$] [b]	2.276	118	13160(202)	
[Cu(t-Bu-pya)$_2$] [c]	2.267	108	11400sh	15350(264)
[Cu(ph$_2$-dpm)$_2$] [d]	2.279	103	8850(456)	14700(2600)

[a] ESR data of the copper(II) complexes with N,N′-diaryl-β-iminoamines are of the chloroform frozen solutions at 77 K. [b] [Cu(t-Bu-sal)$_2$] represents Bis(N-t-butyl-salicylaldiminato)copper(II). [c] [Cu(t-Bu-pya)$_2$] represents Bis(N-t-butyl-pyrrole-2-aldiminato)-copper(II). [d] [Cu(ph$_2$-dpm)$_2$] represents Bis(5,5′-diphenyl-dipyrromethenato)copper(II).

transfer bands, judged from their intensities. In zinc(II) complexes, no band was observed in a region lower than 22000 cm^{-1}.

The spectral data of the copper(II) complexes are summarized in Table IV and the typical spectra are shown in Fig. 3. As shown in Fig. 3, in each spectrum two distinct absorption bands were observed in the ranges 6000–7000 and 13000–15000 cm^{-1}. It should be noted that the intensities of the two bands highly depend on the substituents in the chelate ring. That is, intensities of the bands of the copper(II) complexes with R_2 = phenyl (*cf.* Fig. 1) are much larger than those of the complexes with R_2 = H.

The electronic spectra of the distorted tetrahedral copper(II) complexes have been investigated by many authors for tetrahalogeno- [10], bis(salicylaldimi-nato)- [11], bis(pyrrole-2-aldiminato)- [12] and bis-(dippyromethenato)- [13] copper(II) complexes. The dihedral angles between the two N—Cu—O planes have been determined for some bis(salicylaldiminato) complexes, among which the largest angle (54°) is observed for bis(N-t-butyl-salcylaldiminato)copper(II) complex [14].

According to the preliminary X-ray analysis, the angle of [Cu(L-a)$_2$] is 68° [15]. On the basis of the detailed investigation on the solid state spectra of Cs$_2$[CuCl$_4$] [10], the bands observed at 4800–5550,

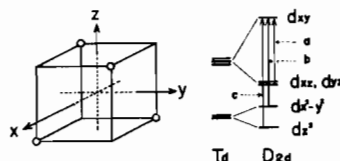Figure 4. The splitting of the 3d orbitals in Cs$_2$[CuCl$_4$]. The energies are: a) 4800–5500 cm^{-1}; b) 7900 cm^{-1}; c) 9050 cm^{-1}.

7800 and 9050 cm^{-1} were assigned to the electronic transitions, $d_{xz}, d_{yz} \rightarrow d_{xy}$, $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{z^2} \rightarrow d_{xy}$, respectively, where x, y, z-axis being shown in Fig. 4. The above results and the spectral data of other related complexes (*cf.* Table IV) being taken into consideration, the bands in the range 6000–7000 cm^{-1} observed for bis(N,N′-diaryl-β-iminoamino)-copper(II) complexes are assigned to the electronic transitions, $d_{xz}, d_{yz} \rightarrow d_{xy}$.

The bands at 13000–15000 cm^{-1} are assumed to be due to the charge-transfer transitions (from ligand to metal), judged from their large ϵ-values (1100–2100). Other d–d transitions, $d_{x^2-y^2}$, $d_{z^2} \rightarrow d_{xy}$ may be obscured by these charge-transfer bands.

As shown in Table IV, the ϵ-values of the copper-(II) complexes with the ligands, H(L-a) ~ H(L-e), are in the range 41 ~ 690. It is well known that the

intensity of the d–d band in the distorted tetrahedral copper(II) complexes are, in general, larger than those of octahedral and planar complexes. Two reasons have been proposed for these facts, that is;

1) the mixing of d–d and 3d–4p transitions [16],
2) the mixing of d–d and charge-transfer transitions [17].

As shown in Table IV, all the lowest-energy bands of the copper(II) complexes of H(L-a) ~ H(L-e), were observed in a narrow region (6000–7000 cm^{-1}), implying that these complexes are of similar coordination geometry to each other. On the other hand, intensity of these bands dramatically varies with the change of the ring substituents. The molar extinction coefficients of the near infrared bands fluctuate in the range 41 ~ 690. Such a large fluctuation of ϵ-values cannot be elucidated by the reason 1), because the tetrahedral distortion from the planar geometry are similar to each other in these complexes and the mixing of 3d and 4p orbitals is mainly determined by the coordination geometry. Thus, the above facts imply that the large ϵ-values observed for [Cu(L-c)$_2$], [Cu(L-d)$_2$] and [Cu(L-e)$_2$] should be due to the reason 2). In fact, it is found that the smaller the energy gap between d–d and CT band, and the larger the ϵ-value of the CT band are, the more intense the d–d band become, as shown in Table IV. Therefore, we may conclude that 3d–4p mixing is not the major factor for the increase of d–d band intensity in distorted tetrahedral copper(II) complexes.
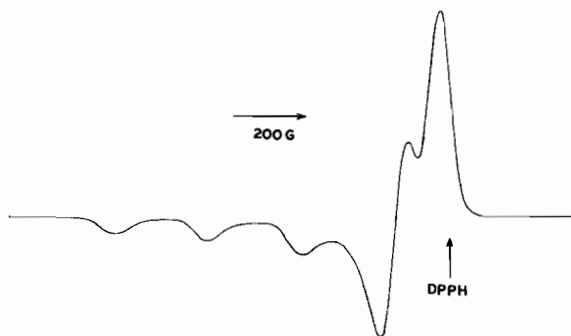

Figure 5. ESR spectrum of [Cu(L-d)$_2$] in chloroform obtained at 77 K.

ESR Spectra of the Copper(II) Complexes

In Fig. 5, the ESR spectrum of [Cu(L-d)$_2$] is shown and the data of other related complexes are summarized in Table IV the $g_{\parallel}$ values and $|A_{\parallel}|$ values are in the ranges 2.18 ~ 2.22 and 115 ~ 135 × 10^{-4} cm^{-1}, respectively. The $|A_{\parallel}|$ values are much smaller than those of the square planar complexes [18]. It has been pointed out that the small $|A_{\parallel}|$ values observed for distorted tetrahedral copper(II) com-

plexes should be attributed to the effect of 3d–4p mixing [19, 20].

As can be seen in the literature [10], distortion from the tetrahedron can be estimated from the energy of d_{xz}, $d_{yz} \rightarrow d_{xy}$ transitions. Since the 6000–7000 cm^{-1} bands observed for the present complexes are assigned to these transitions, it is deduced from the spectral data in Table IV that the tetrahedral distortion from square planar coordination in the present complexes is larger than those of the complexes with salicylaldimines, pyrrole-2-aldimines and dipyrromethenes. However, the $|A_{\parallel}|$ values of the present complexes are not the smallest among those complexes. Since the mixing of 3d–4p orbitals should increase with increasing tetrahedral distortion, the above fact suggests that the extent of 3d–4p mixing is not the only governing factor to decrease the $|A_{\parallel}|$ values in tetrahedral copper(II) complexes.

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