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Absorption Band in the Near-Ultraviolet Region Observed for Binuclear Copper(II) Complexes

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Elucidation of the origin of near-ultraviolet absorption believed to be characteristic of binuclear copper(II) complexes was attempted. The absorption was attributed to charge transfer transitions from nonbonding orbitals of bridging oxygen atoms to the vacant metal *d*-orbital. Appearance of the band in the near-ultraviolet region was interpreted in terms of the red-shift due to the decreasing *s*-character of the nonbonding orbitals enforced by the steric requirement of the complex. On this basis, the spectra of dialkoxo- or dihydroxo- bridged complexes and of copper alkanoates can consistently be explained.

It is well-known that copper(II) alkanoates of a binuclear structure always show an absorption at about 27 kK.[1] A number of investigations have been carried out for the origin of this absorption,[2~7] but the results are still in considerable controversies. A relatively intense absorption band ($\varepsilon=1\sim3\times10^3$) was observed at about 28 kK for many binuclear copper(II) complexes bridged by two alkoxo groups.[8] It was assumed that the band is characteristic of the binuclear structure.

By making use of CD and absorption spectra, we have tried to give a detailed explanation of the origin of the near-ultraviolet bands believed to be characteristic of the binuclear structures of both the copper(II) acetate- and the μ-dialkoxo- types.

Experimental

Optically active N-(3-hydroxypropyl)-(−)1,2-propanediamine $NH_2CH(CH_3)CH_2NH(CH_2)_3OH$ (=pn-prol) and its copper(II) complex $[Cu_2(pn\text{-}prol')_2](ClO_4)_2$ were prepared by the method reported,[8] where pn-prol′ represents deprotonated anion of pn-prol.

The CD and absorption spectra were measured with a JASCO ORD-UV/5 optical rotatory dispersion recorder with a CD attachment. Absorption measurements were carried out over the temperature range 24~−32 °C with a Hitachi EPS-2 spectrometer, a special device being used for temperature control.

Discussion

$[Cu_2(pn\text{-}prol')_2]^{2+}$ has the structural formula as shown in Fig. 1. Its CD and absorption (AB) spectra in methanol are shown in Fig. 2. The band at 28.2 kK is a typical absorption considered to be characteristic of binuclear structure. This band increases in intensity with the lowering of temperature (Fig. 2),

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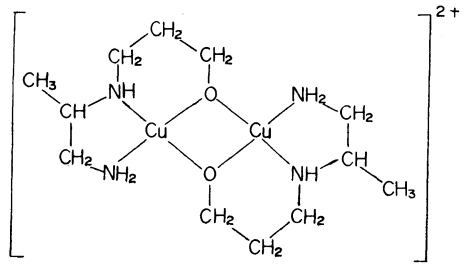

Fig. 1. Structural formula of $[Cu_2(pn\text{-}prol')_2]^{2+}$.

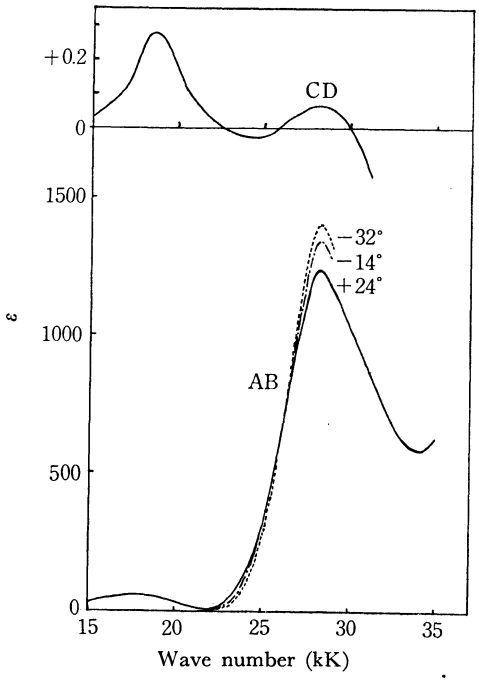

Fig. 2. Absorption and CD spectra of $[Cu_2(pn\text{-}etol')_2](ClO_4)_2$ in methanol.

indicating that it is due to the transition from the ground singlet state. A positive CD band was observed at nearly the same position, and a negative CD band relatively small intensity at 24.8 kK. The temperature dependence of this band could not be confirmed because of experimental difficulty.

Since $[Cu\ pn_2](ClO_4)_2$ has no CD band in the region 23~30 kK,[9] both CD bands are unlikely to be due to d–d transitions and are most probably attributable to charge transfer transitions from the nonbonding orbitals of bridging oxygen atoms to the empty copper d-orbitals.

Although the structure of this compound has not been determined, its skeltal structure can be analogized in high probability with that of $[Cu_2(aca\text{-}prol')_2]$, in which two copper ions, all the coordinating atoms and two carbon atoms bonded with bridging oxygen are practically coplanar, where aca-prol′=$^-OC(CH_3)$-$CHCHC(CH_3)NCH_2CH_2CH_2O^-$.[10] Thus nonbonding orbitals on the oxygen atoms, denoted by p_π and p_π', should be pure 2p-orbitals normal to the coordination plane. The CT-transitions will, therefore, occur from $p_+(=p_\pi+p_\pi')$ or $p_-(=p_\pi-p_\pi')$ to $d_+(=d_{x^2-y^2}+d_{x^2-y^2}')$ or $d_-(=d_{x^2-y^2}-d_{x^2-y^2})$, where p_+, p_-, d_+ and d_- indicate bonding (+) and antibonding (−)-orbitals with respect to the p_π-p_π' and the $d_{x^2-y^2}$·$d_{x^2-y^2}'$ interactions, respectively. However, the transition to the d_+ orbital can not be the origin of the band at 28.2 kK, because the band is attributable to the transition only from the ground singlet state, as demonstrated by measurements of the spectra. This would be understood more easily in terms of electron-formulism, *i.e.*, the possible singlet-singlet CT transitions would be from the $(d_-)^\alpha(d_-)^\beta$ state to the $(d_-)^\alpha(p_-)^\beta$ and the $(d_-)^\alpha(p_+)^\beta$ states, where α and β refer to $m_s=+1/2$ and $-1/2$ respectively; no transitions from the low-lying excited states could be compatible with the fact that the intensity of the band increases with lowering of temperature. Since p_+ and p_- are bonding and antibonding with respect to the p_π-p_π' interaction, the $p_+\leftrightarrow d_-$ and the $p_-\leftrightarrow d_-$ transitions may be assigned to the band at 28.2 and 24.8 kK, respectively. The energy difference between the two bands may be compatible with the energy of the p_π-p_π' interaction considered from the estimated distance 2.3 Å.[10]

Irreducible representations under various symmetries are shown in Table 1 for the p_+, p_- and d_- orbitals together with the direct products of those orbitals. In C_2-symmetry both electric- and magnetic-dipole transitions are allowed for $p_+\leftrightarrow d_-$ and $p_-\leftrightarrow d_-$ transitions, but in D_{2h}-symmetry no electric-dipole transition is allowed for both transitions. In C_{2h}-symmetry, which is a fairly good approximation for the compound, electric-dipole transition is allowed for only the $p_+\leftrightarrow d_-$ transition. Thus, it is clear that assignment of the 28.2 kK band to the $p_+\leftrightarrow d_-$ transition best elucidates the observed intensity ($1\sim3\times10^3$). Accordingly, the $p_-\leftrightarrow d_-$ transition may be assigned to the band at 24.8 kK, since p^+ and p_- are bonding and antibonding with respect to the $p_\pi\cdot p_\pi'$ interaction. The energy difference between the two bands may be compatible with the energy of the p_π-p_π' interaction considered from the estimated O–O distance 2.3 Å.[10] This assignment is also consistent with the fact that the absorption at 24.8 kK is so weak as to be hidden by the lower part of the intense band at 28.2 kK, and that CD intensity of the latter band is very small relative to AB intensity. However, it is safer not to form a final

Table 1. Irreducible representations of p_+, p_- and d_- orbitals and selection rules for the transition between these orbitals under various symmetries

	D_{2h}	C_{2h}	C
$p_+=p_\pi+p_\pi'$	b_{1u}	a_u	a
$p_-=p_\pi-p_\pi'$	b_{3g}	b_g	b
$d_-=d_{x^2-y^2}-d_{x^2-y^2}'$	b_{1g}	a_g	a
$p_+\leftrightarrow d_-$	a_u(——)	a_u(z)	a(z, R_z)
$p_-\leftrightarrow d_-$	b_{2g}(R_y)	b_g(R_xR_y)	b(x, y, R_xR_y)

x, y and z in ( ) denote "allowed for electric-dipole transition of x, y and z-polarization," respectively, and R_x, R_y, R_z in ( ) denote "allowed for magnetic-dipole transition of x, y and z-polarization," respectively.

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conclusion for the origin of the 24.8 kK band until the temperature dependence of the CD band is confirmed, though the present assumption is in harmony with Dubicki's observation of single-crystal spectra of copper(II) acetate.[7]

It is well-known that electronegativity of a nonbonding electron-pair on an oxygen atom is highly dependent on the degree of hybridization of 2s and 2p orbitals. For the present complex, the nonbonding orbital on the oxygen atom can be regarded to be a practically pure $2p_z$ orbital. Accordingly, the CT bands shift to the near-ultraviolet region, as characteristic bands of the binuclear structure. This could be interpreted as follows. In the case of a simple coordination of alkoxo or hydroxo group, the two nonbonding electron pairs should have a considerable *s*-character as has been proved for free water and some similar molecules,[11,12] so that CT bands are observed at a relatively high frequency region. On the other hand, in the case where oxygen atoms function as a bridge in a binuclear complex, the oxygen atoms may be forced to form sp^2 hydridized σ-bonds by steric requirement, leaving p_z-orbital as a nonbonding orbital. Thus the CT band appears in a relatively lower frequency region, frequently showing a distinct peak.

Thus it follows that even in the case of a mononuclear complex an absorption band similar to that observed for binuclear complexes can appear at the near-ultraviolet region, granted that nonbonding orbitals on negatively charged oxygen (or nitrogen) atoms are of mainly *p*-character. In fact, some bis(β-diketonato) copper(II) complexes show a shoulder at 25.8 kK.[13]

Copper(II) Alkanoates. Recently Dubicki measured single-crystal spectra over the temperature range 287~4.2 K and found that the near-ultraviolet spectrum of copper(II) acetate consists of two bands at 27.8 and 30.8 kK, polarized parallel and perpendicular to copper-copper axis, respectively, the two bands being identified as singlet-singlet transitions from the fact that their intensities increase with lowering of temperature. Dubicki assigned these bands to the CT transitions $b_{2u}(p_y) \leftrightarrow b_{1g}(d_{x^2-y^2})$ and $e_g(p_x) \leftrightarrow b_{2u}(d_{x^2-y^2})$, where $b_{2u}(p_y)$ and $e_g(p_x)$ are nonbonding ligand molecular orbitals composed of out-of-plane and in-plane (with respect to the $-C\begin{smallmatrix}O-Cu-\\ \vdots \\ O-Cu-\end{smallmatrix}$ plane) oxygen 2p-orbitals, respectively. However, our conclusion on the elucidation of near-ultraviolet spectra of copper(II) acetate, though being the same as Dubicki's in attributing the band to the CT transitions from nonbonding oxygen orbitals to vacant metal d-orbitals, differs in that only p_x (out-of-plane) orbitals are taken into consideration as the orbitals from which an electron transfers. The in-plane nonbonding orbital (p_y) is regarded as a sp^2-hybridized orbitals, whose energy is much lower than that of the out-of-plane p-orbitals and is thus neglected.

Thus, the bands at 27.8 and 30.8 kK should be assigned to some transitions from the out-of-plane π-orbitals to the metal d-(b_{2u}) orbital. Judging from the observed intensities ($\varepsilon > 100$), the absorptions are not likely to be symmetry-allowed ones.

It should be noted that the appearance of CT bands in such a relatively low-frequency region can also be interpreted in terms of a high *p*-character of the nonbonding orbitals of the negatively charged oxygen atoms.

Possibility of Double Excitations. The possibility of double excitation of d–d transitions for copper(II) acetate and other binuclear metal complexes has been pointed out.[5,14,15] Dubicki could not ignore this possibility, though his discussion appeared in favor of the CT-transition origin.[7] However, in the case of chromium(II) acetate it seems improbable that the double excitations are the origin of the near-ultraviolet bands (ν_{max}=29.2 and 30.8 kK),[4] apart from the problem of absorption intensity, because any combination of the d–d transitions which are most probably distributed within the range 17~25 kK could not account for the observed frequencies 29.2 and 30.8 kK. Similar relations are observed in the case of μ-dialkoxodicopper(II) complexes, *i.e.*, frequencies of the near-ultraviolet bands (~28 kK) are too low to be assigned to some combinations of the d–d transitions (15~18 kK).[18] These facts imply that the near-ultraviolet band is better interpreted in terms of CT transitions than double excitations of d–d transitions at least for the binuclear copper(II) complexes discussed in this paper.

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