[Chem. Pharm. Bull. 25(11)2953—2958(1977)] UDC 547.857.7.04.08 : 543.422.06

Spectral Properties of Mixed-Ligand Copper^{2+} Complexes containing Adenine, 1,10-Phenanthroline and Halogen Anions

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(Received March 14, 1977)

The mixed ligand complexes, Cu_2^{2+} $(AdeH)_2(phen)_2X_2 \cdot 2H_2O$, where X is Cl, Br and ClO_4, have been prepared from aqueous solution. The complexes were characterized by elementary and infrared spectroscopic analyses. In this paper, the IR spectra of these compounds were discussed in some detail and compared to those of binary parent complexes. It was supposed that N9 of adenine ligand coordinated to Cu^{2+} from infrared (IR) spectra. The electron paramagnetic resonance (EPR) spectra of the mixed ligand complexes were recorded on polycrystalline samples at room temperature and *g*-values of the compounds were obtained.

Keywords——Mixed ligand complex; adenine; 1,10-phenanthroline; IR spectra; EPR spectra; metal complexes; purine base; coordination site

The mixed ligand complexes containing adenine as a component of nucleic acids were obtained and they were formulated as $Cu_2(C_5H_5N_5)_2(C_{12}H_8N_2)_2Cl_2 \cdot 2H_2O$, $Cu_2(C_5H_5N_5)_2(C_{12}H_8N_2)_2Br_2 \cdot 2H_2O$ and $Cu_2(C_5H_5N_5)_2(C_{12}H_8N_2)_2(ClO_4)_2 \cdot 2H_2O$. Physical measurements including infrared and EPR spectroscopies have been employed in the characterization of the complexes. Recently the triplet-state EPR spectrum of the mixed ligand complex containing adenine and 1,10-phenanthroline has been reported.[2] In this paper, the other complexes with various halogen anions are reported.

Sletten has demonstrated by X-ray methods that the complex $Cu(Ade)_2 \cdot 4H_2O$ is demeric structure.[3] Recently it has been established that neutral adenine functions as a *syn*, bidentate bridge (*via* N3 and N9) in the copper compound $[Cu_2(AdeH)_4(H_2O)_2 \cdot](ClO_4)_4 \cdot 2H_2O$[4] and $[Cu_2(AdeH)_4Cl_2]Cl_2 \cdot 6H_2O$.[5] Protonated adenine has also been observed to function as a *syn, syn* bridge, *viz.*, in $[Cu_3(AdeH_2)_2Cl_8] \cdot 4H_2O$.[6] In contrast, the nitrogen atom N9 only is coordinated to copper (II) in the complex $[Cu_2(AdeH_2)_2Br_2]Br_2$[7] and (Glycylglycinato)(aquo)(AdeH)Cu monohydrate[8] and (N-salicylidene-N′-methylethylenediamine) (aquo)(9-methyladenine)Cu nitrate dihydrate.[9,10]

The EPR spectrum of the copper complex with adenine separated at pH 7 was examined in polycrystalline samples by Duerst, Baum, and Kokoszka.[11] Jezowska-Trzebiatowska, *et al.* studied the EPR spectra of complexes containing adenine at various pH.[12] In this

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

[2] T. Fujita and T. Sakaguchi, *Chem. Pharm. Bull.* (Tokyo), **25**, 1055 (1977).

[3] E. Sletten, *Chem. Commun.*, 1119 (1967); *idem, Acta Crystallogr., Sect B*, **25**, 1480 (1969).

[4] A. Terzis, A.N. Beauchamp, and R. Rivest, *Inorg. Chem.*, **12**, 1166 (1973).

[5] P. de Meester, D.M.L. Goodgame, K.A. Price, and A.C. Skapski, *Nature* (London), **229**, 191 (1971); P. de Meester and A.C. Skapski, *J. Chem. Soc., A*, 2167 (1971).

[6] P. de Meester and A.C. Skapski, *J. Chem. Soc., Dalton Trans.*, **1972**, 2400.

[7] P. de Meester and A.C. Skapski, *J. Chem. Soc., Dalton Trans.*, **1973**, 424.

[8] T. Sakaguchi and M. Tanno, *Nippon Kagaku Kaishi*, **1974**, 1637; K. Tomita, T. Izuno, and T. Fujiwara, *Biochem Biophys. Res. Commun.*, **54**, 96 (1973).

[9] T.J. Kistenmacher, L.G. Marzilli, and D.J. Szalda, *Acta Crystallogr. Sect. B*, **32**, 186 (1976).

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

[11] R.W. Duerst, S.B. Baum, and G.F. Kokoszka, *Nature* (London), **222**, 665 (1969).

[12] B.J. Jezowska-Trzebiatowska, H. Kozwski, and A. Anyonow, *Bull. Acad. Pol. Sci.*, **22**, 31 (1974).

paper, the mixed ligand complexes containing adenine ligand are reported and the infrared (IR) and electron paramagnetic resonance (EPR) spectra are discussed.

Results and Discussion

The IR spectra have been reported about adenine and its metal complexes.[2,8,13,14] In the present study IR spectra of the mixed ligand complexes containing adenine, Cu^{2+}, 1,10-phenanthroline and halogen ions were discussed.

In adenine the bands at 3290 and 3110 cm^{-1} were assigned to NH_2 stretching.[13] In $Cu_2(AdeH)_2(phen)_2Cl_2 \cdot 2H_2O$[15] many bands assigned to NH_2 stretching were observed in the region 3000—3400 cm^{-1}. Four bands from 2600 to 2975 cm^{-1} were assigned to NH stretching in adenine ligand. In A,[16] no bands assignable to NH stretching were observed in this region. The bands in the region 2600—2900 cm^{-1} are attributed to N9-H stretching[13,17] and therefore, it is likely that Cu^{2+} binds to N9 of adenine in A. A strong absorption at 1630 cm^{-1} was assigned to C=C and C=N stretching due to adenine and 1,10-phenanthroline.

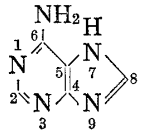

Fig. 1. Structure of Adenine

The structure of $Cu_2(AdeH)_2Cl_4$ has not been determined by X-ray methods. In the IR spectrum of this complex no bands assigned to N9-H stretching from 2900 to 2600 cm^{-1} were seen and it was probable that N9 coordinated to Cu^{2+} in this compound. In $Cu_2(AdeH)_2Cl_4$ the band assigned to NH_2 bending did not shift by complexation and appeared at 1670 cm^{-1}.

In the IR spectrum of A, no bands attributed to NH_2 out-plane deformation from 900 to 950 cm^{-1} were seen and the strong absorptions at 722 and 680 cm^{-1} were assigned to NH_2 rocking.

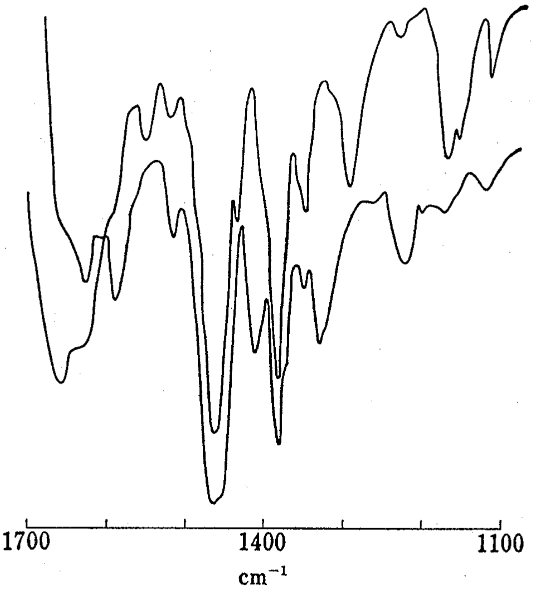

Fig. 2. IR Spectra of $Cu_2(AdeH)_2(phen)_2Br_2 \cdot 2H_2O$ (top) and $Cu_2(AdeH)_2Br_2 \cdot 5H_2O$ (bottom) in Nujol Mulls

In adenine the band at 546 cm^{-1} was attributed to C=C and C=N stretching. Then in $Cu_2(AdeH)_2Cl_4$ three bands in the region 550—600 cm^{-1} were observed. These bands were assigned to C=C, C=N and Cu-N stretching. In A two bands were seen in this region and these bands were assigned to C=C and C=N stretching due to adenine and 1,10-phenanthroline ligands.

The coordination site of $[Cu(AdeH)_2Br_2]Br_2$ prepared in an aqueous acidic solution was determined as N9 by X-ray methods.[7] In the present study, $Cu_2(AdeH)_2Br_4 \cdot 5H_2O$ was prepared but the structure and coordination site of this compound were not determined by X-ray methods. By mixing this parent complex, $Cu_2(AdeH)_2Br_4 \cdot 5H_2O$, and 1,10-phenanthroline, the mixed ligand complex, $Cu_2(AdeH)_2(phen)_2Br_2 \cdot 2H_2O$[18] was obtained. The IR

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[13] C.L. Angell, *J. Chem. Soc.*, **1961**, 504.
[14] T. Sakaguchi and S. Ishino, *Nippon Kagaku Kaishi*, **1974**, 1480.
[15] This complex is denoted by A and 1,10-phenanthroline is denoted by phen in this paper.
[16] $Cu_2(AdeH)_2(phen)_2Cl_2 \cdot 2H_2O$ is denoted by A.
[17] T. Shimanouchi, M. Tsuboi, and Y. Kyogoku, *Adv. Chem. Phys.*, **7**, 435 (1964).
[18] $Cu_2(AdeH)_2(phen)_2Br_2 \cdot 2H_2O$ was denoted by B.

spectra of these compounds were recorded in Nujol Mulls. In the IR spectrum of $Cu_2(AdeH)_2Br_4 \cdot 5H_2O$, a strong band appeared in the region 1660 cm^{-1}, which was assigned to NH_2 bending. In contrast, in $Cu(AdeH)_2 \cdot 4H_2O$ and $Cu_2(AdeH)_4(ClO_4)_4 \cdot 6H_2O$, a strong band assigned to NH_2 bending appeared at 1640 cm^{-1}. In the IR spectrum of B,[18] a shoulder

Table I. Elementary Analysis of Several Binary and Ternary Cu^{2+} Complexes

Compound	C (%)		H (%)		N (%)	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$Cu_2(AdeH)_4(ClO_4)_4 \cdot 6H_2O$	20.46	20.56	2.75	2.46	23.87	23.31
$Cu_2(AdeH)_2Br_4 \cdot 5H_2O$	22.20	22.11	3.18	2.59	25.90	25.89
$Cu_2(AdeH)_2Cl_4$	22.26	21.67	1.87	1.76	25.92	25.53
$Cu_2(AdeH)_2(phen)_2 \cdot Cl_2 \cdot 2H_2O$	47.18	46.92	3.50	3.46	22.17	21.91
$Cu_2(AdeH)_2(phen)_2 \cdot Br_2 \cdot 2H_2O$	42.52	42.85	3.37	3.19	20.43	19.73
$Cu_2(AdeH)_2(phen)_2 \cdot (ClO_4)_2 \cdot 2H_2O$	41.10	40.96	3.05	2.79	19.74	19.73

Table II. IR Data of $Cu_2(AdeH)_2(phen)_2Cl_2 \cdot 2H_2O$(KBr)

Tentative assignment	Adenine	$Cu_2(AdeH)_2Cl_4$	$Cu_2(AdeH)_2(phen)_2 \cdot Cl_2 \cdot 2H_2O$
NH_2 str.	3290m	3390 s	3395 s
	3110 s	3200 s	3280m
		3125 s	3175m
			3050w
NH str.	2975w		
	2790w		
	2690w		
	2600w		
NH_2 bending	1670 s	1670 s	1660 sh
C=C, C=N	1610 s	1618 s	1630 s
Purine Ring vib.	1510w	1520 s, 1585 s	1550m
		1485 s	1520m, 1495m
Ring vib.	1458w	1457 s	1456m
	1426m	1412 s	1432 s, 1402 s
	1375m		1385m
NH ring,	1342m	1364m	1348 s
C–NH_2 str.	1318m	1323 s	1298 s
NH_2 wagging and twisting	1260m	1250w	1230w
	1160w	1220m	1174 s
	1132m	1175m	1152 s
NH		1116 s	1110m
	1028m	1020w, 980w	970m
NH_2 out-plane def.	945m	936m	
	918m		
NH out-plane def.	875w		872m
	850w		852 s
	801m		
CH bending		789 s	795w
			780w
		740 s	735m
NH_2 rocking	728m	725 s	722 s, 680 s
Ring and CN str.	644w	630m	643w
	625w		
C=C, C=N and Cu-N str.		596m	
		572w	560w
	546w	550 s	
			425w

absorption at 1650 cm^{-1} was assigned to NH_2 bending. In the IR spectrum of $Cu_2(AdeH)_2(phen)_2(ClO_4)_2 \cdot 2H_2O$, no bands assignable to N9-H stretching were observed and it was likely that N9 coordinated to Cu^{2+}. A strong absorption appeared at 1655 cm^{-1} and this was assigned to NH_2 bending. This band shifted to lower frequency by complexation. In the IR spectrum of C,[19] two bands at 564 and 432 cm^{-1} were assigned to C=C and C=N vibrations.

In all respects, the infrared spectra of three mixed ligand complexes resembled one another.

In the IR spectrum of $Cu_2(AdeH)_4(ClO_4)_4 \cdot 6H_2O$ whose ClO_4 anions are held in an interaction network of hydrogen bonds,[4] the bands at 1113 and 1088 cm^{-1} are assigned to the asymmetric stretching modes of ionic perchlorate.[20] The bands at 632 and 622 cm^{-1} are assigned to the asymmetric bending modes of ionic perchlorate.[20] The absence of bands in the 900—930 cm^{-1} region and the lack of splitting of 1090 cm^{-1} band substantiate the presence of a noncoordinate anion.

In contrast, in the IR spectrum of C, the symmetric stretching modes of ionic perchlorate about 1101 cm^{-1} are splitting, and a new band appeared at 932 cm^{-1}. Therefore, it may be concluded that the ClO_4^- anion takes part in coordination to the copper (II) ion.[20]

TABLE III. IR Data of $Cu_2(AdeH)_2(phen)_2(ClO_4)_2 \cdot 2H_2O$

Tentative assignment	$Cu_2(AdeH)_4(ClO_4)_2 \cdot 2H_2O$	$Cu_2(AdeH)_2(phen)_2 \cdot (ClO_4)_2 \cdot 2H_2O$
OH str.	3425 s	
NH_2 str.	3325 s	3380 s
	3185 s	3125 s
NH_2 bending	1680 s	1655 s
C=C, C=N	1605 s	1610 s
Purine Ring vib.	1570 m	
	1505 w	1500 w
	1472 s	
Ring vib.		1462 m
	1410 s	1434 s
		1407 m
NH ring, C–NH_2 str.	1355 m	1348 s
	1310 m, 1289 w	1305 s
NH_2 wagging and twisting	1215 s	1232 m
		1205 w
		1188 w
	1150 s	1150 sh
ClO_4^- asym. str.	1113 s	1101 s
	1088 s	
NH	995 w	980 m
NH_2 out-plane def.	940 w	932 w
CH bending	792 s	798 m
		772 m
NH_2 rocking	735 s	726 s
Ring and CN str.	645 w	660 m
		650 m
ClO_4^- bending	632 w	630 s
	622 s	
C=C, C=N	575 w	564 m
		432 m

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19) $Cu_2(AdeH)_2(phen)_2(ClO_4)_2 \cdot 2H_2O$ is denoted by C.

20) B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.*, **1961**, 3091; D.G. Hendricker and R.L. Bonder, *Inorg. Chem.*, **9**, 273 (1970).

EPR Spectra

Carrabine and Sundaralingam[21] reported the structure of di-μ-chloro-bis dichloro(guaninium)copper^{2+} dihydrate and the structure to be that of a dimer consisting of chloro-briged, trigonal-bipyramidally coordinated copper^{2+} ions. The EPR spectrum of a guanine-copper chloride complex was reported by Villa[22] and R.F. Drake, *et al.*[23] The latter reported that assignment of resonance fields was made impossible by the broadening of the spectrum and the presence of monomeric impurities and the full-field spectrum of $Cu(gua)Cl_3 \cdot H_2O$ (gua denots guanine) was very broad, and structureless and g-values of 2.18 can be obtained from the central point in the inflection.

Trinuclear adenine complex $Cu_3Cl_8(C_5H_6N_5)_2 \cdot 4H_2O$ showed only a single broad EPR band in the $g=2$ region,[24] related to that found for $Cu(gua)Cl_3 \cdot H_2O$.[22,23] The mixed ligand complexes, A and C, showed only a single broad band in the $g=2$ region, too. The EPR spectral line shape of these complexes would indicate the exchange interaction to be very small, since the delocalization ability of chloride and perchlorate ions is very low. Therefore, the spectra of these mixed ligand complexes will indicate that the distance Cu-Cu is remarkably small.[12] Consequently, it was assumed that these complexes contained chloride and perchlorate bridges. The mixed ligand complex B showed such a broad band that the g-value of this complex was not determined.

In the present study, a distinct resonance at 1500 G were not observed, which would be assigned to $\Delta M = \pm 2$ band and it was not apparent that the spins at the Cu^{2+} ions were interacting, yielding a triplet and a siglet state. The spectrum of the complex, Cu_3Cl_3(adenine)$_3 \cdot 6H_2O$ was symmetrical[12,24] but the spectra of the mixed ligand complexes were unsymmetrical as that of $Cu(gua)Cl_3 \cdot H_2O$.[22,23] The guanium complex is made up of trigonal bipyramidals sharing equatorial-to-apex with chloro-bridged Cu^{2+}, while many complexes with the bridged Cu^{2+} are square-based pyramid sharing base-to-apex. The mixed ligand complexes, A, B and C, were assumed to be made up of either the former or the latter.

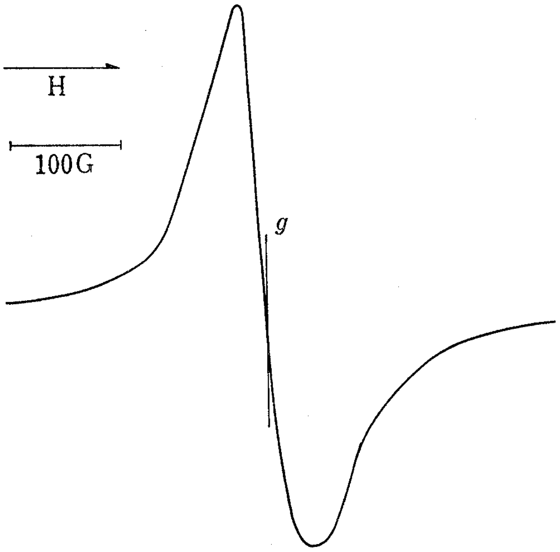

Fig. 3. EPR Spectrum of $Cu_2(AdeH)_2 \cdot (phen)_2Cl_2 \cdot 2H_2O$ with $g=2.12$.

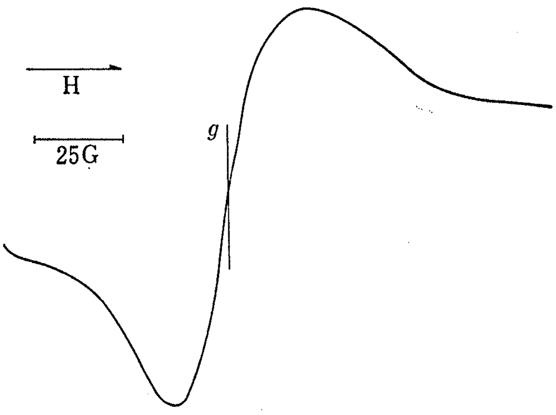

Fig. 4. EPR Spectrum of $Cu_2(AdeH)_2$-$(phen)_2(ClO_2)_2 \cdot 2H_2O$ with $g=2.12$

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[21] J.A. Carrabine and M. Sundaralingam, *J. Am. Chem. Soc.*, **92**, 369 (1970).

[22] J.F. Villa, *Inorg. Chem.*, **9**, 2052 (1973).

[23] R.F. Drake, V.H. Crawford, N.W. Naney, and W.E. Hatfield, *Inorg. Chem.*, **13**, 1246 (1974); J.R. Wasson, J.W. Hall, H.W. Richardson, and W.E. Hatfield, *ibid.*, **16**, 458 (1977).

[24] D.M.L. Goodgame and S.V. Waggett, *Biochim. Biophys. Res.*, **42**, 67 (1971).

Experimental

Apparatus——Infrared spectra were recorded in Nujol or KBr disk on a Hitachi Infrared Spectrometer, Model G3. The EPR spectra were taken on a JES-ME-IX EPR Spectrometer. The spectra were recorded on polycrystalline samples at a room temperature and *g*-values were determined by the methods of Hathaway and Billing.[25]

Reagents——The ligands and other materials were obtained from Wako Pure Chemical Industries Ltd. and Tokyo Kasei Co., Tokyo.

Preparation——$Cu_2(AdeH)_4(ClO_4)$–$6H_2O$ was prepared according to Ref. 4.

The following complexes are new compounds.

$Cu_2(C_5H_5N_5)Cl_4$: In 13 ml of 0.1 M HCl, 0.9 g of adenine hydrochloride was dissolved. In 9 ml of H_2O, 4 g of $CuCl_2 \cdot 2H_2O$ was dissolved. These two solutions were mixed and the solution was heated at 95° for several hours. A yellow polycrystalline compound was obtained. The complex was washed with 0.1 M HCl and methanol.

$Cu_2(C_5H_5N_5)_2(C_{12}H_8N_2)_2Cl_2 \cdot 2H_2O$: In 20 ml of methanol, 200 mg of 1,10-phenanthroline was added to 80 ml of hot water containing $Cu_2(C_5H_5N_5)_2Cl_4$ with stirring. The solution was heated for two hours at a room temperature and then the solution was evaporated. When the solution was cooled, dark green crystals were obtained. They were crystallized from water and dried under a reduced pressure.

$Cu_2(C_5H_5N_5)_2(C_{12}H_8N_2)_2(ClO_4)_2 \cdot 2H_2O$: Method I, in 200 ml of water, 0.578 g of $Cu_2(AdeH)_4(ClO_4)_4 \cdot 6H_2O$ was suspended. In 100 ml of methanol, 0.397 g of 1,10-phenanthroline was dissolved. The two solution were mixed and evaporated. Dark green crystals thus obtained were recrystallized form water and dried under a reduced pressure.

Method II, in 200 ml of an aqueous methanol, 0.270 g of adenine, 0.741 g of $Cu_2(ClO_4)_2 \cdot 6H_2O$ and 0.396 g of 1,10-phenanthroline were dissolved. The solution was refluxed for two hours at 90°. When the solution was cooled, dark green crystals were obtained. They were recrystallized from water and dried under a reduced pressure.

$Cu_2(C_5H_5N_5)_2Br_4 \cdot 5H_2O$: In 50 ml of 0.1 M HCl, 0.338 g of adenine was dissolved and 2.23 g of $CuBr_2$ was dissolved in 10 ml of 0.1 M HCl. The two solutions were mixed with stirring. A brown compound was obtained and washed with water. It was dried under a reduced pressure.

$Cu_2(C_5H_5N_5)_2(C_{12}H_8N_2)_2Br_2 \cdot 2H_2O$: In 100 ml of 50% aqueous methanol solution, 0.530 g of $Cu_2(C_5H_5N_5)_2Br_4 \cdot 5H_2O$ and 0.390 g of 1,10-phenanthroline were suspended. The solution was stirred for two hours at a room temperature. Dark green crystals thus obtained was recrystallized from water and dried under a reduced pressure.

Acknowledgement Thanks are due to Miss H. Oida for elementary analysis.

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25) B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev.*, 5, 143 (1970).