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Correlation between Magnetic and Spectral Properties of Alkoxo-bridged Copper(II) Complexes with N,N-dialkyldiaminealcohols and N,N-dialkylaminoalcohols

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Nine new alkoxo-bridged binuclear (or polynuclear) copper(II) complexes with N,N-dialkyldiaminealcohols, $[Cu(R_2N(CH_2)_nNH(CH_2)_mO)]X$, (where $R = CH_3$ or C_2H_5, $n = 2$ or 3, $m = 2$ or 3, $X = ClO_4$ or $B(C_6H_5)_4$) and with N,N-dialkylaminoalcohols, $[Cu((CH_3)_2N(CH_2)_3O)X]$ (where $X = Cl$, Br), were prepared and characterized. The electronic spectra and temperature dependence of magnetic susceptibilities (80–295 K) of the alkoxo-bridged copper(II) complexes were measured. From the results, the empirical rule was established for the alkoxo-bridged copper(II) complexes, that is, "an intramolecular antiferromagnetic interaction is operative for the complexes which show distinct absorption bands in the near-ultraviolet region (24–29 kK), whereas no antiferromagnetic interaction but a weak ferromagnetic interaction is operative for the compounds which show no distinct absorption bands in the near-ultraviolet region".

Introduction

Uhlig *et al.*[1], and Hein *et al.*[2] studied some binuclear (or polynuclear) copper(II) complexes with N,N-dialkylaminoalcohols (as shown in Figure 1) and classified them into three groups on the basis of their magnetic and spectral properties.

Recently we have reported the preparation, the magnetic and the spectral properties of binuclear copper (II) complexes with some diaminealcohols (as shown in Figure 2).[3,4] These complexes can be classified into two groups, *i.e.*, type A: the complexes which have subnormal magnetic moments at room temperature and show characteristic absorption bands in the near-ultraviolet region (24–29 kK), and type B: the complexes which have normal magnetic moments at room temperature and show no distinct absorption bands in the near-ultraviolet region. The general features of the properties of the compounds is similar to that of Uhlig's compounds. The characteristics of the type A and the type B are similar to those of the first and the second groups of Uhlig's classification, respectively.

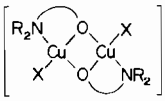

Figure 1. Structure of [Cu(R-n)X], where (R-n) represents $R_2N(CH_2)_nO^-$.

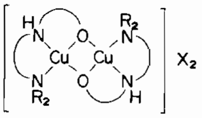

Figure 2. Structure of [Cu(R-n-m)]X, where (R-n-m) represents $R_2N(CH_2)_nNH(CH_2)_mO^-$.

The present investigation was carried out in order to elucidate the correlation between magnetic and spectral properties of the alkoxo-bridged copper(II) complexes comprehensively. Nine new compounds were prepared in this study, that is, $[Cu(R_2N(CH_2)_nNH(CH_2)_mO)]X$ (hereafter abbreviated as [Cu (R-n-m)]X), where R-n-m = CH_3-2-3, CH_3-3-3, CH_3-3-2, C_2H_5-2-3, C_2H_5-3-2, X = ClO_4, $B(C_6H_5)_4$ and $[Cu(R_2N(CH_2)_nO)X]$ (hereafter abbreviated as [Cu(R-n)X]), where R-n = CH_3-3, X = Cl, Br.

Experimental

Preparations

N,N-dialkyldiaminealcohols, $R_2N(CH_2)_nNH(CH_2)_mOH$ (where R = CH_3, C_2H_5, n = 2 or 3, m = 2 or 3), were prepared according to the method of Keller *et al.*[5], by use of N,N-dialkylethylenediamine or N,N-dialkyltrimethylenediamine and ethylenechlorohydrin or trimethylenechlorohydrin. N,N-di-n-butylaminoethanol was prepared according to the method of Hartmen[6], by use of di-n-butylamine and ethylenechlorohydrin. Other N,N-dialkylaminoalcohols were obtained commercially.

TABLE I. Analytical Data of New Compounds.

Complexes	Analysis (%)					
	C		H		N	
	Found	Cald.	Found	Cald.	Found	Cald.
$[Cu(CH_3\text{-}3\text{-}3)]ClO_4$	29.80	29.82	5.94	5.91	8.82	8.69
$[Cu(CH_3\text{-}3\text{-}2)]ClO_4 \cdot H_2O$	25.68	25.93	5.92	5.90	8.71	8.69
$[Cu(H\text{-}3\text{-}2)]B(C_6H_5)_4$	69.54	69.67	6.70	6.65	5.54	5.60
$[Cu(CH_3\text{-}3\text{-}2)]B(C_6H_5)_4 \cdot CH_3OH$	68.63	68.67	7.14	7.38	5.11	5.00
$[Cu(CH_3\text{-}2\text{-}3)]B(C_6H_5)_4 \cdot CH_3OH$	68.39	68.67	7.18	7.38	5.01	5.00
$[Cu(C_2H_5\text{-}3\text{-}2)]B(C_6H_5)_4 \cdot CH_3OH$	69.58	69.44	7.58	7.71	4.75	4.76
$[Cu(C_2H_5\text{-}3\text{-}2)]ClO_4$	31.85	32.14	6.25	6.29	8.24	8.33
$[Cu(CH_3\text{-}3)Cl]$	29.86	29.86	6.06	6.01	6.91	6.96
$[Cu(CH_3\text{-}3)Br]$	24.27	24.45	4.98	4.92	5.54	5.70

$[Cu(C_2H_5\text{-}2\text{-}3)]ClO_4$

N,N-diethyl-N′-γ-hydroxypropylethylenediamine (1.2 g, 0.0072 mol) and methanol solution (10 ml) of NaOH (0,0060 mol) were added to a hot ethanol solution (50 ml) of copper(II) perchlorate (2.3 g, 0.0060 mol). The resulting green solution, after several hours, yielded green prisms, which were filtered and recrystallized from a hot methanol solution. In this procedure, it is to be noted that the use of an excess of diamine-alcohol is necessary in order to avoid the contamination of the blue trinuclear copper(II) complex.[7]

$[Cu(C_2H_5\text{-}2\text{-}3)]B(C_6H_5)_4$

The tetraphenylborate was obtained by adding NaB$(C_6H_5)_4$ to the methanol solution of the corresponding perchlorate. The copper(II) complexes of other N,N-dialkyldiaminealcohols were prepared according to a procedure similar to that described above. All the perchlorates can be recrystallized from a hot methanol solution. The tetraphenyl borates of the copper(II) complexes with N,N-dialkyldiaminealcohols are soluble in DMF, but sparingly soluble in methanol.

[Cu(R-n)X]

The copper(II) complexes with N,N-dialkylamino-alcohols were prepared according to the method of Uhlig *et al.*[1]

The results of elementary analyses of the new compounds are summarized in Table I.

Measurements

Electronic spectra were measured with a Hitachi recording spectrophotometer at room temperature. Magnetic susceptibilities in the range from liquid nitrogen to room temperature were determined by the Faraday method. Magnetic susceptibilities in benzene solutions were determined by the Evans method[8] at 308 K. All the susceptibilities were corrected for the diamagnetism of the constituting atoms by use of the Pascal constants.

Results and Discussion

Magnetic Properties

The temperature dependence of magnetic susceptibility for a magnetically isolated binuclear copper(II) complex was given by the Bleaney and Bowers equation.[9]

$$\chi = \frac{Ng^2\beta^2}{3\,kT}\{1+\frac{1}{3}\exp(-2J/kT)\}^{-1} + N\alpha \qquad (1)$$

where χ is susceptibility per gram atom of copper, N, g, J, β and Nα have the usual meanings. –2J is equal to the seperation of singlet and triplet states. J, g, and Nα were determined by the best fit of the theoretical χ–T curves to the experimentally obtained one, and are tabulated in Table II. The molar susceptibilities were calculated on the basis of the formula weight indicated in Table I and effective magnetic moments were calculated by use of the equation (2).

$$\mu_{eff} = \sqrt{8(\chi - N\alpha)\,T} \qquad (2)$$

The magnetic susceptibilities of the type A complexes generally decrease with lowering of temperature. Some examples are shown in Figure 3. The magnetic behavior of the type A complexes can be interpreted with the equation (1), except for $[Cu(CH_3\text{-}3\text{-}2)]ClO_4$ and $[Cu(C_2H_5\text{-}3\text{-}2)]ClO_4$, for which theoretical interpretation seems to be difficult and is under investigation at present. As seen in Table II, J values of all the type A complexes are negative, indicating that antiferromagnetic interaction is operative in the crystals.

On the other hand, the magnetic susceptibilities of the type B complexes increase with lowering of temperature over the range 80–295 K, obeying the Curie–Weiss law, as shown in Figure 4. The Weiss constants were evaluated by extraporating the χ^{-1}–T curves, and the results are summarized in Table IV. As seen in

TABLE II Magnetic Data of Type A Complexes

Complexes	μ_{eff}(293 K) (B M)	$-2J$ (cm^{-1})	g	$N\alpha \times 10^6$ (e s u /mol)
[Cu(H 2 3)]ClO$_4$	0 65	700	2 10	70
[Cu(H 3 2)]B(C$_6$H$_5$)$_4$	0 96	495	2 06	80
[Cu(H 3 3)]NO$_3$	0 54	795	2 10	50
[Cu(CH$_3$ 2 3)]ClO$_4$	0 93	530	2 08	60
[Cu(CH$_3$ 3 2)]B(C$_6$H$_5$)$_4$	0 95	515	2 08	60
[Cu(CH$_3$ 3 3)]ClO$_4$	0 97	500	2 15	50
[Cu(C$_2$H$_5$ 2 3)]ClO$_4$	0 93	530	2 08	35
[Cu(C$_2$H$_5$ 3 2)]B(C$_6$H$_5$)$_4$	0 87	565	2 08	50
[Cu(C$_2$H$_5$ 2)Br]	0 50	840	2 10	40
[Cu(CH$_3$ 3)Cl]	diamag	>1100	–	–
[Cu(CH$_3$ 3)Br]	0 27	1070	2 10	40

TABLE III Spectral Data of Alkoxo bridged Copper(II) Complexes

Complexes	Type	Reflectance (kK)		Absorption (kK)	
[Cu(H 3 2)]B(C$_6$H$_5$)$_4$	A	17 6	26 5	17 0	28 0
[Cu(CH$_3$ 2 3)]ClO$_4$	A	16 5	25 0	14 9	24 5
[Cu(CH$_3$ 3 2)]ClO$_4$	A	15 4	27 0	15 4	27 0
[Cu(CH$_3$ 2 3)]B(C$_6$H$_5$)$_4$	A	16 8	25 5	15 0	25 4
[Cu(CH$_3$ 3 2)]B(C$_6$H$_5$)$_4$	A	16 3	25 9	15 5	26 9
[Cu(CH$_3$ 3 3)]ClO$_4$	A	16 3	22 6	15 6	24 5
[Cu(C$_2$H$_5$ 3 2)]ClO$_4$	A	16 5	25 0	15 6	26 5
[Cu(C$_2$H$_5$ 3 2)]B(C$_6$H$_5$)$_4$	A	15 5	25 6	15 2	25 6
[Cu(H 3 2)]ClO$_4$	B	17 0	–	16 4	25 6
[Cu(H 3 2)]Cl	B	16 7	–	16 4	27 5
[Cu(n Bu 2)Cl]	B	14 4	–	18 5	25 6
[Cu(n Bu 2)Br]	B	14 3	–	18 0	25 6

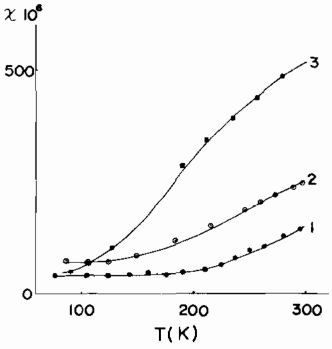

Figure 3 Temperature dependence of magnetic susceptibilities of type A complexes (1) [Cu(C$_2$H$_5$ 2)Br] (2) [Cu (H 2 3)]C10$_4$ (3) [Cu(CH$_3$ 3 3)]C10$_4$

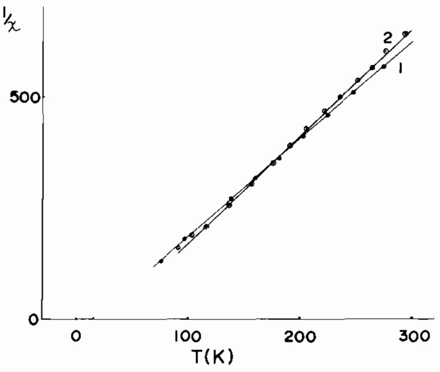

Figure 4 Temperature dependence of magnetic susceptibilities of type B complexes (1) [Cu(H 3 2)]C10$_4$ (2) [Cu (n Bu 2)Br]

the Table all the Weiss constants are positive This implies that ferromagnetic interaction is operative in these complexes, because there can not be found any reason in the copper(II) complexes to cause positive Weiss constants other than ferromagnetic interaction between copper ions[10 11] and furthermore the ESR study[3] for some of the present complexes supports the ferromagnetic interaction

Spectral Properties

The spectral properties of the type A and the type B complexes are summarized in Table III. Some of the reflectance spectra of the type A and the type B complexes are shown in Figure 5 and Figure 6, respectively. It is apparent that all the type A complexes show distinct absorption bands in the near-ultraviolet region (24–29 kK), whereas the type B complexes do not in solid spectra. On the basis of these results, the empirical rule may be established for magnetic and spectral properties of alkoxo-bridged copper(II) complexes: "An intramolecular antiferromagnetic interaction is operative for the complexes which show distinct absorption bands in the near-ultraviolet region (24–29 kK), whereas no antiferromagnetic interaction but a weak ferromagnetic interaction is operative for the complexes which show no distinct absorption bands in the near-ultraviolet region."*

As shown in Figure 7, in the solution spectra of the type A complexes, distinct absorption bands are observed in the near-ultraviolet region, as in the case of reflectance spectra. However, the solution spectra of the type B complexes show quite different spectra from those of the solid state, showing distinct bands in the near-ultraviolet region.[1,3] According to our empirical rule, this fact is indicating that type A complex is formed, at least in part in a solution of type B complex. In order to confirm this, the magnetic moments of the type B complexes in benzene solutions were determined by the Evans method at 308 K. The results are summarized in Table IV. As expected, the type B complexes in benzene solutions show subnormal magnetic moments, indicating that there are equilibriums type A $\rightleftharpoons$ type B in solutions. Thus, the magnetic and spectral properties of type B complexes in solutions are consistent with our empirical rule.

Explanation for the Empirical Rule

In the previous paper,[4] we attributed the near-ultraviolet absorption bands to charge transfer transitions from nonbonding orbitals of bridging oxygen atoms to the vacant copper *d*-orbital, and appearance of the bands in the near-ultraviolet region was interpreted in terms of the red shift due to the decreasing of *s*-character of the nonbonding orbitals enforced by the steric requirement of the complex. As for the mechanism of magnetic interaction in binuclear copper(II) complexes, many experimental evidences have been reported in favour of the superexchange mechanism through the π-paths.[12–17]

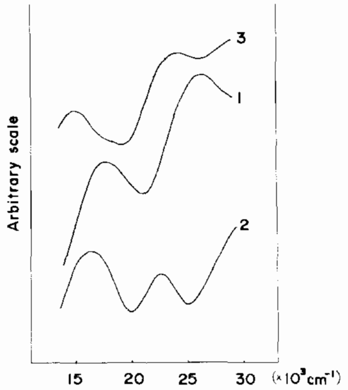

Figure 5. Reflectance spectra of type A complexes. (1): [Cu(H-3-2)]B(C_6H_5)$_4$; (2): [Cu(CH_3-3-3)]ClO_4; (3): [Cu(CH_3-3)Br].

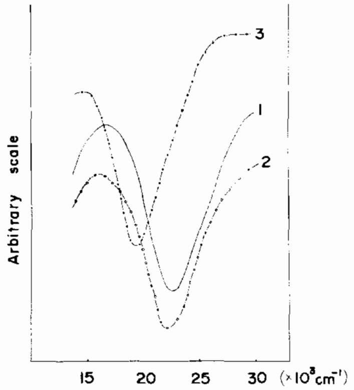

Figure 6. Reflectance spectra of type B complexes. (1): [Cu(H-3-2)]ClO_4; (2): [Cu(H-3-2)]Cl; (3): [Cu(n-Bu-2)Cl].

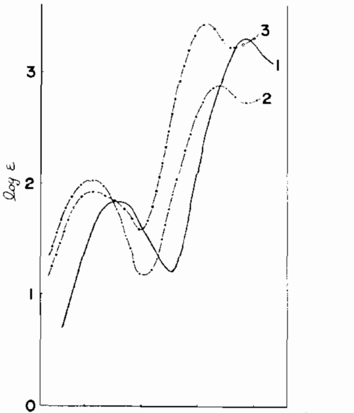

Figure 7. Absorption spectra of type A complexes. (1): [Cu(C_2H_5-2-3)]ClO_4 in MeOH; (2): [Cu(CH_3-3-2)]ClO_4 in MeOH; (3): [Cu(CH_3-3)Cl] in $CHCl_3$.

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* This relation is not very clear-cut in some halogeno complexes such as [Cu(n-Bu-2)Cl], probably due to the presence of CT bands of halogeno-origin. However, it should be noted that the contours of the spectral curves for the type A and B complexes are quite different, as exemplified in Fig. 5 and Fig. 6.

TABLE IV. Magnetic Data of Type B Complexes.

Complexes	μ_{eff}(293 K)[d] (B.M.)	Weiss Constant (degree)	μ_{eff}(308 K) in C_6H_6 (B.M.)
[Cu(H-3-2)]ClO_4	1.93	+15	[a]
[Cu(H-3-2)]Cl	1.88	+16	[a]
[Cu(n-Bu-2)Cl]	1.91	+32	1.1[b]
[Bu(n-Bu-2)Br]	1.90	+36	0.5[c]

[a] The measurement was not carried out because of low solubility for organic solvents. [b] 0.045 mol/l. [c] 0.080 mol/l.
[d] $\mu_{eff} = \sqrt{8(\chi-60)T}$.

On the basis of the above points of view, the simultaneous absence of the near-ultraviolet bands and antiferromagnetic interaction in the type B complexes can be explained in terms of the absence of nonbonding p_π-orbitals of the bridging oxygen atoms. In another words, the establishment of this empirical rule is a strong evidence for the CT-origin of the near-ultraviolet bands and suggesting the spin exchange mechanism through π-paths.

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