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Catalytic Activity of Planar Copper(II) Complexes for the Chemiluminescence of Luminol

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Some planar binuclear copper(II) complexes showed high catalytic activity for the chemiluminescence of luminol in the presence of hydrogen peroxide compared with those of mononuclear planar copper(II) complexes. The formation of singlet O_2 in the reaction mixture of a binuclear copper(II) complex and hydrogen peroxide was assumed to play a key role in the catalytic function of the binuclear copper(II) complexes for the luminol chemiluminescence.

Since the discovery of the chemiluminescence of luminol by Albrecht,[1] many chemists have been interested in the light producing step. White *et al.*[2,3] have established the stoichiometry of the overall reactions as well as the identity of the emitting species. According to them, 3-aminophthalate is the light emitter in protic and approtic solvents.[2-5]

It is well known that hemin catalyzes the chemiluminescence of luminol very effectively in the presence of hydrogen peroxide. It was also shown that some metal complexes cause the luminol chemiluminescence though much less effectively compared with hemin.[6,7] Ojima[7] investigated the catalytic activity of copper(II) complexes for the luminol chemiluminescence, and found that some di-μ-hydroxo binuclear copper(II) complexes show high catalytic activities for the luminol chemiluminescence; howerver, he did not investigate further the function of the binuclear copper(II) complexes for the reaction.

We already showed that some planar binuclear copper(II) complexes, *e.g.*, $[Cu_2(pia)_2]$ and $[Cu_2(et\text{-}2\text{-}3)_2]^{2+}$, *etc.* (for the abbreviations of the complexes, see Fig. 1) show remarkably high reactivities in the redox reactions with ascorbic acid, catechol, *etc.*, compared with the reactivities of planar mononuclear copper(II) complexes.[8-11] More recently we[12] also found that some planar binuclear copper(II) complexes exhibit high catalytic activity for the decomposition of hydrogen peroxide ("catalase-like" function) compared with that of the planar mononuclear copper(II) complexes. These results suggest that the "catalase-like" function of the binuclear copper(II) complexes may be closely related to the specific function of the binuclear copper(II) complexes for the chemiluminescence of luminol observed by Ojima, because these experiments on the luminol chemiluminescence are usually done in the presence of hydrogen peroxide. In order to confirm the above view, in this study, we have investigated the catalytic activity of various planar copper(II) complexes for the luminol chemiluminescence.

Experimental

Materials. Copper(II) complexes cited in Fig. 1 were prepared according to the literature methods. (C),[13] (D),[14] (E),[15] (F),[16] (G),[17] (H),[18] (I),[8] and (J).[19] Luminol (Tokyo Kasei Co.) and hydrogen peroxide (Nakarai's Guaranteed Reagent, 30%) were obtained commercially.

Measurements of Chemiluminescence Intensity. The aqueous solution containing luminol (1.4×10^{-4} mol dm^{-3}), NaOH (2.8×10^{-4} mol dm^{-3}) and H_2O_2 (1.4×10^{-3} mol dm^{-3}) and the dmf solution of copper(II) complexes ($[Cu^{2+}]=2\times10^{-4}$ mol dm^{-3}) were kept standing for 1 d at 18 °C prior to the reaction. The apparatus for the measurement is shown in Fig. 2. The solution of copper(II) complex (0.5 cm^3) was mixed with the luminol solution (30 cm^3) in vessel A by injection from the syringe, and the emitted light was collected on the photomultiplier (RCA 1P28) through the lens, and recorded with a Servocorder type SR651 (Watanabe Instrument Corp.). The temperature of the room was kept at 18 °C throughout the experiments.

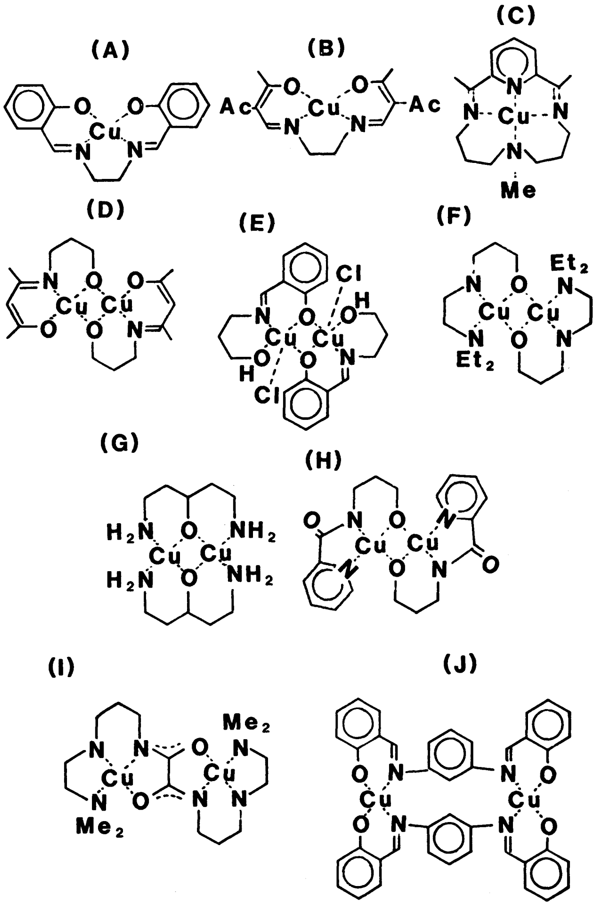


Fig. 1. Copper(II) complexes cited in this paper and their abbreviations. (A) [Cu(salen)], (B)[Cu(J-en)], (C) $[Cu(m\text{-}cr)]^{2+}$, (D) $[Cu_2(pia)_2]$, (E) $[Cu_2(salpa)_2]^{2+}$ (F) $[Cu_2(et\text{-}2\text{-}3)_2]^{2+}$ ($R=C_2H_5$), (G) $[Cu_2(dpl)_2]^{2+}$, (H) $[Cu_2(pc\text{-}1,3)_2]$, (I) $[Cu_2(me\text{-}ox)]^{2+}$, and (J) $[Cu_2\text{-}(sal\text{-}m\text{-}phen)_2]$.

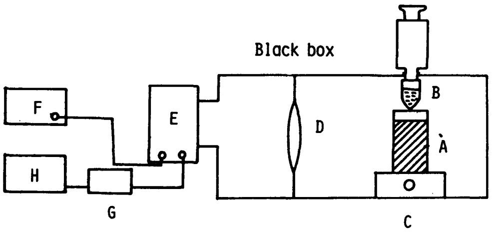


Fig. 2. Apparatus for the measurement of chemiluminescence. A: Luminol solution, B: copper(II) solution, C: magnetic stirrer, D: lens, E, photomultiplier, F: power source (650 V), G: amplifier, H: recorder.

Results and Discussion

Some examples of the time course of luminol chemiluminescence using copper(II) complexes as catalyst are shown in Fig. 3. Planar mononuclear copper(II) complexes, such as [Cu(salen)], [Cu(J-en)], and [Cu(m-cr)]$^{2+}$ showed practically no catalytic activity for the luminol chemiluminescence. In contrast to this, planar binuclear copper(II) complexes, *e.g.*, [Cu_2(pia)$_2$], [Cu_2(et-2-3)$_2$]$^{2+}$, and [Cu_2(pc-1,3)$_2$], exhibited remarkable catalytic activities, whereas binuclear copper(II) complexes, [Cu_2(me-ox)]$^{2+}$ and [Cu_2(sal-m-phen)$_2$] showed no catalytic activity.

The luminol chemiluminescence occurs only when luminol, NaOH, H_2O_2, and a copper(II) complex are mixed in a solution, where NaOH seems to be necessary for the formation of the dianion of luminol. In Table 1 the catalytic activities of various copper(II) complexes for the decomposition of hydrogen peroxide[12] and for the luminol chemiluminescence are shown. It is obvious from the data that the catalytic functions of copper(II) complexes for the decomposition of hydrogen peroxide and for the luminol chemiluminescence are paralell (at least qualitatively) with each other. These facts suggest that the decomposed product of H_2O_2 in the reaction mixture plays a key role in the luminol chemiluminescence.

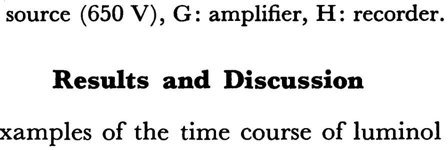


Fig. 4. The assumed intermediate complex between a binuclear copper(II) complex and H_2O_2.

Table 1. Catalytic functions of copper(II) complexes

Complex	Decomposition of H_2O_2	Luminol chemiluminescence
[Cu(salen)]	a)	a)
[Cu(J-en)]	a)	a)
[Cu(m-cr)]$^{2+}$	a)	a)
[Cu_2(pia)$_2$]	$t_{1/2} \approx 1$ min$^{b)}$	220$^{c)}$
[Cu_2(et-2-3)$_2$]$^{2+}$	$t_{1/2} < 0.5$ min	320
[Cu_2(salpa)$_2$]$^{2+}$	$t_{1/2} \approx 3$ min	380
[Cu_2(dpl)$_2$]$^{2+}$	$t_{1/2} \approx 10$ min$^{d)}$	50
[Cu_2(pc-1,3)$_2$]	$t_{1/2} < 0.2$ min	290
[Cu_2(me-ox)]$^{2+}$	a)	a)
[Cu_2(sal-m-phen)$_2$]	a)	a)

a) Practically zero. b) $t_{1/2}$ denotes the half-life time of H_2O_2 in the reaction mixture of a copper(II) complex and ten times excess of H_2O_2 in methanol at 25°C. c) This denotes the highest value of chemiluminescence intensity (*cf.* Fig. 3). d) In water.

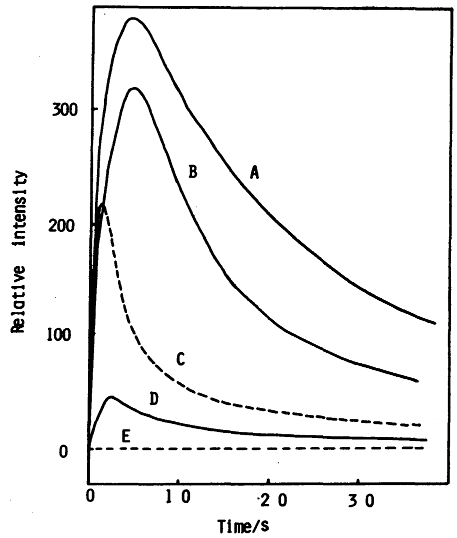


Fig. 3. Chemiluminescence intensity as a function of time. A: [Cu_2(salpa)$_2$]$^{2+}$, B: [Cu_2(et-2-3)$_2$]$^{2+}$, C: [Cu_2(pia)$_2$], D: [Cu_2(dpl)$_2$]$^{2+}$, E: [Cu(salen)].

The decomposition reaction is essentially a redox-disproportionation reaction between two H_2O_2 molecules *e.g.*,

$$2H_2O_2 \longrightarrow 2H_2O + O_2.$$

However, the rate of the reaction is very slow in the absence of catalysis. In the preliminary report,[12] we discussed the catalytic function of binuclear copper(II) complexes for the decomposition of hydrogen peroxide, and assumed that the first step is the formation of a H_2O_2 complex as depicted in Fig. 4-a and the second step is the approaching of another H_2O_2 molecule to the vacant site of the H_2O_2-binuclear complex, forming the intermediate complex as shown in Fig. 4-b; the third step is the two-electron transfer from one H_2O_2 molecule to another through the copper atoms, resulting in a formation of O_2 and $2H_2O$. In the cases of [Cu_2(me-ox)]$^{2+}$ and [Cu_2(sal-m-phen)$_2$], the formation of the intermediate complex is impossible because of the long Cu–Cu distance.[8,12] This may explain the very low catalytic activity of these complexes for the decomposition of hydrogen peroxide.

In the intermediate complex as shown in Fig. 4-a or 4-b, a H_2O_2 molecule bidentately coordinates to the two copper(II) ions with its nonbonding filled 2p orbitals. When two electrons are transfered from the peroxide to the two copper(II) ions, a single electron is left in each oxygen 2p orbital which was used for the coordination. These orbitals will immediately form a π bond pairing the electron spins, because the two Cu–O

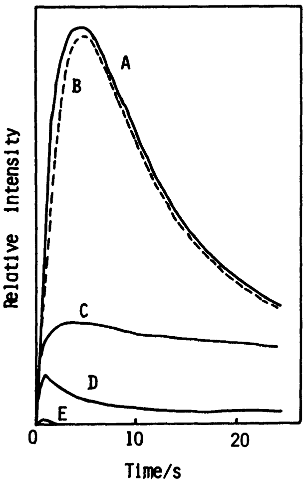
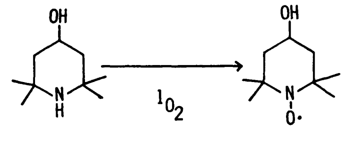


Fig. 5. Chemiluminescence intensity in the $[Cu_2(\text{et-2-3})_2]^{2+}$ system in the presence of DABCO(R= [DABCO]/[Luminol]). A: R=0, B: R=100, C: R=1000, D: R= 2500, E: R=10000.

bonds should be nearly paralell to each other due to the steric requirement of the Cu_2–O_2 bonding system. Thus, the H_2O_2 molecule will become a singlet dioxygen molecule losing two protons. Accordingly, it seems that singlet dioxygen molecule (denoted as $^1O_2$ hereafter) plays a key role in the catalytic function of the binuclear copper(II) complexes for the luminol chemiluminescence.

It is well known that $^1O_2$ reacts with luminol to induce chemiluminescence. Thus, we have measured the luminol chemiluminescence in the NaClO–H_2O_2 system, because the NaClO–H_2O_2 system is one of the simplest ways to generate $^1O_2$ in the laboratory.[20] The luminol chemiluminescence was observed in the NaClO–H_2O_2 system, as expected. When a large excess of 1,4-diazabicyclo[2.2.2]octane (DABCO, one of the scavenger[21] of $^1O_2$) was added to this system, the intensity of chemiluminescence was greatly quenched. This fact indicates that the luminol chemiluminescence in the NaClO–H_2O_2 system is caused by the generation of $^1O_2$ in this system.[22] In Fig. 5, the time courses of luminol chemiluminescence in the presence of $[Cu_2(\text{et-2-3})_2]^{2+}$ and DABCO are shown. These clearly indicate that the intensities of luminol chemiluminescence by $[Cu_2(\text{et-2-3})_2]^{2+}$ are greatly depressed by the presence of DABCO, similarly to the case of the NaClO–H_2O_2 system. Such a quenching effect by DABCO was also observed for all the luminol chemiluminescence catalyzed by the binuclear copper(II) complexes examined in this study.

It is well known that 2,2,6,6-tetramethyl-4-piperidinol reacts with $^1O_2$ to yield the nitroxide radical, as shown below.[23] We could observe the ESR signal due to the nitroxide radical in the reaction mixture of a binuclear copper(II) complex (*e.g.*, $[Cu_2(\text{pia})_2]$), H_2O_2 and 2,2,6,6-tetramethyl-4-piperidinol. Thus, we may conclude that the $^1O_2$ produced by the simultaneous two-electron transfer from H_2O_2 to two copper(II) ions plays a key role in the catalytic function of the binuclear copper(II) complexes for the luminol chemiluminescence.



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