Synthesis and Characterization of a New Family of Binuclear Copper(II) Complexes with a Flexible Bridge and the π–π Type Charge-transfer Interaction with 1,3,5-Trinitrobenzene

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Copper(II) complexes with unsymmetrical quadridentate Schiff bases, composed of the 1 : 1 : 1 condensation products of salicylaldehyde derivatives (salicylaldehyde, 2-hydroxy-1-naphthalenecarbaldehyde, *o*-hydroxyacetophenone), diamine (ethylenediamine, trimethylenediamine), and acetylacetone, react electrophilically with hexamethylene di-isocyanate or *m*-xylene di-isocyanate in 2:1 mol ratio to produce the binuclear copper(II) complexes with a hexamethylene dicarbamoyl or *m*-xylene dicarbamoyl bridging group. The binuclear copper(II) complexes were characterized by elemental analyses, melting points, molecular weights, and i.r., e.s.r., and electronic spectra. The binuclear copper(II) complex containing a naphthalene moiety as π-electron donor interacts with 1,3,5-trinitrobenzene (tnb) to form a 1 : 1 molecular complex exhibiting a new absorption band attributable to the charge transfer between the naphthalene moiety and tnb, both in the solid and in solution. The 1 : 1 molecular complex between the mononuclear parent complex and tnb showed the charge-transfer band in the solid but not in solution.

Binuclear metal complexes in which the ligand framework is positioned to promote the substrate bindings are of current interest,[1] since the structural unit is thought to be involved in a variety of biological processes such as oxygen transport and oxygen activation.[2] Recently a number of binuclear metal complexes have been designed and synthesized in order that the ligand framework can structurally interact with an organic substrate or oxygen molecule.[1,3] A metal complex containing a six-membered di-iminato- or acetylacetonato-chelate ring can be an effective starting compound for the preparation of a binuclear metal complex, since it is expected that such a complex would react with electrophilic reagents containing two reaction sites to produce a binuclear complex selectively. From this viewpoint we are interested in metal complexes containing a nucleophilic centre.[4]

In this study, we report the synthesis and properties of binuclear copper(II) complexes produced by the electrophilic substitution reaction of unsymmetrical quadridentate Schiff-base copper(II) complexes and a di-isocyanate (hexamethylene di-isocyanate or *m*-xylene di-isocyanate), according to the reaction procedure shown in Figure 1, where the unsymmetrical quadridentate Schiff base is composed of a 1:1:1 condensation product of a salicylaldehyde derivative, diamine, and acetylacetone. The binuclear copper(II) complexes were characterized by elemental analyses, melting points, molecular weights, and i.r., e.s.r., and electronic spectra. The π–π type charge-transfer interaction between the binuclear copper(II) complex and 1,3,5-trinitrobenzene (tnb) was examined based on the electronic spectra, and compared with that between the parent copper(II) complex and tnb.

Experimental

Synthesis of Parent Copper(II) *Complexes*.—The unsymmetrical quadridentate copper(II) complexes used in this work [CuL] (L = L^1—L^4) were prepared by the procedure reported earlier,[5,6] and identified by elemental analyses and melting points.

Binuclear Copper(II) *Complexes*.—The binuclear copper(II) complexes were prepared by the electrophilic substitution

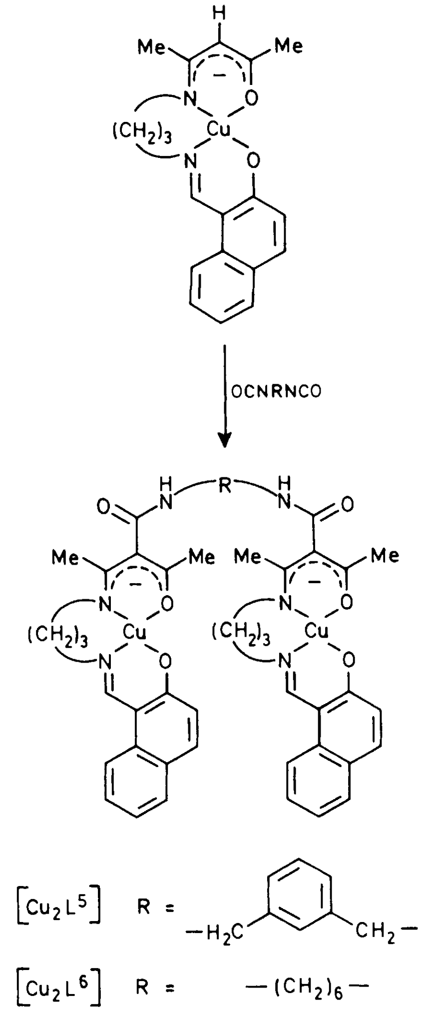
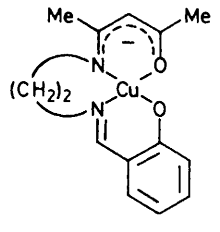
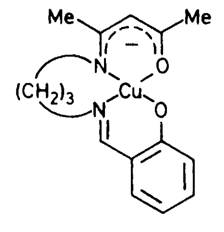


Figure 1. Scheme for the reaction of the mononuclear copper(II) complex [CuL^3] to give the binuclear copper(II) complexes [Cu_2L^5] and [Cu_2L^6]



$[CuL^1]$



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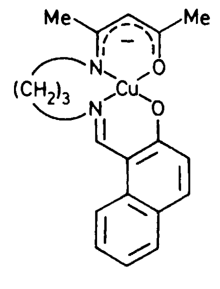
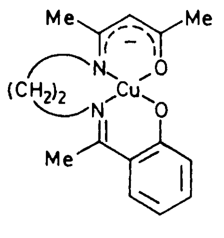
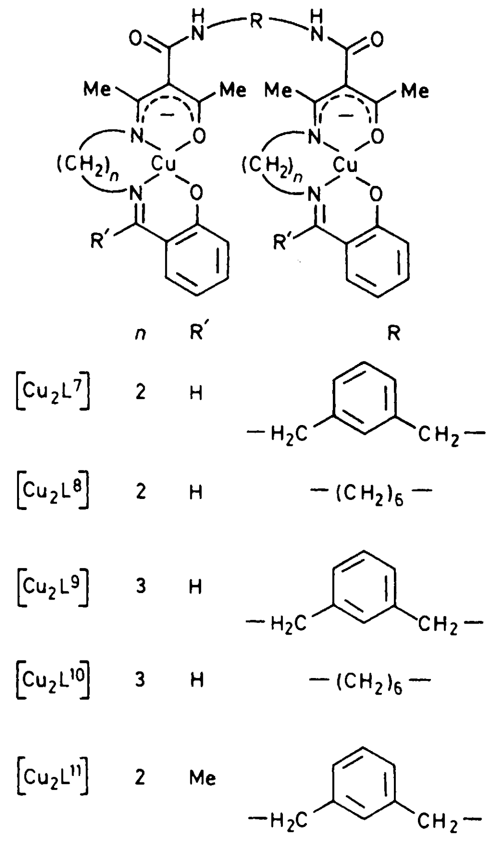


$[CuL^3]$



$[CuL^4]$



reaction at the γ-position of the acetylacetonate residue of the parent copper(II) complex with hexamethylene di-isocyanate or *m*-xylene di-isocyanate, according to the reaction procedure shown in Figure 1. The reaction procedure is exemplified by the preparation of $[Cu_2L^9]$ in detail. To a solution of $[CuL^2]$ (20 mmol) in benzene (50 cm^3) was added a solution of *m*-xylene di-isocyanate (10 mmol) in benzene (30 cm^3). The mixture was refluxed for 6 h and the solution volume was reduced by half and n-hexane (20 cm^3) was added. The resulting precipitate was filtered off, washed with benzene and diethyl ether, and dried *in vacuo*. The other binuclear copper(II) complexes were prepared by a similar method using dichloromethane or benzene as reaction solvent.

Charge-transfer Complexes between Copper(II) *Complexes and* 1,3,5-*Trinitrobenzene*.—$[CuL^3]$·tnb. To a solution of $[CuL^3]$ (190 mg) in dichloromethane (10 cm^3) was added a solution of 1,3,5-trinitrobenzene (tnb) (18.2 mg) in acetone (10 cm^3). The mixture was warmed for several minutes on a water-bath and allowed to stand for several hours, during which time fine dark red crystals precipitated. They were filtered off, washed with diethyl ether, and dried *in vacuo*.

$[Cu_2L^6]$·tnb. A dark green solution of $[Cu_2L^6]$ (10 mmol) in chloroform (30 cm^3) and a colourless solution of tnb (30 mmol) in acetone were mixed and warmed for 30 min on a water-bath, and the colour changed from green to red. The solution was adsorbed on a Florisil column. Acetone and chloroform were eluted to remove unreacted starting materials, and then *NN*-dimethylformamide (dmf) was eluted to give a dark red solution. The solution was collected, the volume reduced to *ca.* 10 cm^3, and diethyl ether was added. The resulting precipitates were collected, washed with diethyl ether, and dried *in vacuo*.

Physical Measurements.—Melting points were measured on a Yanagimoto micromelting-point apparatus and are uncorrected. Elemental analyses were performed by Mr. Shinichi Miyazaki at the Technical Service Center of Kumamoto University. Thermogravimetric analyses (t.g.a.) were carried out on a Shimadzu TGC 20 type microthermobalance at the heating rate of 5 °C min^{-1}, using *ca.* 10 mg of the sample for each run. Molecular weights were estimated in chloroform solution on a Corona 114 vapour pressure osmometer. Visible and u.v. spectra in $CHCl_3$ solution were recorded with a Hitachi 323 spectrophotometer, and electronic spectra in Nujol mulls were measured on a Shimadzu UV-200 spectrophotometer. I.r. spectra were recorded as KBr discs or Nujol mulls with a Shimadzu IR-410 spectrophotometer. E.s.r. spectra (*X*-band) were measured in dmf solution at room temperature and liquid-nitrogen temperature on a JEOL-FEAX spectrometer, using Mn^{2+} doped in MgO as reference.

Results and Discussion

Syntheses.—The γ-positions of the six-membered di-iminato- and acetylacetonato-chelate rings have been found to be very reactive nucleophilic centres.[7] The present copper(II) complexes with unsymmetrical quadridentate Schiff bases, composed of 1:1:1 condensation products of a salicylaldehyde derivative, diamine, and acetylacetone, react with an electrophilic reagent containing two reaction sites such as hexamethylene di-isocyanate or *m*-xylene di-isocyanate to produce the binuclear copper(II) complexes selectively and almost quantitatively. The structural parameters associated with the co-ordination sphere such as the distortion of the co-ordination environment and those of the bridging moiety such as the orientation of two co-ordination planes and the metal–metal distance can be varied easily and independently.

Elemental analytical data, melting points, and molecular weights estimated by vapour pressure osmometry are given in Table 1. Some of the complexes tend to crystallize as solvates. The solvents in the crystals were detected by t.g.a., where the weight losses corresponding to those expected from the

Table 1. Elemental analytical data, melting points, and molecular weights

Complex	Analysis* (%) C	H	N	M.p. (°C)	*M**
$[Cu_2L^{10}]\cdot 0.5CH_2Cl_2$	54.0	5.80	10.15	133 (de-	758
	(54.1)	(5.80)	(9.85)	comp.)	(811.9)
$[Cu_2L^6]\cdot 0.5CH_2Cl_2$	58.6	5.85	8.80	167—170	906
	(58.5)	(5.60)	(8.80)		(912.0)
$[Cu_2L^9]\cdot 0.5C_6H_6$	59.3	5.35	9.65	165—167	891
	(59.2)	(5.45)	(9.65)		(831.9)
$[Cu_2L^5]$	61.85	5.15	8.60	198—203	951
	(61.85)	(5.20)	(9.00)		(932.0)
$[Cu_2L^{11}]$	57.95	5.40	10.1	259—260	
	(57.75)	(5.35)	(10.1)		
$[CuL^3]\cdot$tnb	51.3	3.90	11.85		
	(51.35)	(3.95)	(11.95)		
$[Cu_2L^6]\cdot$tnb$\cdot H_2O$	54.85	5.55	10.75		
	(54.65)	(5.05)	(11.05)		

* Calculated values are in parentheses.

Table 2. Electronic spectroscopic data in chloroform

Complex	$10^{-3}\tilde{\nu}/cm^{-1}(\varepsilon/dm^3\ mol^{-1}\ cm^{-1})$ *d–d*	Other
$[Cu_2L^{10}]$	16.7 (160)	26.5 (4 500)
$[Cu_2L^6]$	16.9 (170)	25.0 (6 700), 25.8 (6 400)
$[Cu_2L^9]$	16.5 (120)	26.7 (4 300)
$[Cu_2L^5]$	17.1 (140)	24.9 (5 400), 25.8 (5 200)

elemental analyses were observed. The molecular weights estimated by vapour pressure osmometry agree with the formation of the binuclear species.

Infrared Spectra.—The i.r. spectra of the binuclear copper(II) complexes differ from those of the component compounds, most notably in the absence of the intense band at *ca.* 2 250 cm^{-1} assignable to the C=N stretching mode of isocyanates. The binuclear copper(II) complexes possess new i.r. absorptions at *ca.* 1 650 and 3 250br cm^{-1} assignable to ν(C=O) and ν(NH) of the substituted -CONH- group, based on the analogy of the reaction products of *NN'*-ethylenebis(acetylacetoneiminato)-copper(II) and isocyanates.[8]

Electronic Spectra of the Binuclear Copper(II) *Complexes.*—Visible and u.v. spectra were measured in chloroform solution at room temperature, and the absorption maxima and absorption coefficients are given in Table 2. The spectra consist of a band in the visible region assignable to the *d–d* transition with an absorption coefficient of *ca.* 150 dm^3 mol^{-1} cm^{-1} and several bands in the u.v. region assignable to charge-transfer transitions. The *d–d* transition of the $NCH_2CH_2CH_2NCu$ chelated complex has a lower wavenumber than that of the NCH_2CH_2NCu chelated complex, suggesting that the co-ordination geometry of the former complex is distorted from square planar, compared to that of the latter.[9] The electronic spectra of the binuclear copper(II) complexes resemble those of the corresponding parent copper(II) complexes both in band maxima and absorption coefficients; no effects of substitution on the formation of the binuclear species were observed.

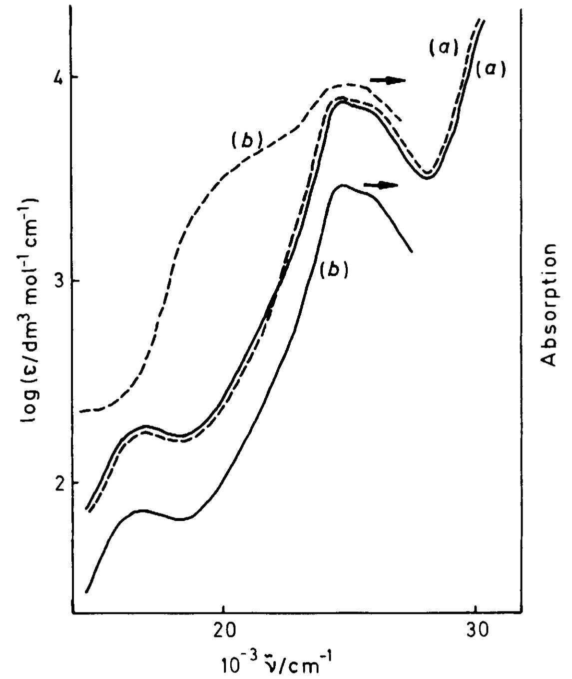


Figure 2. Electronic spectra of $[CuL^3]$ (———) and $[CuL^3]\cdot$tnb (— — —) in chloroform solution (*a*) and in Nujol mull (*b*)

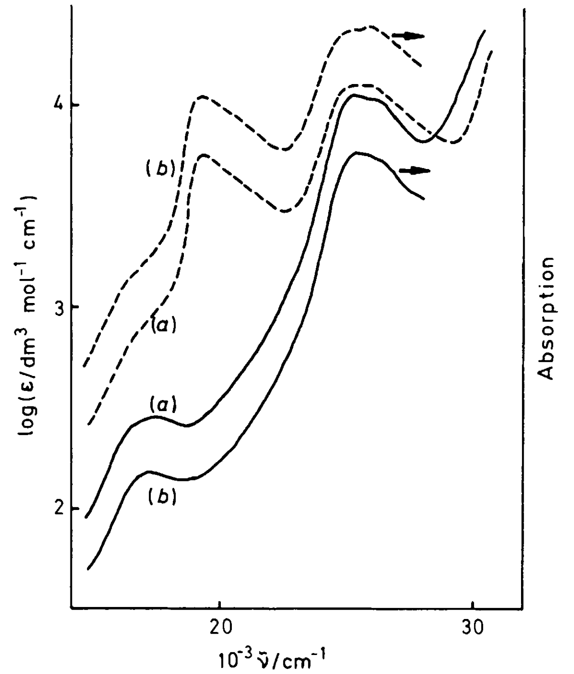


Figure 3. Electronic spectra of $[Cu_2L^6]$ (———) and $[Cu_2L^6]\cdot$tnb (— — —) in chloroform solution (*a*) and in Nujol mull (*b*)

Interaction with 1,3,5-*Trinitrobenzene.*—The green copper(II) complex containing a naphthalene moiety as π-electron donor, $[CuL^3]$, forms a red 1 : 1 charge-transfer complex, $[CuL^3]\cdot$tnb, with 1,3,5-trinitrobenzene as π-electron acceptor. The electronic spectra of the 1 : 1 molecular complex in chloroform solution and in a Nujol mull, along with the spectrum of the parent complex, are shown in Figure 2. The spectrum of the 1 : 1 charge-transfer complex $[CuL^3]\cdot$tnb shows a new absorption band attributable to a charge-transfer interaction between the naphthalene moiety of the complex and tnb. However, in chloroform solution, the band disappeared and the spectrum is

Table 3. E.s.r. parameters * in dmf

Complex	g_0	$g_\parallel$	$g_\perp$	A_0	$A_\parallel$	$A_\perp$
$[Cu_2L^8]$	2.113	2.188	2.076	93	210	35
$[Cu_2L^{10}]$	2.122	2.216	2.075	76	191	18
$[Cu_2L^6]$	2.125	2.237	2.069	82	179	33
$[Cu_2L^7]$	2.115	2.188	2.079	90	210	31
$[Cu_2L^9]$	2.124	2.238	2.067	77	177	28
$[Cu_2L^5]$	2.121	2.219	2.072	84	185	34
$[CuL^3]\cdot$tnb	2.120	2.233	2.064	78	182	26
$[Cu_2L^6]\cdot$tnb	2.130	2.221	2.085	82	185	30

* $g_\perp$ and $A_\parallel$ were calculated from the equations $g_0 = (g_\parallel + 2g_\perp)/3$ and $A_0 = (A_\parallel + 2A_\perp)/3$, using the observed values of g_0, A_0, $g_\parallel$, and $A_\parallel$.

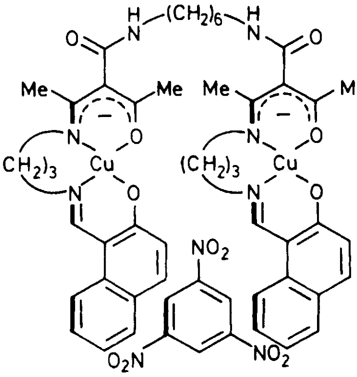


Figure 4. Proposed structure for $[Cu_2L^6]\cdot$tnb

consistent with that of the parent complex in band maxima and absorption coefficient, where the tnb molecule shows no absorptions in the region. This indicates that there is no charge-transfer interaction between $[CuL^3]$ and tnb in chloroform solution (*ca.* 2×10^{-4} mol dm^{-3}). This behaviour is the same in the case of the 1 : 2 charge-transfer complexes between bis[1-(*N*-alkyliminomethyl)-2-naphtholato)metal(II) and tnb.[10]

The binuclear copper(II) complex $[Cu_2L^6]$ forms a 1:1 molecular complex with tnb. The electronic spectra of the molecular complex $[Cu_2L^6]\cdot$tnb in chloroform solution and Nujol mull, along with the spectrum of the component complex $[Cu_2L^6]$ for comparison, are shown in Figure 3. The molecular complex exhibits a new band attributable to the charge-transfer transition between the naphthalene moiety and tnb in Nujol mull and even in chloroform solution (*ca.* 5×10^{-5} mol dm^{-3}). As shown in Figure 3, the spectrum of the molecular complex in Nujol resembles that in chloroform, suggesting that the charge-transfer interaction observed in the solid is preserved in solution. This indicates an intramolecular charge-transfer interaction, whose possible structure is shown in Figure 4.

E.S.R. Spectra.—E.s.r. spectra were measured in dmf solution at room temperature and at liquid-nitrogen temperature, and the parameters obtained are given in Table 3. The e.s.r. spectra of the complexes showed an axial pattern. Based on the $g_\parallel$ and $A_\parallel$ values, the complexes can be classified into two groups, that is, the $\overline{NCH_2CH_2NCu}$ and $\overline{NCH_2CH_2CH_2NCu}$ chelated complexes, where the $A_\parallel$ values of the latter are smaller than for the former complexes, and the reverse is the case for the $g_\parallel$ values. This tendency can be explained by tetrahedral distortion of the co-ordination environment, as already known for structurally well characterized complexes.[9] In fact, one of the $\overline{NCH_2CH_2CH_2NCu}$ chelated complexes, $[CuL^2]$, assumes a distorted tetrahedral co-ordination geometry with a dihedral angle of 19.1° between the two OCuN planes.[6] The spectra of the binuclear copper(II) complexes and the molecular complexes with tnb resemble those of the corresponding parent complexes. This implies that the metal–metal interaction is very weak in these complexes.[11]

Acknowledgements

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