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Electronic Structures of Square Planar Cobalt(II), Nickel(II) and Copper(II) Complexes with some N_4-macrocyclic Ligands [1]

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ESR and absorption spectra were measured for the square planar cobalt(II), nickel(II) and copper(II) complexes with some 14, 15 and 16-membered N_4-macrocyclic ligands, such as (14-a), H(14-b), H_2(14-c), H_2(15-c) and H_2(16-c) (for the abbreviations, see Fig. 2 in the text). On the basis of the ESR spectra of the cobalt(II) complexes, the splitting schemes for the cobalt d-orbitals were grouped into two types, (1) $[Co(14\text{-}a)]^{2+}$ and $[Co(14\text{-}b)]^{+}$ where no or little π-antibonding interaction is present and (2) [Co(14-c)], [Co(15-c)] and [Co(16-c)] where a considerable π-antibonding interaction is present. The electronic spectra of the cobalt(II), nickel(II) and copper(II) complexes were reasonably interpreted in terms of the model proposed.

Introduction

In order to understand the various properties such as electronic spectrum, magnetism or reactivity of square planar complexes, the detailed knowledge is necessary about the splitting of the d-orbitals in the central ions. In square planar complexes, the highest d-orbital is undoubtedly d_{xy}, as shown in Fig. 1 [2–5] (throughout this paper, the molecular axes were adopted as shown in Fig. 1). Since the other four d-orbitals (d_{xz}, d_{yz}, d_{z^2}, $d_{x^2-y^2}$) are energetically close to each other, it is very difficult to theoretically predict the energy order of these four d-orbitals. Therefore, many investigators have attempted to determine the energy order of the d-orbitals of square planar nickel(II) and copper(II) complexes on the basis of experimental data such as absorption [6, 7], circular dichroism [8–10], magnetic circular dichroism [11, 12] and single crystal polarized spectra [13–16]. In general, however, unambiguous assignments of the bands to the d–d transitions seem to be difficult because of the incompleteness of the theory for the intensities of d–d transitions [14, 15].

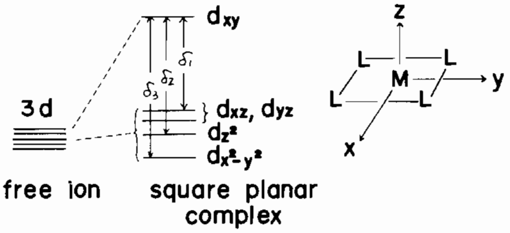

Figure 1. The splitting scheme of 3d orbitals in square planar complexes.

In connection with this situation, it should be noted that the important information about the splitting of d-orbitals may be available from the study of the ground state electronic configuration of square planar cobalt(II) complexes, where an unpaired electron houses in one of the four 3d orbitals, $d_{x^2-y^2}$, d_{xz}, d_{yz} and d_{z^2}. The ground state of low-spin cobalt(II) complexes has been discussed by many workers on the basis of the ESR spectra. Very recently, detailed studies on the ESR and electronic spectra of low-spin square planar cobalt(II) complexes were reported by Hitchman [17] and the present authors [18, 19]. In the present study, we have measured the ESR and electronic spectra of cobalt(II), nickel(II) and copper(II) complexes with N_4-macrocycles (Fig. 2), and elucidated the splitting of d-orbitals on the basis of our recent result obtained for the cobalt(II) complexes.

Experimental

The N_4-macrocycles were prepared according to the methods described in the literature; (14-a) [20], H(14-b) [21], H_2(14-c), H_2(15-c), and H_2(16-c) [22] (for the abbreviations of the ligands, see Fig. 2). For the ESR measurements, all the cobalt(II) complexes were diluted in the corresponding nickel(II) complexes. ESR spectra were measured with a JEOL ESR apparatus model JES-ME-3X at room temperature and 77 K using an X-band. DPPH was used as a standard marker. Absorption and reflectance spectra were measured with a Shimadzu Multipurpose MPS-5000 at room temperature.

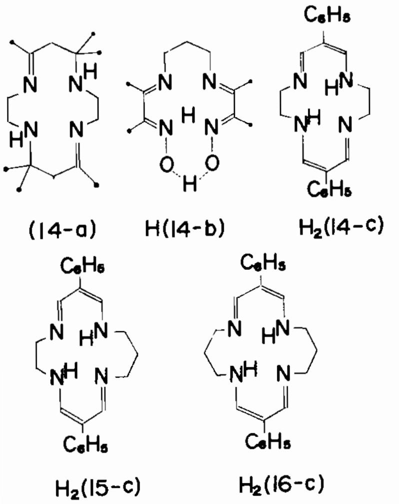

Figure 2. The N_4-macrocyclic ligands used in this paper and their abbreviations.

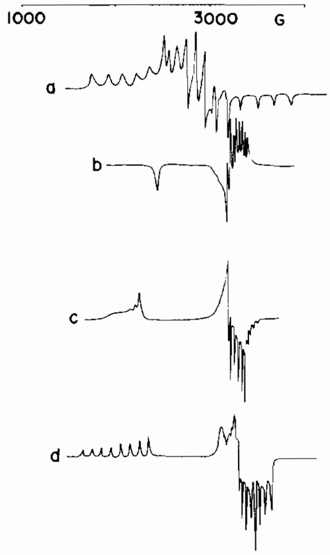

Figure 3. ESR spectra of cobalt(II) complexes obtained at 77 K: a) $[Co(14\text{-}b)]^+$, b) [Co(14-c)], c) [Co(15-c)], d) [Co(16-c)].

Results and Discussion

ESR Spectra of Cobalt(II) Complexes

In Fig. 3, the powder ESR spectra of $[Co(14\text{-}b)]^+$, [Co(14-c)], [Co(15-c)] and [Co(16-c)] are shown. It is clear that the ESR pattern of $[Co(14\text{-}b)]^+$ is quite different from those of the other three complexes. That is, an absorption with a large hyperfine splitting ($|A_3| = 173 \times 10^{-4}$ cm^{-1}) is observed around the g = 2.0 region; on the other hand, two absorptions with small hyperfine splittings ($|A_2|$, $|A_3| < 50 \times 10^{-4}$ cm^{-1}) are observed for [Co(14-c)], [Co(15-c)] and [Co(16-c)]. According to our criterion [19], the above fact is indicative that an unpaired electron lies in the d_{z^2} orbital for $[Co(14\text{-}b)]^+$, while in the d_{yz} orbital for [Co(14-c)], [Co(15-c)] and [Co(16-c)].

Judging from the result obtained from the single crystal ESR study of [Co(acen)] [23], where H_2acen denotes N,N′-bis(1-acetonylethylidene)ethylenediamine, the lowest absorption in the ESR spectra of [Co(14-c)], [Co(15-c)] and [Co(16-c)] should correspond to g_x. As seen in Fig. 3 and Table I, the g_x and $|A_x|$ values increase with increasing size of macrocyclic rings. According to our calculation (*cf.* Fig. 2 and 8 in Ref. 19), $|A_x|$ is expected to increase with increasing g_x value, which are consistent with the present experimental results, and this corresponds to the decreasing energy separation between the ground state, $(d_{xy})^2(d_{yz})^1$ and the excited state, $(d_{xy})^2(d_{z^2})^1$ with increasing size of macrocyclic rings in [Co(14-c)], [Co(15-c)] and [Co(16-c)].

Electronic Spectra of $M(14\text{-}a)^{2+}$, $M(14\text{-}b)^+$ and M(14-c) (M = Co, Ni, Cu)

In the electronic spectrum of [Ni(14-c)], a shoulder is observed around 1.6 μm^{-1}, and it shifts to a lower energy region with increasing size of the macrocyclic ring as seen in Fig. 4. In [Co(14-c)], as shown in Fig. 5, a distinct band (logϵ ~ 2.34) is observed at 1.17 μm^{-1}, which should be a spin-allowed d–d transition judging from its intensity. This band can be assigned to the electronic transition, $d_{x^2-y^2} \rightarrow d_{yz}$ on the basis of the results obtained for the *cis*-$[CoN_2O_2]$ and $[CoN_4]$ type complexes with quadridentate Schiff bases [17–19].

TABLE I. ESR Parameters of Cobalt(II) and Copper(II) Complexes.

Ligands	Cobalt(II) Complexes		Copper(II) Complexes	
	g_1[a]	$\|A_1\|$ (10^{-4} cm^{-1})	$g_\parallel$	$\|A_\parallel\|$ (10^{-4} cm^{-1})
$H_2(14\text{-}c)$	2.676	~0	2.123	211
$H_2(15\text{-}c)$	2.874	46	2.140	198
$H_2(16\text{-}c)$	3.252	147	2.165	190

[a] g_1 corresponds to the absorption of the lowest magnetic field (*cf.* Fig. 3).

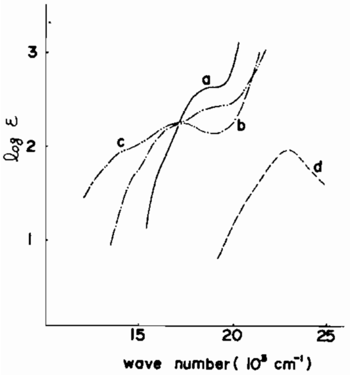

Figure 4. Absorption spectra of nickel(II) complexes: a) [Ni(14-c)] (in CH_2ClCH_2Cl), b) [Ni(15-c)] (in CH_2ClCH_2Cl), c) [Ni(16-c)] (in CH_2ClCH_2Cl), d) $[Ni(14\text{-}a)]^{2+}$ (in DMF).

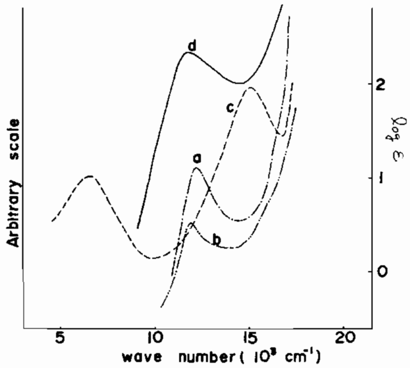

Figure 5. Electronic spectra of cobalt(II) complexes: a) [Co(14-c)] (reflectance), b) [Co(15-c)] (reflectance), c) [Co(16-c)] (reflectance), d) [Co(14-c)] (absorption, in CH_2ClCH_2Cl).

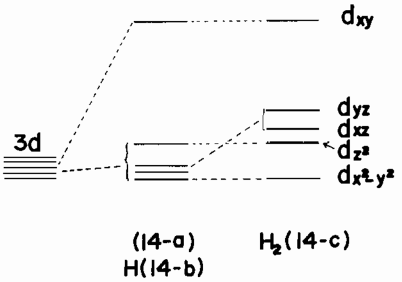

Figure 6. The splitting scheme of 3d orbitals in $[Co(14\text{-}a)]^{2+}$, $[Co(14\text{-}b)]^+$ and [Co(14-c)].

From the g_x-value of [Co(14-c)], we can estimate the energy gap between the states, $(d_{xy})^2(d_{yz})^1$ and $(d_{xy})^2(d_{z^2})^1$ to be 0.25 μm^{-1}, making use of the results of our calculation [19]. Taking the interelectronic repulsion energy into consideration (with the assumption of reasonable values for F_2 and F_4 [24], *e.g.*, $F_2 = 10F_4 = 0.07$ μm^{-1}), we concluded that the d_{yz} orbital is higher in energy (~0.35 μm^{-1}) than the d_{z^2} orbital in [Co(14-c)]. The energy gap between d_{yz} and $d_{x^2-y^2}$, which can be estimated from the absorption band in the near-infrared region, is dependent on the values of F_2 and F_4, and roughly estimated at 0.60 μm^{-1}, if $F_2 = 10F_4 = 0.07$ μm^{-1} is assumed. On this assumption the nephelauxetic ratio (F(complex)/F(free ion)) is 0.40 [25], which is a reasonable value compared with those found for low-spin type 3d-metal complexes [26]. Thus, we obtain a splitting scheme of d-orbitals in [Co(14-c)] as shown in Fig. 6. It should be noted that the $d_{x^2-y^2}$ orbital is almost non-bonding in all the complexes under discussion, because none of the coordinated nitrogen atoms have in-plane π-orbitals. Unfortunately, we could not obtain good spectra and failed to identify a band corresponding to the $d_{x^2-y^2} \rightarrow d_{z^2}$ transition in $[Co(14\text{-}a)]^{2+}$ and $[Co(14\text{-}b)]^+$, because they react with molecular oxygen very sensitively. However for these complexes the energy gaps between d_{z^2} and d_{xz}, d_{yz} orbitals can be estimated to be smaller than 0.50 μm^{-1} from their g-values [27], with the assumption of $F_2 = 10F_4 = 0.07$ μm^{-1}. Thus, the orbital energies of the cobalt(II) complexes of (14-a), $(14\text{-}b)^-$ and $(14\text{-}c)^{2-}$ are schematically shown in Fig. 6. This result is now compared with the spectra of the corresponding nickel(II) and copper(II) complexes, and we will show how successfully our orbital energy scheme interpretes the experimental data. The specific feature of the spectra of Ni(II) and Cu(II) complexes is that the lowest d–d bands of Ni(II) and Cu(II) complexes of (14-a) and $(14\text{-}b)^-$ are always observed in a higher energy region than those of $(14\text{-}c)^{2-}$ (*cf.* Table II and Fig. 7). These facts can

TABLE II. The Lowest Absorption Peaks of Ni(II) and Cu(II) Complexes with 14-Membered N_4-macrocyclic Ligands.

Ligands	Ni(II) (μm^{-1})	Cu(II) (μm^{-1})
(14-a)	2.27	1.99
H(14-b)	>2.0	2.12
H_2(14-c)	1.65sh	1.60

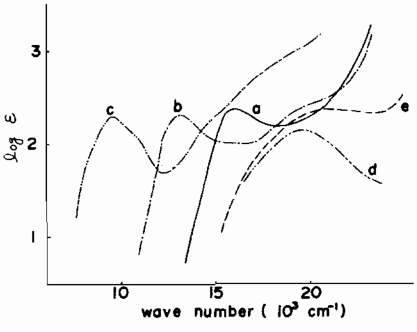

Figure 7. Absorption spectra of copper(II) complexes: a) [Cu(14-c)] (in CH_2ClCH_2Cl), b) [Cu(15-c)] (in CH_2ClCH_2Cl), c) [Cu(16-c)] (in CH_2ClCH_2Cl), d) [Cu(14-a)] $(Bph_4)_2$ (in DMF), e) $[Cu(14\text{-}b)]ClO_4 \cdot H_2O$ (in acetone).

be reasonably interpreted in terms of our model (Fig. 6) on the assumption that the lowest d–d bands in [Ni(14-c)] and [Cu(14-c)] are due to the electronic transitions, d_{xz}, $d_{yz} \rightarrow d_{xy}$ (*cf.* Table II). The above facts indicate that the d_{yz} and d_{xz} orbitals suffer remarkable antibonding effects in [M(14-c)] complexes (M = Co(II), Ni(II), Cu(II)) as a consequence of the interaction with π-orbitals of the ligands.

Electronic Spectra of the Complexes of $(14\text{-}c)^{2-}$, $(15\text{-}c)^{2-}$ and $(16\text{-}c)^{2-}$

In the reflectance spectrum of [Co(16-c)] (Fig. 5), two bands are observed at 0.70 and 1.50 μm^{-1}. From the above discussion, it is most reasonable to assign the 0.70 and 1.50 μm^{-1} bands to the electronic transitions, $d_{x^2-y^2} \rightarrow d_{yz}$ and $d_{yz} \rightarrow d_{xy}$, respectively. Accordingly, the orbital scheme for Co(14-c), Co(15-c) and Co(16-c) can be assumed as shown in Fig. 8, where the ligand field splitting reduces with increasing size of the macrocyclic ring. The spectra of the copper and nickel complexes with the same series of ligands are shown in Fig. 4 and 7, respectively, where the same trend is seen for the variation of the ring size. Thus, it is obvious that our model (Fig. 8) is also valid qualitatively for the copper and nickel complexes. As clearly shown in Fig. 8, the antibonding effect of the d_{xy}, d_{yz} (or d_{xz}) orbitals decreases with increasing size of the macrocyclic ring. These facts are quite compatible with the generally accepted view [28–30] that the ligand field effect decreases with increasing size of macrocyclic rings of the ligands.

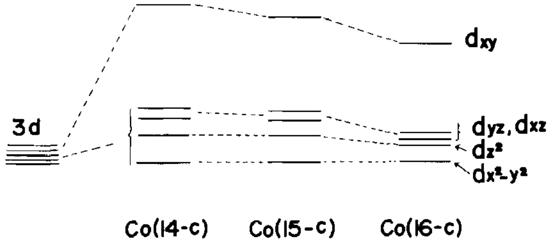

Figure 8. The splitting scheme of 3d orbitals in [Co(14-c)], [Co(15-c)] and [Co(16-c)]. The energy gap between d_{xy} and d_{yz} orbitals was estimated from the spectral data of corresponding nickel(II) complexes.

ESR Spectra of Copper(II) Complexes

In Fig. 9, the ESR spectra of copper(II) complexes are shown. As shown in Fig. 9 and Table I, the $g_{\parallel}$ ($=g_z$) value decreases in the order [Cu(16-c)], [Cu(15-c)] and [Cu(14-c)]. According to Maki and McGarvey [31],

$$g_{\parallel} = 2 - \frac{8\lambda\alpha^2\beta^2}{\Delta[(xy)-(x^2-y^2)]} \qquad (1)$$

where $\Delta[(xy) - (x^2 - y^2)]$ and λ are the energy separation between d_{xy} and $d_{x^2-y^2}$ orbitals and the spin–orbit coupling constant, respectively, and α, β are the coefficients in the following molecular orbitals [31, 32].

$$\begin{aligned} \psi^1 &= \alpha d_{xy} - \alpha'\psi_{lig} \\ \psi^2 &= \beta d_{x^2-y^2} - \beta'\psi_{lig} \end{aligned} \qquad (2)$$

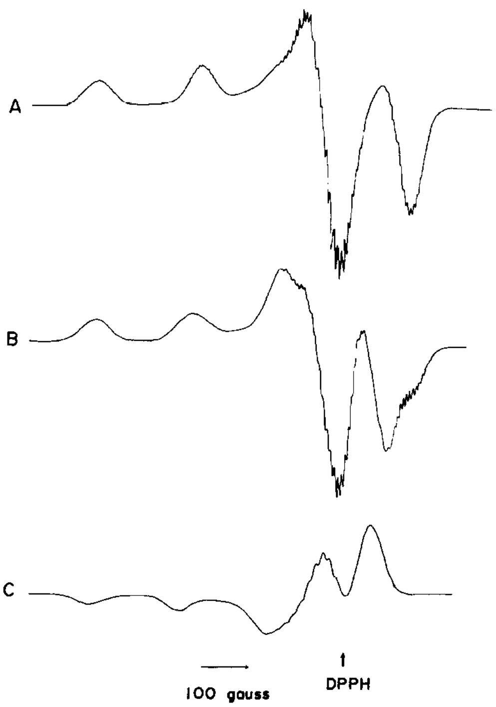

Figure 9. ESR spectra of copper(II) complexes obtained at 77 K: A) [Cu(14-c)] (in [Ni(14-c)]), B) [Cu(15-c)] (in $CHCl_3$), C) [Cu(16-c)] (in [Ni(16-c)]).

In the complexes with N_4-macrocyclic ligands, β can be set to unity, thus $g_{\parallel}$ is a function of α and $\Delta[(xy) - (x^2 - y^2)]$. If we assume the orbital energy scheme of Figs. 6 and 8 for the copper(II) complexes, α and $1/\Delta[(xy) - (x^2 - y^2)]$ both increase with increasing ring size, thereby the $g_{\parallel}$ is enlarged according to the equation (1). Thus, our model (Figs. 6 and 8) is quite compatible with the experimental results.

In the region of $g_{\perp}$ ($= g_x$ and g_y), many peaks due to the ligand superhyperfine splitting (~8 gauss) are observed for [Cu(14-c)] and [Cu(15-c)], whereas nine hyperfine structures (~14 gauss) are observed for [Cu(16-c)]. In the latter case, the nine peaks may be due to the nuclear spins of the coordinated four nitrogen atoms [33]. In the former case, the peaks are likely to be superhyperfine splitting due to the coordinated nitrogen atoms and the hydrogen atoms adjacent to the carbon atom of C–N bonds (*cf.* Fig. 10). Similar superhyperfine structures due to the

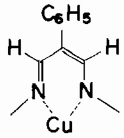

Figure 10. The molecular arrangement in Cu complexes.

TABLE III. Some d–d Transition Energies in Cobalt(II) and Nickel(II) Complexes.

Cobalt(II) Complexes	Energies[a]
$d_{x^2-y^2} \longrightarrow d_{yz}$	$(\delta_3 - \delta_1) + 15F_2 - 75F_4$
$d_{z^2} \longrightarrow d_{yz}$	$(\delta_2 - \delta_1) - 5F_2 + 25F_4$
Nickel(II) Complexes	
$d_{yz} \longrightarrow d_{xy}$	$\delta_1 - 3F_2 - 20F_4$
$d_{z^2} \longrightarrow d_{xy}$	$\delta_2 - 4F_2 - 15F_4$
$d_{x^2-y^2} \longrightarrow d_{xy}$	$\delta_3 - 35F_4$

[a] For δ_1, δ_2 and δ_3, see Fig. 1.

hydrogen atoms in the ligands are known in many Schiff base complexes [34, 35]. The absence of the proton superhyperfine structure in [Cu(16-c)] is reasonably interpreted in terms of the fact that the Cu–N bonds in [Cu(16-c)] are weak compared to those of [Cu(15-c)] and [Cu(14-c)], as is evidently deduced from our orbital energy scheme of Figs. 6 and 8.

The same procedures as described in this paper have been performed for the square planar metal complexes of *cis*-[MN_2O_2], [MN_2S_2] and [MS_4] types, whose results will be reported in a separate paper [36].

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