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Binuclear Schiff Base Complexes of Nickel(II) or Copper(II) Linked by Dithiols as a Bridging Group

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Abstract

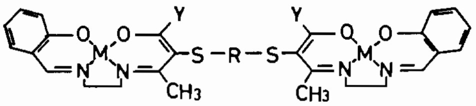
Binuclear Schiff base complexes of nickel(II) or copper(II) were synthesized by bridging unsymmetrical Schiff base complexes of nickel(II) and copper(II) with 2,5-dimercapto-1,3,4-thiadiazole or 2-mercaptoethyl ether.

Although the magnetic susceptibility and ESR measurements showed that copper(II)–copper(II) interaction of the binuclear copper(II) complexes is very weak in the solid state, they catalyzed chemiluminescence of luminol by hydrogen peroxide in DMF solution, suggesting that small amounts of the complexes might be present in the form of the appropriate copper(II)–copper(II) distance to activate hydrogen peroxide in solution.

Introduction

Many studies of rigid binuclear copper(II) complexes have been reported: their magnetic properties and catalytic activites have been the subject of recent extensive investigations [1–7]. The binuclear copper(II) complexes with flexible bridging groups have particularly drawn attention for their structural resemblance to Type-III copper proteins in the biological system: Nishida *et al.* reported that the flexible binuclear copper(II) complexes exhibit a catalytic activity for the oxidation of N,N,N′N′-tetramethyl-1,4-diaminobenzene (TMPD) by dioxygen [8, 9].

In this paper, new type binuclear complexes of nickel(II) or copper(II), in which mononuclear Schiff base complexes are linked by dithiols, are reported, and their magnetic properties and catalytic activity on chemiluminescence of luminol are studied. The abbreviation of the complexes used in this study is shown in Fig. 1.



M = Ni(II), Cu(II)
Y = methyl, phenyl
HS–R–SH = 2,5-dimercapto-1,3,4-thiadiazole --- A
2-mercaptoethyl ether ------------------------------ B
D(M, –SRS–, Y)

Fig. 1. The abbreviation of the binuclear Schiff base complexes linked by dithiols.

Experimental

Synthesis

[N-(2-bromo-1-methyl-3-oxobutylidene)-N′-salicylideneethylenediaminato] copper(II), Cu(L-Br, CH_3), was prepared by the method previously described [10]. Other derivatives were prepared by a similar method.

Binuclear Copper(II) Complexes

The acetone solution (8 ml) of 2,5-dimercapto-1,3,4-thiadiazole (0.3 g, 2.0 mmol) was added dropwise to 60 ml of dichloromethane solution of 1.5 g (4.0 mmol) Cu(L-Br, CH_3), which was then stirred below −10 °C for 2 h. After the solution was concentrated to *ca.* 10 ml under reduced pressure, it was chromatographed on alumina. The reduced product of [N-(1-methyl-3-oxobutylidene)-N′-salicylideneethylenediaminato] copper(II), Cu(L-H, CH_3) was first eluted with dichloromethane and was followed by the binuclear copper(II) complex with a small amount of acetone in dichloromethane. The reddish purple crystals of the binuclear copper(II) complex were recrystallized from dichloromethane with a small amount of methanol. Other binuclear complexes were also prepared using a similar method. With the exception of D(Ni,B,CH_3), the binuclear metal(II) complexes linked by 2-mercaptoethyl ether were not obtained because of the decomposition of the ligand. Yields of the binuclear complexes were less than 20% based on the starting mononuclear complexes.

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Measurements

^{1}H NMR spectra were recorded with a JEOL-MH 100 spectrophotometer in ppm, using TMS as the internal standard. The electronic spectra were measured on a Hitachi 215 spectrophotometer. A Hitachi 115 Vapor Pressure osmometer was used for the determination of molecular weights using dichloromethane as a solvent. A PA 155 Vibrating Sample magnetometer, operated at 10 kG, was used to measure magnetic susceptibility of the compounds. The ESR spectra (X-band) were measured with a JEOL-1X spectrophotometer. Chemiluminescence was observed with a Shonic CL TD-7 Chemiluminescence Counter. No filters were used for the measurements.

Results and Discussion

Although a free bridged ligand, D(2H,A,CH$_3$), was not obtained from the direct reaction of N-(2-bromo-1-methyl-3-oxobutylidene)-N′-salicylideneethylenediamine and 2,5-dimercapto-1,3,4-tridiazole because of the decomposition of the ligand, it was obtained by elimination of the copper(II) ion from the D(Cu,A,CH$_3$) complex by passing gaseous hydrogen sulfide. A free ligand, D(2H,B,CH$_3$), was also obtained by elimination of the nickel(II) ion from the D(Ni,B,CH$_3$) complex by passing gaseous hydrogen chloride.

The results of elemental analyses, molecular weights and electronic spectra are listed in Table I.

The elemental analytical data show that the binuclear metal(II) complexes form adducts with one molecule of dichloromethane. The molecular weights measurements give an indication of the formation of the binuclear metal(II) complexes. The complexes are highly soluble in dichloromethane, soluble in chloroform, but sparingly soluble in other common organic solvents.

The binuclear nickel(II) complexes show the *d–d* absorption bands at 540–550 nm which are characteristic of a square planar nickel(II) complex. The bands are shifted to the shorter wavelengths compared with those of the starting mononuclear complexes. A similar tendency was also observed in the case of the binuclear copper(II) complexes.

The results of ^{1}H NMR spectra are shown in Table II.

The ^{1}H NMR signals of the methine proton of the starting mononuclear compounds disappear in the

TABLE I. Elemental Analyses, Molecular Weights and Electronic Spectra.[a]

Complexes	Found				Calculated				λ_{max}[b] (nm)
	C	H	N%	MW	C	H	N%	MW	
D(Ni,A,CH$_3$)	44.31	3.71	10.07	800	44.48	3.86	10.04	837.2	375 412 440sh 545
D(Ni,A,C$_6$H$_5$)	51.31	3.46	8.98	1029	51.23	3.57	9.74	961.3	393 407 440sh 545
D(Cu,A,CH$_3$)	43.80	3.72	10.26	793	43.92	3.81	9.93	846.8	380 547
D(Cu,A,C$_6$H$_5$)	50.40	3.45	8.90	976	50.72	3.74	8.66	970.9	380sh 550
D(Ni,B,CH$_3$)	48.62	4.87	7.02	910	48.04	4.89	6.79	825.1	376 415 445sh 550

[a]The calculated values are for the adducts with one molecule of dichloromethane [b]Measured in chloroform. sh = shoulder

TABLE II. ^{1}H NMR Spectra of the Free Ligands and Nickel(II) Complexes.[a]

Compounds	δ values (ppm) in CDCl$_3$		
	methyl	methylene	aromatic and azomethine
D(2H,A,CH$_3$)	2.54(s,12H)	4.06(br.s, 8H)	7.56–8.45(m,10H)
D(2H,B,CH$_3$)	2.54(s,12H)	2.90(m,4H) 3.86(m,8H) 4.36(m,4H)	7.52–8.35(m,10H)
D(Ni,A,C$_6$H$_5$)	2.61(s,6H)	3.30–3.80(m,8H)	6.93–7.99(m,20H)
D(Ni,B,CH$_3$)	2.54(s,6H) 2.67(s,6H)	2.77–2.90(m,4H) 3.53(br.s,8H) 3.70–3.89(m,4H)	7.43–8.09(m,10H)

[a]s = singlet, d = doublet, m = multiplet, and br = broad, the ^{1}H NMR spectrum of D(Ni,A,CH$_3$) was not obtained because of its poor solubility.

binuclear compounds, which indicates the replacement of the methine proton with the bridging groups. The ^{1}H NMR spectra of D(Ni,B,CH_3) and D(2H,B,CH_3) also show the new proton signals of the methylene protons due to the bridging group of B, which indicates replacement on the methine carbon.

Magnetic Properties of the Binuclear Copper(II) Complexes

The ESR spectra of the binuclear copper(II) complexes were obtained at 77 K using an X-band for the dichloromethane frozen solutions. The spectra of the binuclear copper(II) complexes showed an axial pattern with $|A| \simeq 200$ G, which resembles those of the mononuclear copper(II) complexes. This suggests that the copper(II)–copper(II) interaction is negligibly weak in the complexes.

Magnetic susceptibilities of the binuclear copper(II) complexes were measured on solid samples in the temperature range from liquid nitrogen to room temperature. χ_A *vs.* T^{-1} plots for these complexes showed that they obey the Curie law. The effective magnetic moments (μ_{eff}) at room temperature and near liquid nitrogen temperature are as follows: 1.82 BM at 290 K and 1.85 BM at 80 K for D(Cu,A,CH_3); 1.80 BM at 290 K and 1.86 BM at 80 K for D(Cu,A,C_6H_5). The magnetic moments are almost independent of temperature. These results also suggest that the copper(II)–copper(II) interaction of the complexes is very weak.

Catalytic Activity of the Binuclear Copper(II) Complexes

As shown in Fig. 2, no chemiluminescence was observed when the N,N-dimethylformamide (DMF) solution of Cu(L-H, CH_3) was mixed with the DMF solution of luminol containing small amounts of hydrogen peroxide, indicating no catalytic activity of the mononuclear complex. On the other hand, chemiluminescence was accelerated by the addition of the binuclear complex of D(Cu,A,CH_3) or D(Cu,A,C_6H_5) to the luminol solution.

It has been reported that the catalytic activity of the binuclear copper(II) complexes on chemiluminescence of luminol, oxidation of TMPD, and decomposition of hydrogen peroxide is closely related to the presence of two adjacent copper(II) ions with the optimum copper(II)–copper(II) distance [8].

From the magnetic results of the binuclear copper(II) complexes of D(Cu,A,CH_3) and D(Cu,A,C_6H_5), however, the interaction of copper(II)–copper(II) is very weak, suggesting that the distance between the two copper(II) ions must be great in the solid state.

It has been further reported that the value of μ_{eff} of a binuclear *m*-xylidenebis(Cu(salprn)) complex was 1.92 BM/metal center in the solid state and 1.49 BM/metal center in solution, respectively [3]. The reduced moment is ascribed to the fact that the average proximity of the two metal centers in the binuclear complex increases in solution, resulting in an increase in their magnetic interactions.

In the present case, small amounts of the complex might also be present in the form of the appropriate copper(II)–copper(II) distance in solution (see below).

A relatively weak carbon–sulfur bonding may easily permit the rotation of the Schiff base complexes around the carbon–sulfur axis, resulting in the formation of a dredging conformation in solution. The dredging model shows that the shortest distance of the two copper(II) ions is 5 Å, which is enough

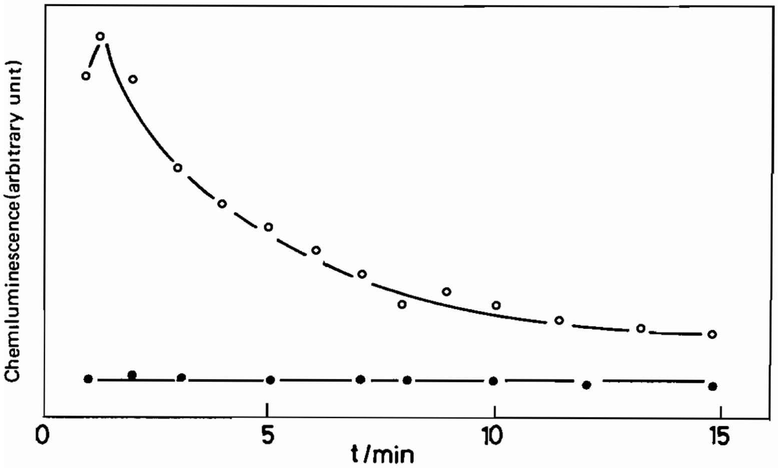
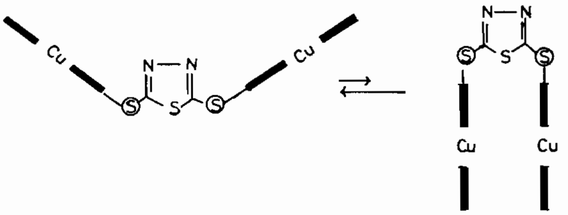


Fig 2. Time course of chemiluminescence in the reaction mixture of luminol and the complexes in DMF solution at 293 K, [complex] = 4.00 × 10^{-4} mol dm^{-3}, [luminol] = 6.00 × 10^{-3} mol dm^{-3}, [H_2O_2] = 3 00 × 10^{-2} mol dm^{-3}. (○) D(Cu,A,CH_3); (●) Cu(L-H,CH_3).



to catalyse chemiluminescence of luminol [8]. However, the catalytic activity is smaller than that of the binuclear complexes which show strong magnetic interactions of copper(II)–copper(II) ions in the solid state [11].

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References

1 J A. Fee, *Struct Bonding (Berlin)*, *23*, 1 (1975).
2 S. K Mandel and K. Nag, *J. Chem. Soc., Dalton Trans*, 2429 (1983).
3 B. C. Whitmore and R. Eisenberg, *Inorg. Chem*, *22*, 1 (1983).
4 M. P. Brown, R. J. Poddephatt, M. Rashidi and K. R. Seddon, *Inorg. Chim. Acta*, *23*, L33 (1977)
5 T. Izumitani, M. Nakamura, H. Ōkawa and S. Kida, *Bull Chem Soc Jpn.*, *55*, 2122 (1982), and articles cited therein.
6 Y. Nishida, N. Oishi and S. Kida, *Inorg. Chim Acta*, *46*, L69 (1980).
7 N. Oishi, Y. Nishida, K. Ida and S Kida, *Bull Chem Soc. Jpn.*, *53*, 2847 (1980)
8 N. Oishi, Y. Nishida and S. Kida, *Chem Lett*, 1031 (1981).
9 Y. Nishida, M. Takeuchi, N Oishi and S. Kida, *Inorg. Chim. Acta*, *75*, 169 (1983).
10 K. Kasuga, T. Nagahara, T. Masuda, S. Kiyota and Y Yamamoto, *Bull. Chem. Soc. Jpn.*, *57*, 1631 (1984).
11 K. Kasuga, T. Oishi, T. Nagahara and Y. Yamamoto, unpublished work.