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Infrared and Electron Spin Resonance Study of the Dimeric Form of the Mixed Ligand Complex containing Adenine

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The ternary complex $[Cu(AdeH)(Ade)(phen)_2OH]_2 \cdot 2H_2O$ has been prepared and compared with the binary complexes. The mixed ligand complex was characterized from elementary analysis and infrared spectra. From the shift of the aromatic carbon-aliphatic nitrogen stretching in infrared spectra, it is expected that the amino group of adenine ligand would not coordinate to copper(II), and consequently, it is likely that N9 of adenine ligand coordinates to copper(II) in the mixed ligand complex.

The triplet state electron spin resonance spectra of the mixed ligand complex were recorded and the results interpreted in terms of a dipole-dipole interaction between pairs of copper(II) ions in a dimeric complex.

Keywords——ESR spectra; IR spectra; adenine; mixed ligand complex; dimeric form; triplet state; copper(II) complex; Hamiltonian; bimetallic copper complex; coordination site

Mixed ligand complexes play an important role in biological processes. Some enzymes are known to be activated by metal ions, and metal ions have been shown to have crucial effect on the biological activity.

We have synthesized (glycylglycinato)(aqua)(AdeH)Cu(II) monohydrate,[2] and Tomita, *et al.*[3] have demonstrated by X-ray methods that the nitrogen atom 9 alone is coordinated to copper(II) in this complex. However, nitrogen atom 7 alone is coordinated to copper(II) in the complexes (glycylglycinato)(aqua)(9-methyladenine)copper(II) tetrahydrate[4] and (N-salicylidene-N′-methylethylenediamine)(aqua)(9-methyladenine)copper(II) nitrate dihydrate.[5]

Results and Discussion

Electron Spin Resonance (ESR) Spectra of $[Cu(AdeH)(Ade)(phen)_2OH]_2 \cdot 2H_2O$

In this paper two basic assumptions were made. First, it was assumed that zero-field splitting parameter E is so small as to be considered equal to zero. Second, we assumed that the band at about 3000 gauss resulted from a simple paramagnetism of monomeric impurity present in the mixed ligand complex. Unfortunately, we are unable to offer a conclusive evidence to support this assumption, but band shape studies do not conflict with this assignment. Having made these two assumptions, the spectra may be interpreted using the analysis of Wasserman, Synder, and Yager[6] as adapted by Wasson, Shyr, and Trapp.[7]

The X-band ESR spectra of powdered samples of the mixed ligand complex recorded at room temperature are illustrated in Fig. 2. Assignments of the observed transitions are summarized in Table I.

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[1] Location: *Yayoi-cho, Chiba, 280, Japan.*

[2] T. Sakaguchi and M. Tanno, *Nippon Kagaku Kaishi*, **1974**, 1637.

[3] K. Tomita, T. Izuno, and T. Fujiwara, *Biochem. Biophy. Res. Commun.*, **54**, 96 (1973).

[4] T.J. Kistenmacher, L.G. Marzilli, and D.J. Szalda, *Acta Crysrallogr. Sec. B*, **1976**, B32(1), 186.

[5] D.J. Szalda, T.J. Kistenmacher, and L.G. Marzilli, *Inorg. Chem.*, **14**, 2623 (1975).

[6] E. Wasserman, L.C. Synder, and W.A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

[7] J.R. Wasson, C.-I. Shyr, and C. Trapp, *Inorg. Chem.*, **7**, 469 (1968).

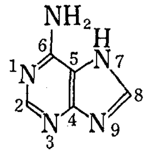

Fig. 1. Structure of Adenine (denoted by AdeH)

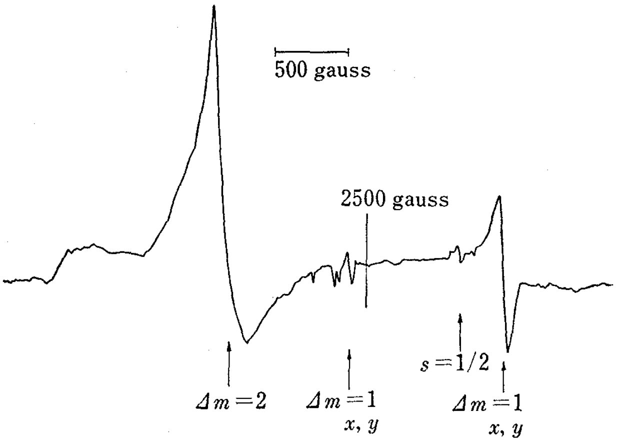

Fig. 2. X-Band ESR Spectrum of Polycrystalline $[Cu\ (AdeH)\ (Ade)\ (phen)_2\ OH]_2 \cdot 2H_2O$ at Room Temperature

The Hamiltonian for the triplet state of dimeric copper complexes[8] is shown. The effective spin Hamiltonian (with S=1)[6]

$$\mathscr{H} = H \cdot g \cdot S\beta + DS_z^2 + E(S_x^2 - S_y^2) - (2/3)D$$

leads one to expect an ESR spectrum containing seven bands, one isotropic $\Delta M = \pm 2$ transition and six $\Delta M = \pm 1$ transitions. This form of the Hamiltonian assumes that the principal axes for zero-field splitting are coincident with the g tensor.

If $E=0$, then the resonance fields are[6]

$$H_{xy1}^2 = (g_e/g_{xy})^2 H_0(H_0 - D')$$
$$H_{xy2}^2 = (g_e/g_{xy})^2 H_0(H_0 + D')$$
$$H_{z1} = (g_e/g_z)|H_0 - D'|$$
$$H_{z2} = (g_e/g_z)|H_0 + D'|$$

where $H_0 = h\nu/g_e\beta$, $D' = D/g_e\beta$, and $g_e = g$ value of a free electron. At room temperature, splitting of H_{xy} into H_x and H_y is either incomplete or unobservable, so that an approximation to axial symmetry is made initialy. With assignment of the $\Delta M=1$ transitions, H_{xy1} and H_{xy2}, the value of g_{xy} and D are obtained, but the value of g_z is not obtained. It can be deduced that the $\Delta M=2$ transition (which we expect to see when $D < h\nu$) and the $\Delta M=1$ band H_{z1} should occur close together in the low-field region.[9] Accordingly, the band at the lowest field cannot be assigned unambiguously, though its isotropic nature and its similarity to the low-field band observed in $Cu(Ade)_2 \cdot 4H_2O$[10] are strongly suggestive of $\Delta M=2$.

In line with magnetic susceptibility data, the triplet state characteritics of the ESR spectrum reveal the presence of pairwise magnetic exchange in $[Cu(AdeH)(Ade)(phen)_2OH]_2 \cdot 2H_2O$[11] and the mixed ligand complex is an oxygen-bridged bimetallic complex.

TABLE I. ESR Data for $[Cu(AdeH)(Ade)(phen)_2OH]_2 \cdot 2H_2O$ at 9.50 GHz

H_{xy1}	2350 gauss	g_{xy}	2.30 cm⁻¹
H_{xy2}	3450 gauss	D	0.116 cm⁻¹
$\Delta M=2$	1500 gauss		

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[8] G.F. Kokoszka, *Coord. Chem. Rev.*, **5**, 209 (1970).

[9] D.M.L. Goodgame and S.V. Waggett, *Biochem. Biophys. Res. Commun.*, **42**, 63 (1971).

[10] D.M.L. Goodgame and K.A. Price, *Nature* (London), **220**, 783 (1968); R.W. Duerst, S.J. Baum, and G.F. Kokoszka, *ibid.*, **222**, 665 (1969).

[11] Adenine and 1,10-phenanthroline are denoted by AdeH and phen in this paper; B. Jezowska-Trzebiatowska, H. Kosewski, and A. Antonow, *Bull. Acad. Pol. Sci.*, **22**, 31 (1974).

Infrared (IR) Spectra

The infrared spectra of adenine ligand has been reported in some detail and band assignments have been proposed.[2],[12] Furthermore, we have reported the IR spectra of the copper complex of adenine.[2]

In the mixed ligand complex, the bands at 3235 and 3055 cm^{-1} are assigned to NH_2 stretching, and the band at 2700 cm^{-1} was assigned to NH stretching.[2] In the region of

TABLE II. IR Data of Adenine and $[Cu(AdeH)(Ade)(phen)_2OH]_2 \cdot 2H_2O$

Tentative assignment	Adenine	$[Cu(AdeH)(Ade)(phen)_2OH]_2 \cdot 2H_2O$
NH_2 str.	3290m	3235 s
	3110 s	3055 s
NH str.	2975w	
	2790w	
	2690w	2700w
	2600w	
NH_2 in-plane sym. def.	1670 s	1680m
C=C, C=N	1610 s	1610 s
Purine ring vib.		1540w
	1510w	1522w
		1511w
		1498w
Ring vib.	1458w	1455m
	1426m	1428 s
	1375m	1396 s
		1365m
NH ring, C–NH_2 str.	1342m	1349w
	1318m	1325m
NH_2 out-plane sym. def.	1260m	1262m
		1232w
	1160w	1196 s
	1132m	1142 s
NH		1110m
		1099w
	1028m	1030 s
		978m
NH_2 out-plane sym. def.	945m	962w
	918m	911m
NH out-pane def.	875w	876m
		860w
	850w	852w
		846 s
	801m	804w
CH bending		778w
		768w
		738w
NH_2 in-plane asym. def.	728m	728 s
		714w
		690w
Ring and CN str.	644w	659m
		646w
	625w	629w
C=C, C=N, and Cu–N str.		595w
		571m
	546m	550m
		510w
Cu–N str.		462w

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12) C.L. Angell, *J. Chem. Soc.*, 504 (1961).

1810—1910 cm^{-1} no bands due to either adenine[2] or 1,10-phenanthroline[13-15] were seen, and then at least these bands were not assigned to NH and CH stretchings. But these bands can not be assigned.

In the spectrum of adenine ligand the band at 1670 cm^{-1} is assigned to NH_2 deformation.[16] Therefore, in the spectrum of the mixed ligand complex the band at 1680 cm^{-1} can be assigned also to NH_2 deformation, which is shifted to higher wave numbers.

The strong bands at 1610 and 1540 cm^{-1} in the spectrum of the mixed ligand complex could therefore be attributed to the C=C and C=N vibrations in the ring system of adenine and 1,10-phenanthroline. The bands at 1522 and 1511 cm^{-1} can be accounted for, in the main, by C=C and C=N stretching mode.

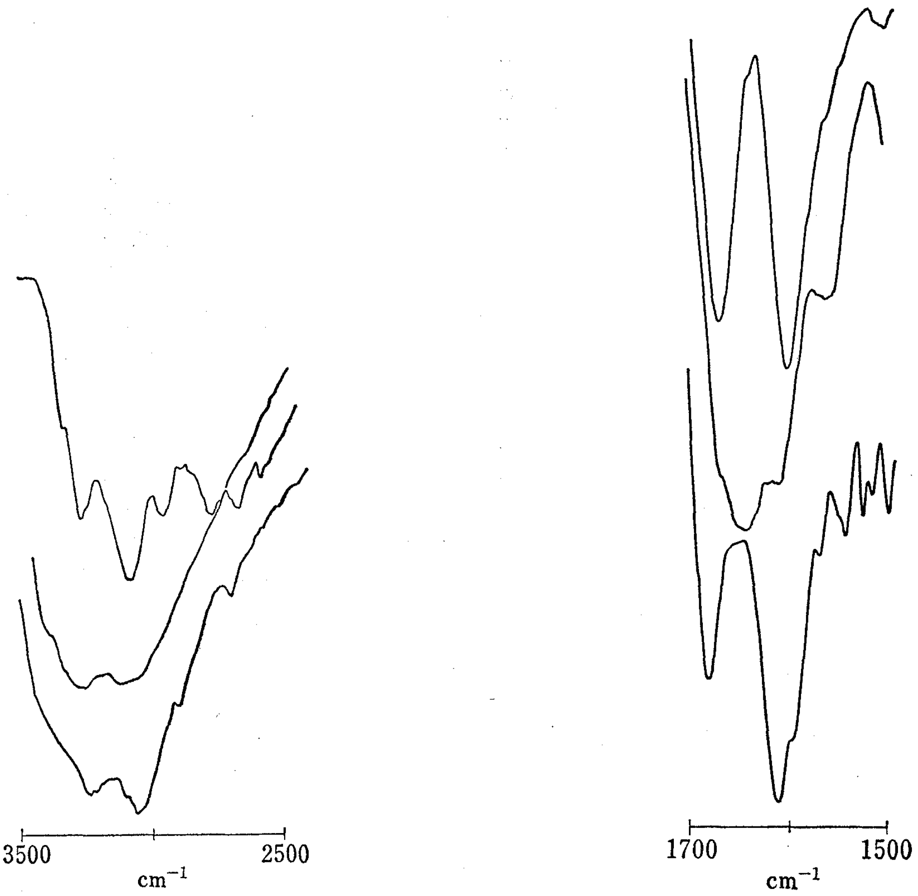

Fig. 3. IR Spectrum of Adenine (upper), $[Cu(AdeH)_2OH]_2\,6H_2O$ (center) and $[Cu(AdeH)(Ade)(phen)_2OH]_2 \cdot 2H_2O$ (bottom)

Ring stretching modes are also expected to occur in the 1500—1350 region and the spectrum shows at 1498, 1455, 1428, 1396, 1365 and 1349 cm^{-1}. The band of medium intensity at 1325 cm^{-1} may arise from the aromatic carbon-aliphatic nitrogen stretching frequency.[17] The most characteristic absorptions for aromatic ring systems occur in the 900—700 cm^{-1} region. The bands at 876, 860, 852, and 846 cm^{-1} can be assigned to NH out-of-plane deformation due to the adenine ligand.[2] The aromatic carbon-aliphatic nitrogen

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13) A.A. Schilt and R.C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).
14) M.F.A. EI-Sayed and R.K. Sheline, *J. Inorg. Nucl. Chem.*, **6**, 187 (1958).
15) E. Dinjus, I. Gorski, and H. Wasther, *Z. anorg. allg. Chem.*, **422**, 75 (1976).
16) T. Sakaguchi and S. Ishino, *Nippon Kagaku Kaishi*, 1480 (1974).
17) L.J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, 1962, p. 257, p. 280.

stretching is shifted to a higher frequency and appeares at 1325 cm^{-1}. This shift may be expected, as the lone pair of electrons on the amino groups would not be engaged in the bonding.[18] Similar shifts have been observed for this mixed ligand complex and Cu(AdeH)GlyGly·H_2O whose N9 of adenine ligand coordinates to cooper(II). Consequently, it is likely that the N9 of adenine ligand coordinates to copper(II) in $[Cu(AdeH)(Ade)(phen)_2OH]_2 \cdot 2H_2O$. Though in adenine there are only two bands of NH out-of-plane deformation 875 and 850 cm^{-1}, in the mixed ligand complex the bands at 911, 876, 860, and 852 cm^{-1} are assigned to NH out-of-plane deformation. From this assignment, it is assumed that N7 of adenine is protonated.

Experimental

Apparatus——Infrared spectra were taken as KBr pellets on a Hitachi Infrared spectrometer, Model EPI-G3. The ESR spectra were recorded on a JES-ME-IX ESR spectrometer operating at 100 Hz. The spectra were recorded on polycrystalline samples at room temperature.

Reagents——The ligands used were obtained from Wako Pure Chemical Industries, Tokyo, and Tokyo Kasei Co. They were reagent grade samples and were used without further purification.

Preparation of Mixed-Ligand Complex——The complex $[Cu(AdeH)_2OH]_2 \cdot 6H_2O$ was prepared according to the method of Jezowska-Trzebiatowska, *et al.*[19] $[Cu(AdeH)(Ade)(phen)_2OH]_2 \cdot 2H_2O$: A solution of $[Cu(AdeH)_2OH]_2 \cdot 6H_2O$ dissolved in 100 ml of hot water was heated on a water-bath and 0.198 g of 1,10-phenanthroline was added into this solution. The color of the solution changed from violet to blue-green. The mixture was further heated for 30 min. After 20 min, a white-blue polycrystalline material formed, which was collected and washed with water. The product was dried under a reduced pressure. *Anal.* Calcd. for $[Cu(C_5H_5N_5)(C_5H_4N_5)(C_{12}H_8N_2)_2OH]_2 \cdot 2H_2O$: C, 56.03; H, 3.88; N, 26.91. Found: C, 55.68; H, 3.77, N, 26.91.

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[18] J.C. Fanning and L.T. Taylor, *J. Inorg. Nucl. Chem.*, 27, 2217 (1965).

[19] B. Jezowska-Trzebiatowska, H. Kosewski, and A. Antonow, *Bull. Acad. Pol. Sci.*, 22, 31 (1974).