Binuclear Metal Complexes. X.[1] Preparation and Magnetism of Mononuclear and Binuclear Copper(II) Complexes of Schiff Bases Derived from 4,6-Diacetylresorcine and Polyamines

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New binuclear complexes $Cu_2X_2dar(en\text{-}R)_2$ and $[Cu_2dar(dien)_2](ClO_4)_2\cdot H_2O$ were synthesized, $H_2dar(A)_2$ being a Schiff base prepared from 4,6-diacetylresorcinol and an amine A; A stands for *N,N*-dialkylethylenediamine(=en-R, R=C_2H_5 or *iso*-C_3H_7) or diethylenetriamine(=dien). Mononuclear complexes CuXHdar(en-R) were also prepared for comparison. Two copper(II) ions of the binuclear complexes are separated from each other by the benzene ring. Magnetic susceptibilities of the compounds were measured in the temperature range 77.4~300 K. It was found by means of the plots of χ_A^{-1} *versus* T that all the compounds obey the Curie-Weiss law. The Weiss constants for the binuclear complexes (−10~−34 K) indicate the presence of antiferromagnetic interactions between copper(II) ions through the conjugated π-system of 4,6-diacetylresorcinol moiety, whereas those of the mononuclear complexes are practically zero, showing that the intermolecular interaction is negligibly small.

A number of reports[2-4] have appeared on polynuclear copper(II) complexes which exhibit subnormal magnetic moments. In most of them the copper(II) ions are kept in close proximity by bridging groups.

Some polynuclear copper(II) complexes which exhibit magnetic moments lower than 1.73 B.M., in spite of the considerably long distance between the metal ions, are polymeric copper(II) complexes formed by a catena-μ-group such as pyrazine,[5] quinoxaline[6] and their derivatives,[7,8] and binuclear copper(II) complexes of complicated ligands such as 1,2,4,5-tetraaminobenzene-derivatives[9] and oxamide-derivatives.[10] The magnetic behaviors of these complexes could be explained on the basis of antiferromagnetic exchange interaction between the copper(II) ions through the π-conjugated system of the ligand. In order to obtain an additional information on long distance spin-coupling in binuclear copper(II) complexes, we have prepared a new class of binuclear copper(II) complexes with the use of di-Schiff bases of 4,6-diacetylresorcinol. The complexes obtained are $Cu_2X_2dar(en\text{-}R)_2$ (X=Cl or Br and R=C_2H_5(Et) or *iso*-C_3H_7(*i*-Pr)) and $[Cu_2dar(dien)_2](ClO_4)_2\cdot H_2O$, where $H_2dar(en\text{-}R)_2$ and $H_2dar(dien)_2$ are the di-Schiff bases of 4,6-diacetylresorcine with *N,N*-dialkylethylenediamines and diethylenetriamine, respectively. Two copper(II) ions are separated from each other by 4,6-diacetylresorcinol moiety.

The mononuclear copper(II) complexes CuXHdar(en-R) (X=Cl or Br and R=Me, Et or *i*-Pr) were prepared, $H_2dar(en\text{-}R)$ denoting the mono-Schiff bases prepared from 4,6-diacetylresorcinol and *N,N*-dialkylethylenediamine. The new compounds were characterized on the basis of elemental analyses, and IR and visible spectra. Magnetic properties of the binuclear complexes were discussed in comparison with those of the mononuclear complexes.

Experimental

Syntheses. 4,6-Diacetylresorcinol was synthesized according to Baker's method.[11]

$Cu_2X_2dar(en\text{-}R)_2$ Complexes. These complexes were prepared by practically the same method. A typical procedure is as follows for $Cu_2Cl_2dar(en\text{-}Et)_2$. *N,N*-Diethylethylenediamine (232 mg, 2 mmol) and 2,2-dimethoxypropane (1 g) were added to an anhydrous methanolic solution (50 ml) of 4,6-diacetylresorcinol (194 mg, 1 mmol) and the reaction mixture was refluxed for 4~5 hr. To this solution were added anhydrous copper(II) chloride (268 mg, 2 mmol) and triethylamine (202 mg, 2 mmol), and the mixture was refluxed for 1~2 hr. Triethylamine was added as a proton-acceptor, without which the binuclear complexes could not be obtained probably due to the decomposition of the Schiff base. The brown needles separated were collected and washed with anhydrous methanol.

$[Cu_2dar(dien)_2](ClO_4)_2\cdot H_2O$. To an anhydrous methanolic solution (50 ml) of 4,6-diacetylresorcinol (194 mg) were added $[Cu(dien)H_2O](ClO_4)_2$ (750 mg), 2,2-dimethoxypropane (1 g) and triethylamine (202 mg). The mixture was heated under stirring for 2 hr and concentrated to 20 ml to give pink prisms which were filtered and recrystallized from methanol.

CuXHdar(en-Me) and CuXHdar(en-Et) Complexes. These complexes were prepared by practically the same method. A typical procedure is as follows for CuClHdar(en-Me). *N,N*-Dimethylethylenediamine (88 mg, 1 mmol) and 2,2-dimethoxypropane (1 g) were added to an anhydrous ethanolic solution (50 ml) of 4,6-diacetylresorcinol (194 mg, 1 mmol) and the reaction mixture was refluxed for 2~3 hr. Anhydrous copper(II) chloride (134 mg, 1 mmol) and triethylamine (101 mg, 1 mmol) were added to the solution which was refluxed for 1 hr and allowed to stand at room temperature overnight. The blue prisms separated were collected and washed with anhydrous ethanol.

CuClHdar(en-i-Pr). *N,N*-di(*iso*-propyl)ethylenediamine (144 mg, 1 mmol) and 2,2-dimethoxypropane (1 g) were added to an anhydrous methanolic solution (50 ml) of 4,6-diacetylresorcinol (194 mg, 1 mmol), and the reaction mixture was refluxed for 2~3 hr. Anhydrous copper(II) chloride (134 mg, 1 mmol) and triethylamine (101 mg, 1 mmol) were added to the solution which was refluxed for 1 hr. The hot solution gave the binuclear complex $Cu_2Cl_2dar(en\text{-}i\text{-}Pr)_2$ as brown crystals, which were filtered and the filtrate was allowed to stand overnight. The brown needles obtained from the filtrate were collected and washed with anhydrous methanol.

Analytical data are given in Table 1.

Measurements. Infrared spectra were measured with a

Table 1. Elemental analyses of complexes

Complex	C(%)		H(%)		N(%)	
	Calcd	Found	Calcd	Found	Calcd	Found
$Cu_2Cl_2dar(en\text{-}Et)_2$	45.05	45.00	6.19	6.17	9.55	9.46
$Cu_2Br_2dar(en\text{-}Et)_2$	39.12	39.17	5.37	5.27	8.29	8.21
$Cu_2Cl_2dar(en\text{-}i\text{-}Pr)_2\cdot MeOH$	48.06	47.59	7.17	7.00	8.30	8.04
$Cu_2Br_2dar(en\text{-}i\text{-}Pr)_2$	42.69	43.20	6.06	6.17	7.66	7.41
$[Cu_2dar(dien)_2](ClO_4)_2\cdot H_2O$	30.60	30.36	4.57	4.50	11.89	11.79
CuClHdar(en-Me)	46.41	46.36	5.28	5.29	7.73	7.75
CuBrHdar(en-Me)	41.43	41.52	4.71	4.88	6.89	6.55
CuClHdar(en-Et)	49.23	48.96	5.91	6.15	7.16	6.93
CuBrHdar(en-Et)	44.20	43.99	5.33	5.79	6.44	6.19
CuClHdar(en-*i*-Pr)·1/2MeOH	51.15	51.49	6.72	7.00	6.45	6.39

Hitachi Grating Infrared Spectrometer model 215 in the region 4000~650 cm^{-1} on a KBr disk. Reflectance spectra were measured with a Shimadzu Multipurpose Spectrometer model MPS-50L at room temperature. Magnetic susceptibilities were determined by the Faraday method in the range from liquid nitrogen temperature to room temperature. Effective magnetic moments $\mu_{\rm eff}$ were calculated by the equation

$$\mu_{\rm eff} = 2.828\sqrt{(\chi_A - N\alpha)T}$$

where χ_A is the atomic susceptibility corrected for diamagnetism by the use of Pascal's constants[12] and $N\alpha$ denotes the temperature independent paramagnetism of copper(II) ions.

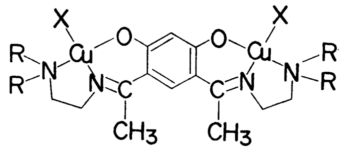
Results and Discussion

The yield of the binuclear complex $Cu_2X_2dar(en\text{-}R)_2$ is highly dependent on the substituent R. We were successful in obtaining $Cu_2X_2dar(en\text{-}i\text{-}Pr)_2$ in a high yield and $Cu_2X_2(en\text{-}Et)_2$ in a low yield, all the attempts to obtain $Cu_2X_2(en\text{-}Me)_2$ being unsuccessful. Attempts to prepare the binuclear complexes, $[Cu_2dar(en\text{-}R)_2Sol_2](ClO_4)_2$ (Sol denotes a solvent molecule, such as water, methanol or ethanol) were unsuccessful. This is probably because the desired compounds decompose in the solvent into monomeric species. On the other hand, $[Cu_2dar(dien)_2](ClO_4)_2\cdot H_2O$ was easily obtainable. It seems that the larger chelate effect operates for $[Cu_2dar(dien)_2](ClO_4)_2\cdot H_2O$ as compared with $[Cu_2dar(en\text{-}R)_2Sol_2](ClO_4)_2$. The ligand field effect can contribute to the stabilization of $[Cu_2dar(dien)_2](ClO_4)_2\cdot H_2O$.

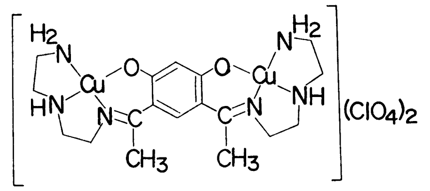
Table 2. IR and visible spectral data of complexes

Complex	IR (cm^{-1})		Reflectance ($\times 10^3$ cm^{-1})	
	C=O	C=N	d-d	C.T.
$Cu_2Cl_2dar(en\text{-}Et)_2$	—	1590	16.1	20.9
$Cu_2Br_2dar(en\text{-}Et)_2$	—	1595	16.0	20.6
$Cu_2Cl_2dar(en\text{-}i\text{-}Pr)_2\cdot MeOH$	—	1595	15.7	20.8
$Cu_2Br_2dar(en\text{-}i\text{-}Pr)_2$	—	1595	15.4	20.0
$[Cu_2dar(dien)_2](ClO_4)_2\cdot H_2O$	—	1580	17.9	—
CuClHdar(en-Me)	1650	1600	15.6	22.5
CuBrHdar(en-Me)	1650	1600	15.7	22.0
CuClHdar(en-Et)	1630	1580	15.6	22.2
CuBrHdar(en-Et)	1630	1595	15.7	21.4
CuClHdar(en-*i*-Pr)·1/2MeOH	1650~1620	1600~1580	16.1	21.6

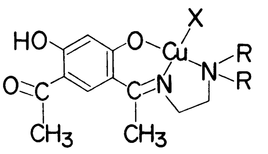
The infrared and visible spectral data of the binuclear and the mononuclear complexes are given in Table 2. In the binuclear copper(II) complexes no absorption band was found in the region 1700~1600 cm^{-1}, while in the mononuclear copper(II) complexes a strong band due to the C=O stretching vibration of free acetyl group was found near 1630 cm^{-1}. The absorption band which is attributable to the C=N stretching vibration is observed in the region 1600~1580 cm^{-1}. This band is superposed by the skeletal vibration of the aromatic ring. The broad and strong band around 1100 cm^{-1} in $[Cu_2dar(dien)_2](ClO_4)_2\cdot H_2O$ is attributable to the non-coordinated perchlorate ion. The reflectance spectra of $Cu_2X_2dar(en\text{-}R)_2$ and CuXHdar(en-R) show a ligand field band in the region 16.1~15.4 kK. A band was observed at 20~22.5 kK in addition to the d-d band. Since no such a band is present in the spectrum of $[Cu_2dar(dien)_2](ClO_4)_2\cdot H_2O$, and the bands for $Cu_2Cl_2dar(en\text{-}R)_2$ and CuClHdar(en-R) are located at higher energy region as com-



$Cu_2X_2dar(en\text{-}R)_2$ X=Cl, Br R=Et, *i*-Pr



$[Cu_2dar(dien)_2](ClO_4)_2$



CuXHdar(en-R) X=Cl, Br
R=Me, Et, *i*-Pr

Fig. 1. Proposed structures of complexes.

Table 3. Magnetic data of complexes

Complex	θ(K)	μ_{eff}(T)	
Cu_2Cl_2dar(en-Et)$_2$	−20	1.66 (78.1)	1.80 (288.0)
Cu_2Br_2dar(en-Et)$_2$	−12	1.66 (83.7)	1.75 (290.0)
Cu_2Cl_2dar(en-*i*-Pr)$_2$·MeOH	−34	1.66 (81.0)	1.85 (297.8)
Cu_2Br_2dar(en-*i*-Pr)$_2$	−10	1.62 (80.6)	1.75 (297.8)
[Cu_2dar(dien)$_2$]-(ClO_4)$_2$·H_2O	−17	1.69 (83.9)	1.75 (297.8)
CuClHdar(en-Me)	−1	1.76 (83.6)	1.78 (297.8)
CuBrHdar(en-Me)	−2	1.75 (78.3)	1.79 (297.8)
CuClHdar(en-Et)	−2	1.73 (86.0)	1.76 (293.0)
CuBrHdar(en-Et)	0	1.74 (84.1)	1.78 (295.4)
CuClHdar(en-*i*-Pr)·1/2MeOH	0	1.74 (81.2)	1.74 (297.8)

pared with those for the bromo homologues, it is natural to assign the band to the charge transfer band from the halogen ion to the copper(II) ion. This implies that the halogen ion is coordinated to the copper(II) ion. It is thus concluded that the complexes have the structures given in Fig. 1.

The magnetic susceptibilities of the binuclear and mononuclear copper(II) complexes were measured over the temperature range 77.4~300 K. The effective magnetic moments at room temperature and near liquid nitrogen temperature are given in Table 3. The effective magnetic moments of the binuclear copper(II) complexes and those of the mononuclear copper(II) complexes show nearly the same values; all the values being larger than the spin-only value, 1.73 B.M. Although the magnetic moment of each mononuclear copper(II) complex near liquid-nitrogen temperature is nearly equal to that at room temperature, the magnetic moments of the binuclear copper(II) complexes are considerably lower than those at room temperature. The reciprocal of $\chi_A - 60\times10^{-6}$ was plotted against temperature. Typical examples for the binuclear and the mononuclear complexes are shown in Fig. 2. The magnetism for the complexes is interpreted in terms of the Curie-Weiss law, $\chi_A = C/(T-\theta)$. The Weiss constants of the complexes are also given in Table 3. The Weiss constants of the mononuclear complexes are nearly zero. This fact clearly indicates that the intermolecular magnetic spin-exchange interaction is negligibly small. On the other hand, the Weiss constants of binuclear copper(II) complexes are in the range −10~−34 K. In comparison with the magnetic properties of mononuclear copper(II) complexes, the antiferromagnetisms of the binuclear copper(II) complexes are attributable to an intramolecular spin-exchange interaction through the π-pathway of 4,6-diacetylresorcine moiety.

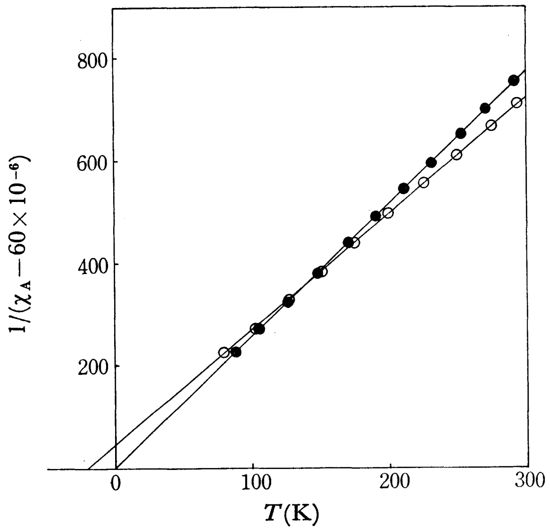


Fig. 2. Plots of reciprocal atomic susceptibilities of (○) Cu_2Cl_2dar(en-Et)$_2$ and (●) CuClHdar(en-Et) as a function of temperature.

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