The Crystal and Molecular Structure of the Aquabis(cyclo-L-histidyl-L-histidylato)dicopper(II) Perchlorate Hydrate $[H_2O\ Cu_2(C_{12}H_{13}N_6O_2)_2](ClO_4)_2\cdot 3.5H_2O$

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The crystal structure of the title compound has been determined by a three-dimensional X-ray structure analysis, using 4563 counter intensity data. The crystals are monoclinic, with $a=22.97(2)$, $b=15.89(1)$, $c=10.00(1)$ Å, $\beta=100.1(1)°$, space group $P2_1$, and $Z=4$. The structure was solved by the Patterson and Fourier technique and was refined by the block-diagonal least-squares method to $R=0.061$. The unit cell contains two crystallographically independent complex cations, the structure of which are very similar to each other. The complex cation is dimeric; there are two Cu atoms, and each of the two cyclo-L-histidyl-L-histidylato ligands bridges two metal atoms. Except for the aqua ligand, the main body of the complex has an approximate twofold axis which passes through the two metal atoms and relates the ligands to each other. The two Cu atoms have different coordination geometries. One Cu atom has a flattened tetrahedral coordination by 4N atoms, whereas the other is surrounded by 2N and 3O atoms and is intermediate between the square pyramid and the trigonal bipyramid.

There has been considerable interest in the structures of the metal chelates of amino acid anhydride as simple model compounds for the biomolecules.[1] Although some infrared and visible spectral studies have been made of these complexes,[2] the stereochemical details of the complexes have not yet been elucidated. Since no X-ray structure has been reported as yet, we wish to report here the preparation and X-ray structure of the title compound. A preliminary communication on the structure of the complex has already been published.[3]

Experimental

Preparation of the Complex. $HISH_2$[$HISH_2$=cyclo(L-histidyl-L-histidyl)] was prepared following the procedure of Abderhalden *et al.*[4] A suspension of equimolar amounts of $HISH_2$(0.585g, 2 mmol) and copper(II) perchlorate hexahydrate (0.741 g, 2 mmol) in hot methanol was stirred until both substances had been completely dissolved. Lithium hydroxide monohydrate (0.084 g, 2 mmol) was then added, and the resultant solution was allowed to stand for one day at room temperature. The blue crystals were separated out. The square prisms were obtained upon recrystallization from a hot aqueous solution. Yield, 0.393 g (41.2%).

Found: C, 30.26; H, 3.63; N, 17.68%. Calcd for $[H_2O\ Cu_2(C_{12}H_{13}N_6O_2)_2](ClO_4)_2\cdot 3.5H_2O$: C, 30.23; H, 3.70; N, 17.63%.

X-Ray Data Collection. The specimen employed for data collection had dimensions of $0.22\times0.25\times0.28$mm. Preliminary X-ray photographic studies, using oscillation, Weissenberg, and precession techniques, revealed the approximate unit-cell dimensions, the Laue symmetry of $2/m$, and the systematic absences of $0k0$ for $k=2n+1$. These extinctions indicate that the space group is $P2_1$, since the compound is optically active.

Crystal Data: $Cu_2(C_{12}H_{13}N_6O_2)_2(ClO_4)_2(H_2O)_{4.5}$, $a=22.97(2)$, $b=15.89(1)$, $c=10.00(1)$Å, $\beta=100.1(1)°$, $U=3596.3$Å^3, $Z=4$, $D_x=1.76$, $D_m=1.74$ g cm^{-3}, space group $P2_1$, λ(Mo$K\alpha$)$=0.7107$Å, μ(Mo$K\alpha$)$=78.0$ cm^{-1}.

The cell dimensions were determined by the least-squares treatment using 48 θ values measured accurately on a Philips PW1100 diffractometer. Intensity data with $3°\leqq 2\theta \leqq 50°$ were collected at room temperature by the use of graphite-monochromated Mo$K\alpha$ radiation. The ω-2θ scan technique was employed. The scan range was $(0.9+0.3\tan\theta)°$, and the scan speed, 2°/min; the background was counted for 15 s at each end of the scan. The three standard reflections, 080, 900, and 004, measured every 150 min, showed no appreciable decay. A total of 4563 intensities with $I_{top}-2\sqrt{I_{top}}>I_{back}$ were classified as observed, where I_{top} is the intensity (count/s) measured at the top of the peak and I_{back} is the mean background intensity (count/s), obtained from the preliminary background measurements for 5 s on each side of the peak. The Lorentz-poralization corrections were made, and relative structure factors were derived.[5] No absorption correction was applied.

Structure Determination and Refinement. The four copper stoms were located from a three-dimensional Patterson map, and the positions of the remaining non-hydrogen atoms were determined by successive Fourier syntheses. The structure was initially refined by the isotropic block-diagonal least-squares method. In the course of refinement, it was found that the 15O atoms of perchlorate ions and all the water molecules of crystallization were somewhat disordered. Therefore, isotropic temperature factors were assigned to them throughout the refinement. Six cycles of the anisotropic least-squares refinement resulted in convergence at $R=0.061$. No parameter was observed to shift by $>0.1\,\sigma$. The function minimized was $\sum w(F_o-|F_c|)^2$, with $w=1/\sigma(F_o)^2$ being used. The scattering factors for the neutral Cu, Cl, O, N, and C atoms were taken from Ref. 6. No attempt was made to locate the hydrogen atoms. The absolute crystal structure was determined on the basis of the known configuration of the cyclo-L-histidyl-L-histidilato ligand. The final atomic coordinates which give the absolute crystal structure are presented in Table 1, along with their temperature factors. The observed and calculated structure factors have been deposited at the Chemical Society of Japan (Document No. 7721). All the calculations were performed on a FACOM 270-30 computer at Osaka City University. The programs used included a local version of the UNICS.[7]

Results and Discussion

The structural formula of cyclo-L-histidyl-L-histidyl ($HISH_2$) is shown in Fig. 1. The middle 2,5-piperadinedione moiety ($DKPH_2$) takes a planar structure. Since the C(5) and C(7) atoms have an S absolute configuration, both the C(4) and C(9) atoms lie on one side of the ring plane of the $DKPH_2$. The $HISH_2$ molecule

TABLE 1. FRACTIONAL POSITIONAL PARAMETERS ($\times 10^4$) AND ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$), WITH e.s.d.'s IN PARENTHESES

The temperature factors are of the form: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})]$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(A)	3870(1)	6565(1)	6382(2)	10(0)	31(1)	88(2)	−1(1)	14(1)	−1(2)
Cu(B)	3752(1)	4382(1)	5687(2)	8(0)	29(1)	71(2)	0(1)	6(1)	3(2)
Cu′(A)	8482(1)	4020(1)	11101(2)	11(0)	25(1)	58(2)	−8(1)	12(1)	−24(2)
Cu′(B)	9240(1)	5000(1)	8651(2)	9(0)	21(1)	55(2)	−2(1)	0(1)	−6(2)
Cl	8070(2)	9384(3)	8932(4)	16(1)	39(2)	95(5)	−7(3)	7(3)	−1(6)
Cl′	611(2)	6600(3)	6797(4)	16(1)	40(2)	83(4)	7(2)	15(3)	10(6)
Cl″	7168(2)	6660(4)	5639(6)	20(1)	55(3)	215(8)	9(3)	23(5)	81(9)
Cl‴	4266(3)	8217(7)	9916(9)	35(2)	176(8)	323(14)	64(7)	33(9)	−192(19)
C(1)	3376(7)	6160(12)	8802(15)	20(4)	53(10)	70(19)	−16(11)	11(14)	4(23)
C(2)	2414(7)	6320(11)	8279(15)	20(4)	46(10)	66(18)	11(10)	14(13)	10(20)
C(3)	2651(6)	6515(9)	7176(14)	9(3)	16(6)	108(19)	0(8)	10(11)	1(20)
C(4)	2380(6)	6750(10)	5747(14)	9(3)	33(8)	70(16)	9(8)	−6(11)	−10(19)
C(5)	2285(6)	5983(9)	4843(14)	10(3)	27(7)	90(19)	−1(8)	13(12)	30(20)
C(6)	2853(6)	5520(10)	4925(13)	17(4)	29(7)	37(15)	−2(9)	−22(12)	−5(17)
C(7)	2432(6)	4197(10)	5663(14)	7(3)	39(9)	79(16)	−2(8)	2(10)	18(19)
C(8)	1827(6)	4624(10)	5344(14)	11(3)	42(9)	60(16)	−16(8)	−16(11)	2(19)
C(9)	2550(6)	4031(10)	7263(13)	15(3)	33(7)	67(16)	26(9)	3(12)	42(20)
C(10)	3114(6)	3534(10)	7685(15)	12(3)	32(8)	84(18)	−6(8)	10(12)	6(20)
C(11)	3155(7)	2835(11)	8481(15)	17(4)	36(9)	95(20)	−7(9)	−12(14)	19(22)
C(12)	4047(8)	3155(12)	7980(17)	19(4)	38(9)	128(23)	−2(10)	0(16)	−5(24)
C′(1)	4351(7)	6810(11)	3910(17)	16(4)	37(9)	146(24)	−12(9)	31(15)	7(24)
C′(2)	5326(7)	6707(11)	4442(15)	18(4)	45(9)	99(20)	−15(10)	28(14)	19(23)
C′(3)	5096(6)	6657(10)	5593(16)	14(3)	21(7)	139(22)	2(9)	35(14)	−24(22)
C′(4)	5382(7)	6501(11)	7058(16)	18(4)	33(8)	114(21)	−14(10)	−4(14)	−17(23)
C′(5)	5366(6)	5543(11)	7404(17)	11(3)	32(8)	140(24)	1(9)	21(14)	−43(23)
C′(6)	4735(6)	5207(9)	6964(13)	14(3)	27(8)	57(16)	6(8)	−3(12)	3(18)
C′(7)	5033(6)	4148(10)	5488(13)	9(3)	37(8)	77(17)	−2(8)	21(11)	−11(20)
C′(8)	5679(5)	4400(10)	6007(15)	4(3)	34(7)	119(20)	6(8)	5(11)	−16(22)
C′(9)	4922(6)	4358(12)	3915(14)	13(3)	48(9)	81(17)	1(10)	21(12)	22(23)
C′(10)	4320(6)	4024(12)	3232(14)	15(3)	54(9)	69(17)	0(10)	15(12)	−54(23)
C′(11)	4187(8)	3731(15)	1902(21)	22(5)	83(15)	182(31)	10(14)	−9(19)	−99(36)
C′(12)	3374(7)	3794(12)	2863(15)	19(4)	56(11)	77(19)	−6(11)	5(14)	−13(23)
C″(1)	8496(7)	2430(10)	9613(14)	20(4)	27(7)	57(16)	−5(9)	27(13)	−13(18)
C″(2)	7655(7)	2286(10)	8251(15)	16(4)	27(8)	97(19)	−12(8)	22(14)	−24(20)
C″(3)	7669(6)	3023(9)	8942(13)	13(3)	25(7)	57(16)	−17(8)	16(11)	−21(17)
C″(4)	7231(5)	3743(9)	8747(15)	5(3)	24(7)	113(19)	6(7)	15(12)	10(19)
C″(5)	7417(5)	4447(10)	7850(13)	9(3)	28(7)	61(15)	−2(8)	3(10)	3(18)
C″(6)	8058(5)	4737(8)	8367(13)	9(3)	12(6)	68(16)	4(6)	−6(10)	4(15)
C″(7)	8371(5)	4309(10)	6282(13)	8(3)	27(7)	81(17)	−4(7)	5(11)	−11(19)
C″(8)	7718(5)	4149(9)	5645(12)	10(3)	24(7)	54(14)	−11(7)	12(10)	−25(16)
C″(9)	8675(6)	3435(9)	6387(15)	13(3)	21(7)	106(20)	10(8)	−1(13)	−24(19)
C″(10)	9359(6)	3506(9)	6810(13)	13(3)	21(7)	56(15)	2(7)	31(11)	5(17)
C″(11)	9773(7)	2993(11)	6391(15)	20(4)	42(9)	62(17)	10(10)	9(13)	−23(21)
C″(12)	10207(6)	4006(11)	7775(14)	15(3)	34(7)	82(17)	20(9)	31(12)	−11(21)
C‴(1)	8431(7)	5581(11)	12620(18)	19(4)	30(8)	150(25)	−1(10)	50(17)	−18(24)
C‴(2)	9249(7)	5585(11)	14199(14)	17(4)	38(8)	62(17)	−21(9)	14(3)	−1(20)
C‴(3)	9249(6)	4865(10)	13473(12)	16(3)	41(8)	30(14)	−24(9)	14(11)	−12(18)
C‴(4)	9675(6)	4161(10)	13593(14)	19(4)	27(8)	67(16)	−1(8)	−2(12)	2(18)
C‴(5)	10089(6)	4178(8)	12510(13)	14(3)	14(7)	68(16)	−2(7)	−6(11)	11(16)
C‴(6)	9727(5)	4342(10)	11117(13)	7(3)	32(7)	66(15)	8(8)	11(10)	−20(19)
C‴(7)	10225(6)	5643(9)	10771(14)	9(3)	26(7)	75(18)	−7(8)	−22(11)	12(19)
C‴(8)	10646(6)	5465(10)	12164(15)	13(3)	33(8)	89(20)	−11(9)	14(13)	−21(20)
C‴(9)	9867(6)	6454(10)	11019(14)	14(3)	31(8)	61(16)	1(8)	−19(12)	−23(19)
C‴(10)	9462(6)	6748(9)	9757(13)	11(3)	29(8)	63(16)	−7(8)	4(11)	−3(18)
C‴(11)	9304(8)	7550(11)	9444(16)	23(4)	41(9)	88(20)	−5(10)	19(15)	13(23)
C‴(12)	8793(7)	6685(10)	7865(15)	17(4)	23(7)	111(21)	−3(9)	22(14)	8(21)
N(1)	3266(5)	6408(8)	7532(11)	11(3)	28(6)	79(14)	2(6)	7(10)	−39(5)
N(2)	2859(6)	6093(10)	9312(12)	21(4)	58(8)	71(16)	4(9)	24(12)	17(20)
N(3)	1795(5)	5462(8)	5119(12)	16(3)	22(6)	80(16)	−4(7)	−8(11)	8(15)
N(4)	2922(5)	4719(7)	5350(11)	8(2)	25(6)	70(14)	−1(6)	7(9)	−9(14)
N(5)	3647(5)	3734(8)	7358(12)	13(3)	37(7)	73(14)	17(7)	−2(10)	12(16)
N(6)	3769(7)	2606(10)	8672(14)	28(4)	48(8)	110(19)	4(10)	15(14)	18(21)
N′(1)	4472(5)	6692(9)	5175(13)	11(3)	35(7)	124(17)	−7(7)	36(11)	2(19)
N′(2)	4862(6)	6793(9)	3393(14)	24(4)	43(8)	129(19)	−13(9)	45(14)	−10(20)

TABLE 1. (Continued)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N′(3)	5794(5)	5050(9)	6800(13)	10(3)	37(7)	138(18)	17(8)	−20(11)	−65(20)
N′(4)	4602(5)	4562(8)	6146(11)	9(2)	39(7)	67(13)	2(7)	5(9)	9(16)
N′(5)	3824(5)	4084(9)	3799(12)	10(3)	47(7)	86(15)	1(8)	−2(10)	−15(19)
N′(6)	3569(6)	3562(12)	1729(14)	14(3)	104(13)	117(19)	−7(11)	−2(13)	−97(26)
N″(1)	8215(5)	3126(7)	9787(11)	9(2)	24(6)	61(13)	−9(6)	−2(9)	−21(14)
N″(2)	8192(6)	1926(8)	8740(12)	23(4)	26(6)	79(16)	−1(8)	21(12)	−35(16)
N″(3)	7322(5)	4204(7)	6438(10)	14(3)	21(6)	57(12)	1(6)	9(9)	−30(14)
N″(4)	8450(5)	4694(7)	7650(10)	8(2)	22(5)	53(13)	−9(5)	5(9)	−20(13)
N″(5)	9626(5)	4125(8)	7665(11)	14(3)	29(6)	65(13)	3(7)	25(9)	−12(15)
N″(6)	10302(6)	3331(9)	7053(13)	18(3)	36(7)	96(17)	4(7)	11(12)	4(18)
N‴(1)	8726(5)	4876(8)	12484(12)	9(3)	33(6)	98(15)	−7(7)	20(10)	−29(17)
N‴(2)	8745(6)	6027(9)	13688(13)	27(4)	28(7)	99(17)	−14(8)	30(13)	−26(18)
N‴(3)	10547(5)	4807(9)	12866(12)	8(2)	49(8)	81(15)	−8(7)	−11(9)	52(17)
N‴(4)	9819(4)	4961(8)	10333(10)	10(2)	25(5)	40(11)	−3(7)	4(8)	−1(15)
N‴(5)	9138(5)	6210(7)	8783(12)	9(3)	18(5)	100(16)	−5(6)	6(10)	−15(15)
N‴(6)	8871(6)	7498(8)	8236(13)	22(3)	23(6)	111(18)	1(7)	8(12)	15(17)
O(1)	3305(4)	5922(6)	4679(9)	11(2)	34(5)	77(12)	−12(5)	31(8)	12(13)
O(2)	1393(4)	4197(6)	5330(11)	7(2)	26(6)	180(16)	−3(5)	5(9)	2(15)
O(3W)	3648(6)	7796(8)	6152(13)	28(4)	36(6)	168(18)	8(8)	34(13)	2(18)
O(4)	8610(6)	9534(11)	9785(13)	30(4)	109(12)	136(18)	−43(11)	−36(13)	44(24)
O(5)	7723(6)	8798(10)	9560(12)	32(4)	92(11)	115(16)	−32(10)	20(13)	43(22)
O(6)	8157(5)	9046(8)	7662(11)	25(3)	42(6)	126(15)	11(8)	22(11)	−8(17)
O(7)	7757(6)	10145(9)	8701(14)	35(4)	44(7)	197(21)	21(9)	32(14)	−24(21)
O′(1)	4339(4)	5607(7)	7461(10)	13(2)	31(5)	105(14)	5(6)	20(9)	3(14)
O′(2)	6079(4)	3996(8)	5612(12)	6(2)	52(7)	206(19)	0(7)	6(10)	−66(20)
O′(3W)	7801(6)	3656(9)	12086(12)	31(4)	80(9)	109(15)	−55(9)	69(12)	−73(19)
O′(4)	50(5)	7001(9)	6710(14)	21(3)	61(8)	230(23)	3(8)	49(14)	−11(23)
O′(5)	617(5)	6176(10)	5550(13)	19(3)	86(10)	161(19)	28(9)	17(12)	−92(22)
O′(6)	760(7)	6087(12)	7990(14)	51(5)	100(12)	137(20)	2(3)	−41(17)	104(26)
O′(7)	1069(6)	7251(9)	6943(15)	21(3)	68(9)	233(23)	1(9)	17(14)	66(24)
O″(1)	8140(4)	4994(6)	9603(8)	10(2)	23(4)	60(10)	4(5)	6(7)	5(13)
O″(2)	7594(4)	3985(8)	4431(9)	17(2)	65(7)	65(11)	−13(7)	3(8)	−48(16)
O″(4)	7509(10)	7303(16)	6481(22)	a)					
O″(5)	6850(9)	6226(14)	6495(19)	a)					
O″(6)	7608(9)	6160(15)	5229(20)	a)					
O″(7)	6829(9)	7129(14)	4719(19)	a)					
O‴(1)	9302(4)	3814(6)	10731(9)	12(2)	24(5)	73(11)	−9(5)	9(8)	−13(12)
O‴(2)	11047(4)	5962(7)	12514(10)	13(2)	52(7)	89(13)	−23(6)	−14(9)	−6(16)
O‴(4)	4603(11)	8952(18)	10363(24)	a)					
O‴(5)	4531(8)	7730(13)	9019(18)	a)					
O‴(6)	3699(9)	8424(14)	8981(20)	a)					
O‴(7)	4170(11)	7748(18)	11077(25)	a)					
O(8W)	7716(6)	6624(10)	9775(14)	a)					
O(9W)	6513(7)	6015(12)	9585(16)	a)					
O(10W)	1097(7)	2574(11)	5121(16)	a)					
O(11W)	4809(9)	1477(14)	9188(19)	a)					
O(12W)	8512(10)	7715(17)	11708(23)	a)					
O(13W)	6503(11)	654(18)	8160(24)	a)					
O(14W)	3205(12)	321(19)	7490(26)	a)					

Atom	B(Å²)	Atom	B(Å²)	Atom	B(Å²)	Atom	B(Å²)
O″(4)	1330(68)	O″(5)	1154(59)	O″(6)	1200(61)	O″(7)	1116(56)
O‴(4)	1530(81)	O‴(5)	1064(53)	O‴(6)	1152(58)	O‴(7)	1585(84)
O(8W)	702(35)	O(9W)	905(46)	O(10W)	843(42)	O(11W)	1182(59)
O(12W)	1420(73)	O(13W)	1510(78)	O(14W)	1668(89)		

a) Isotropic temperature factors ($\times 10^2$) with e.s.d.'s in parentheses.

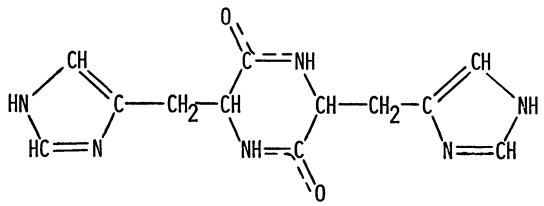


Fig. 1. The schematic drawing of cyclo(L-histidyl-L-histidyl)

has four donor atoms: two N atoms of the respective imidazole groups (Im) and two O atoms in the $DKPH_2$. In the cyclo-L-histidyl-L-histidylato ligand ($HISH^-$) of the present complex, one of the NH groups in the $DKPH_2$ is deprotonated; the resulting "anionic" N atom also coordinates to the Cu atom.

There are two crystallographically independent complex cations in the unit cell; a stereoscopic view of them is given in Fig. 2, where the atom numbering

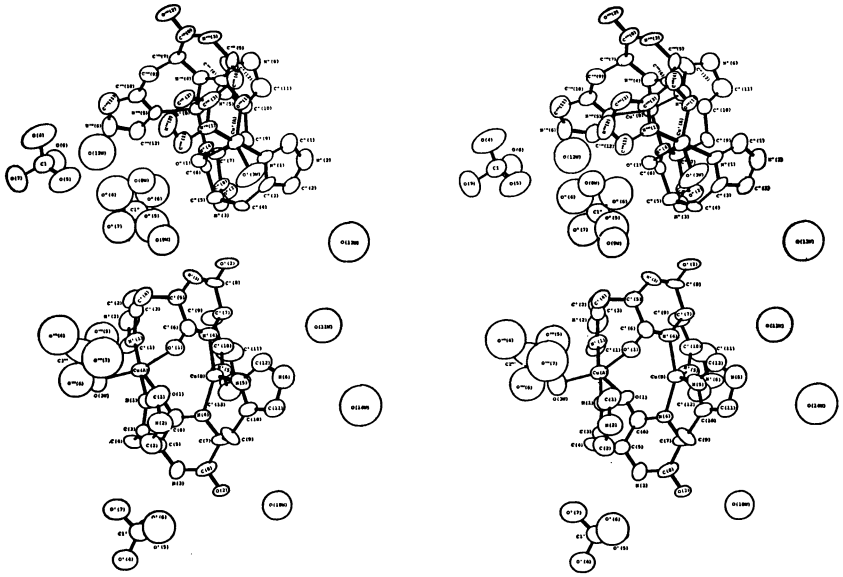


Fig. 2. Stereoscopic view of aquabis(cyclo-L-histidyl-L-histidylato)dicopper(II) perchlorate hydrate, looking down along the c axis.

TABLE 2. BOND DISTANCES (d/Å), WITH e.s.d.'s IN PARENTHESES

Cu(A)–N(1)	1.97(1)	Cu(A)–N′(1)	2.00(1)	Cu′(A)–N″(1)	1.96(1)	Cu′(A)–N‴(1)	1.95(1)
Cu(A)–O(1)	2.21(1)	Cu(A)–O′(1)	2.06(1)	Cu′(A)–O″(1)	2.20(1)	Cu′(A)–O‴(1)	2.01(1)
Cu(A)–O(3W)	2.02(1)			Cu′(A)–O′(3W)	2.07(1)		
Cu(B)–N(4)	1.95(1)	Cu(B)–N′(4)	1.95(1)	Cu′(B)–N″(4)	1.97(1)	Cu′(B)–N‴(4)	1.96(1)
Cu(B)–N(5)	2.01(1)	Cu(B)–N′(5)	1.98(1)	Cu′(B)–N″(5)	2.00(1)	Cu′(B)–N‴(5)	1.95(1)
C(1)–N(1)	1.31(2)	C′(1)–N′(1)	1.26(2)	C″(1)–N″(1)	1.31(2)	C‴(1)–N‴(1)	1.33(2)
C(1)–N(2)	1.38(2)	C′(1)–N′(2)	1.36(2)	C″(1)–N″(2)	1.30(2)	C‴(1)–N‴(2)	1.38(2)
C(2)–C(3)	1.35(2)	C′(2)–C′(3)	1.35(2)	C″(2)–C″(3)	1.36(2)	C‴(2)–C‴(3)	1.36(2)
C(2)–N(2)	1.37(2)	C′(2)–N′(2)	1.37(2)	C″(2)–N″(2)	1.37(2)	C‴(2)–N‴(2)	1.38(2)
C(3)–C(4)	1.50(2)	C′(3)–C′(4)	1.52(2)	C″(3)–C″(4)	1.51(2)	C‴(3)–C‴(4)	1.48(2)
C(3)–N(1)	1.41(2)	C′(3)–N′(1)	1.42(2)	C″(3)–N″(1)	1.40(2)	C‴(3)–N‴(1)	1.42(2)
C(4)–C(5)	1.51(2)	C′(4)–C′(5)	1.56(3)	C″(4)–C″(5)	1.54(2)	C‴(4)–C‴(5)	1.56(2)
C(5)–C(6)	1.49(2)	C′(5)–C′(6)	1.54(2)	C″(5)–C″(6)	1.54(2)	C‴(5)–C‴(6)	1.52(2)
C(5)–N(3)	1.46(2)	C′(5)–N′(3)	1.47(2)	C″(5)–N″(3)	1.44(2)	C‴(5)–N‴(3)	1.45(2)
C(6)–N(4)	1.34(2)	C′(6)–N′(4)	1.31(2)	C″(6)–N″(4)	1.25(2)	C‴(6)–N‴(4)	1.30(2)
C(6)–O(1)	1.28(2)	C′(6)–O′(1)	1.28(2)	C″(6)–O″(1)	1.29(2)	C‴(6)–O‴(1)	1.29(2)
C(7)–C(8)	1.53(2)	C′(7)–C′(8)	1.54(2)	C″(7)–C″(8)	1.54(2)	C‴(7)–C‴(8)	1.58(2)
C(7)–C(9)	1.60(2)	C′(7)–C′(9)	1.58(2)	C″(7)–C″(9)	1.55(2)	C‴(7)–C‴(9)	1.57(2)
C(7)–N(4)	1.48(2)	C′(7)–N′(4)	1.44(2)	C″(7)–N″(4)	1.48(2)	C‴(7)–N‴(4)	1.45(2)
C(8)–N(3)	1.35(2)	C′(8)–N′(3)	1.30(2)	C″(8)–N″(3)	1.31(2)	C‴(8)–N‴(3)	1.30(2)
C(8)–O(2)	1.20(2)	C′(8)–O′(2)	1.24(2)	C″(8)–O″(2)	1.23(2)	C‴(8)–O‴(2)	1.22(2)
C(9)–C(10)	1.51(2)	C′(9)–C′(10)	1.53(2)	C″(9)–C″(10)	1.56(2)	C‴(9)–C‴(10)	1.51(2)
C(10)–C(11)	1.36(2)	C′(10)–C′(11)	1.39(3)	C″(10)–C″(11)	1.37(2)	C‴(10)–C‴(11)	1.35(2)
C(10)–N(5)	1.36(2)	C′(10)–N′(5)	1.36(2)	C″(10)–N″(5)	1.38(2)	C‴(10)–N‴(5)	1.41(2)
C(11)–N(6)	1.44(2)	C′(11)–N′(6)	1.43(2)	C″(11)–N″(6)	1.39(2)	C‴(11)–N‴(6)	1.43(2)
C(12)–N(5)	1.37(2)	C′(12)–N′(5)	1.35(2)	C″(12)–N″(5)	1.33(2)	C‴(12)–N‴(5)	1.34(2)
C(12)–N(6)	1.34(2)	C′(12)–N′(6)	1.34(2)	C″(12)–N″(6)	1.33(2)	C‴(12)–N‴(6)	1.35(2)
Cl–O(4)	1.40(1)	Cl′–O′(4)	1.43(1)	Cl″–O″(4)	1.46(2)	Cl‴–O‴(4)	1.43(3)
Cl–O(5)	1.44(2)	Cl′–O′(5)	1.42(1)	Cl″–O″(5)	1.40(2)	Cl‴–O‴(5)	1.40(2)
Cl–O(6)	1.43(1)	Cl′–O′(6)	1.44(2)	Cl″–O″(6)	1.40(2)	Cl‴–O‴(6)	1.50(2)
Cl–O(7)	1.41(1)	Cl′–O′(7)	1.47(2)	Cl″–O″(7)	1.33(2)	Cl‴–O‴(7)	1.43(3)

scheme is also given. Both of the complex cations can be represented by the same formula, $[Cu(HISH)_2Cu(H_2O)]^{2+}$. The four $HISH^-$ ligands in the two complex cations are crystallographically independent of each other. The atom-numbering scheme for the $HISH^-$ is shown in Fig. 2; the same numbering was used for these four ligands, but primes are utilized in order to distinguish between these ligands. The bond lengths and angles are listed in Tables 2 and 3 respectively.

The two complexes have a close resemblance in

TABLE 3. BOND ANGLES (ϕ/°)

N(1)–Cu(A)–O(1)	90.7(4)	N″(1)–Cu′(A)–O″(1)	91.2(4)
N(1)–Cu(A)–O(3W)	90.0(5)	N″(1)–Cu′(A)–O′(3W)	86.8(5)
N(1)–Cu(A)–O′(1)	87.5(5)	N″(1)–Cu′(A)–O‴(1)	87.2(4)
N′(1)–Cu(A)–O(1)	87.5(4)	N‴(1)–Cu′(A)–O″(1)	90.9(4)
N′(1)–Cu(A)–O(3W)	91.2(6)	N‴(1)–Cu′(A)–O′(3W)	90.3(5)
N′(1)–Cu(A)–O′(1)	92.1(5)	N‴(1)–Cu′(A)–O‴(1)	94.6(4)
O(1)–Cu(A)–O(3W)	104.9(4)	O″(1)–Cu′(A)–O′(3W)	108.1(4)
O(1)–Cu(A)–O′(1)	104.2(4)	O″(1)–Cu′(A)–O‴(1)	102.9(4)
O(3W)–Cu(A)–O′(1)	150.8(4)	O′(3W)–Cu′(A)–O‴(1)	148.5(5)
N(1)–Cu(A)–N′(1)	178.1(5)	N″(1)–Cu′(A)–N‴(1)	176.8(5)
N(4)–Cu(B)–N(5)	91.6(5)	N″(4)–Cu′(B)–N″(5)	91.5(5)
N(4)–Cu(B)–N′(4)	155.4(5)	N″(4)–Cu′(B)–N‴(4)	148.8(5)
N(4)–Cu(B)–N′(5)	98.2(5)	N″(4)–Cu′(B)–N‴(5)	99.6(5)
N(5)–Cu(B)–N′(4)	98.0(5)	N″(5)–Cu′(B)–N‴(4)	96.2(5)
N(5)–Cu(B)–N′(5)	135.3(6)	N″(5)–Cu′(B)–N‴(5)	142.2(5)
N′(4)–Cu(B)–N′(5)	90.7(5)	N‴(4)–Cu′(B)–N‴(5)	92.6(5)
C(1)–N(1)–C(3)	107.3(13)	C′(1)–N′(1)–C′(3)	109.6(14)
C″(1)–N″(1)–C″(3)	103.5(11)	C‴(1)–N‴(1)–C‴(3)	109.0(12)
Cu(A)–N(1)–C(1)	124.6(10)	Cu(A)–N′(1)–C′(1)	124.5(11)
Cu′(A)–N″(1)–C″(1)	126.8(9)	Cu′(A)–N‴(1)–C‴(1)	124.8(10)
Cu(A)–N(1)–C(3)	128.1(9)	Cu(A)–N′(1)–C′(3)	125.9(10)
Cu′(A)–N″(1)–C″(3)	129.4(10)	Cu′(A)–N‴(1)–C‴(3)	126.2(10)
N(1)–C(1)–N(2)	110.5(13)	N′(1)–C′(1)–N′(2)	108.9(13)
N″(1)–C″(1)–N″(2)	113.0(13)	N‴(1)–C‴(1)–N‴(2)	107.8(13)
C(1)–N(2)–C(2)	106.2(13)	C′(1)–N′(2)–C′(2)	108.6(14)
C″(1)–N″(2)–C″(2)	109.2(13)	C‴(1)–N‴(2)–C‴(2)	108.6(13)
C(3)–C(2)–N(2)	108.9(14)	C′(3)–C′(2)–N′(2)	107.0(14)
C″(3)–C″(2)–N″(2)	103.8(12)	C‴(3)–C‴(2)–N‴(2)	108.1(12)
C(2)–C(3)–N(1)	107.2(12)	C′(2)–C′(3)–N′(1)	105.7(12)
C″(2)–C″(3)–N″(1)	110.4(12)	C‴(2)–C‴(3)–N‴(1)	106.5(13)
C(2)–C(3)–C(4)	132.5(13)	C′(2)–C′(3)–C′(4)	131.7(14)
C″(2)–C″(3)–C″(4)	129.1(12)	C‴(2)–C‴(3)–C‴(4)	131.1(12)
C(4)–C(3)–N(1)	120.2(13)	C′(4)–C′(3)–N′(1)	122.3(14)
C″(4)–C″(3)–N″(1)	119.8(12)	C‴(4)–C‴(3)–N‴(1)	122.4(13)
C(3)–C(4)–C(5)	111.2(12)	C′(3)–C′(4)–C′(5)	110.5(13)
C″(3)–C″(4)–C″(5)	112.2(12)	C‴(3)–C‴(4)–C‴(5)	113.9(12)
C(4)–C(5)–C(6)	109.4(11)	C′(4)–C′(5)–C′(6)	109.4(12)
C″(4)–C″(5)–C″(16)	111.5(10)	C‴(4)–C‴(5)–C‴(6)	109.7(11)
C(4)–C(5)–N(3)	112.3(12)	C′(4)–C′(5)–N′(3)	112.6(14)
C″(4)–C″(5)–N″(3)	111.4(12)	C‴(4)–C‴(5)–N‴(3)	110.2(11)
C(6)–C(5)–N(3)	114.1(12)	C′(6)–C′(5)–N′(3)	111.4(13)
C″(6)–C″(5)–N″(3)	112.4(11)	C‴(6)–C‴(5)–N‴(3)	111.5(11)
C(5)–C(6)–N(4)	122.7(13)	C′(5)–C′(6)–N′(4)	123.6(13)
C″(5)–C″(6)–N″(4)	122.3(11)	C‴(5)–C‴(6)–N‴(4)	124.3(12)
C(5)–C(6)–O(1)	118.5(13)	C′(5)–C′(6)–O′(1)	114.7(12)
C″(5)–C″(6)–O″(1)	112.9(12)	C‴(5)–C‴(6)–O‴(1)	115.3(12)
N(4)–C(6)–O(1)	118.6(13)	N′(4)–C′(6)–O′(1)	121.7(13)
N″(4)–C″(6)–O″(1)	124.8(11)	N‴(4)–C‴(6)–O‴(1)	120.4(11)
C(6)–O(1)–Cu(A)	118.1(8)	C′(6)–O′(1)–Cu(A)	120.4(9)
C″(6)–O″(1)–Cu′(A)	113.9(8)	C‴(6)–O‴(1)–Cu′(A)	121.5(9)
C(5)–N(3)–C(8)	124.6(12)	C′(5)–N′(3)–C′(8)	126.5(12)
C″(5)–N″(3)–C″(8)	127.4(11)	C‴(5)–N‴(3)–C‴(8)	127.5(11)
C(6)–N(4)–C(7)	123.1(11)	C′(6)–N′(4)–C′(7)	122.6(12)
C″(6)–N″(4)–C″(7)	124.7(11)	C‴(6)–N‴(4)–C‴(7)	123.3(10)
C(6)–N(4)–Cu(B)	111.9(9)	C′(6)–N′(4)–Cu(B)	112.0(10)
C″(6)–N″(4)–Cu′(B)	112.8(8)	C‴(6)–N‴(4)–Cu′(B)	112.7(8)
C(7)–N(4)–Cu(B)	124.6(9)	C′(7)–N′(4)–Cu(B)	124.5(9)
C″(7)–N″(4)–Cu′(B)	121.6(8)	C‴(7)–N‴(4)–Cu′(B)	122.9(9)
C(8)–C(7)–C(9)	105.8(11)	C′(8)–C′(7)–C′(9)	105.0(12)
C″(8)–C″(7)–C″(9)	106.0(11)	C‴(8)–C‴(7)–C‴(9)	105.4(11)
C(8)–C(7)–N(4)	114.0(12)	C′(8)–C′(7)–N′(4)	115.2(12)

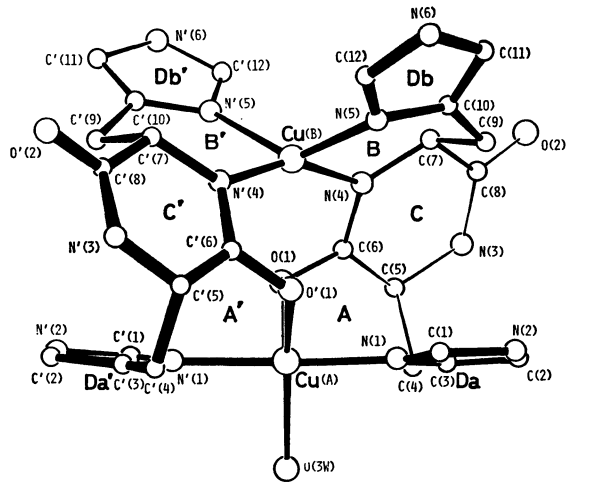
TABLE 3. (Continued)

C″(8)–C″(7)–N″(4)	113.8(11)	C‴(8)–C‴(7)–N‴(4)	113 4(12)
C(9)–C(7)–N(4)	107.6(10)	C′(9)–C′(7)–N′(4)	110.7(11)
C″(9)–C″(7)–N″(4)	109.0(10)	C‴(9)–C‴(7)–N‴(4)	109.5(11)
C(7)–C(8)–N(3)	119.6(13)	C′(7)–C′(8)–N′(3)	119.7(13)
C″(7)–C″(8)–N″(3)	117.8(11)	C‴(7)–C‴(8)–N‴(3)	118.9(12)
C(7)–C(8)–O(2)	118.3(14)	C′(7)–C′(8)–O′(2)	118.9(13)
C″(7)–C″(8)–O″(2)	119.0(12)	C‴(7)–C‴(8)–O‴(2)	117.0(14)
N(3)–C(8)–O(2)	122.2(13)	N′(3)–C′(8)–O′(2)	121.4(12)
N″(3)–C″(8)–O″(2)	123.2(12)	N‴(3)–C‴(8)–O‴(2)	124.1(13)
C(7)–C(9)–C(10)	110.7(12)	C′(7)–C′(9)–C′(10)	110.3(12)
C″(7)–C″(9)–C″(10)	112.1(11)	C‴(7)–C‴(9)–C‴(10)	112.7(11)
C(9)–C(10)–C(11)	123.9(14)	C′(9)–C′(10)–C′(11)	125.0(15)
C″(9)–C″(10)–C″(11)	126.4(13)	C‴(9)–C‴(10)–C‴(11)	126.2(13)
C(9)–C(10)–N(5)	125.0(14)	C′(9)–C′(10)–N′(5)	123.2(13)
C″(9)–C″(10)–N″(5)	122.7(12)	C‴(9)–C‴(10)–N‴(5)	124.5(13)
C(11)–C(10)–N(5)	111.1(13)	C′(11)–C′(10)–N′(5)	111.3(14)
C″(11)–C″(10)–N″(5)	110.9(12)	C‴(11)–C‴(10)–N‴(5)	109.0(12)
C(10)–C(11)–N(6)	104.5(14)	C′(10)–C′(11)–N′(6)	103.0(17)
C″(10)–C″(11)–N″(6)	102.7(13)	C‴(10)–C‴(11)–N‴(6)	105.2(14)
C(10)–N(5)–C(12)	107.1(13)	C′(10)–N′(5)–C′(12)	106.4(13)
C″(10)–N″(5)–C″(12)	106.3(12)	C‴(10)–N‴(5)–C‴(12)	108.2(12)
C(10)–N(5)–Cu(B)	124.3(9)	C′(10)–N′(5)–Cu(B)	120.0(9)
C″(10)–N″(5)–Cu′(B)	128.0(9)	C‴(10)–N‴(5)–Cu′(B)	126.3(9)
C(12)–N(5)–Cu(B)	123.5(11)	C′(12)–N′(5)–Cu(B)	124.2(11)
C″(12)–N″(5)–Cu′(B)	125.6(10)	C‴(12)–N‴(5)–Cu′(B)	125.1(10)
N(5)–C(12)–N(6)	109.2(15)	N′(5)–C′(12)–N′(6)	110.6(14)
N″(5)–C″(12)–N″(6)	109.0(12)	N‴(5)–C‴(12)–N‴(6)	108.5(12)
C(11)–N(6)–C(12)	108.2(14)	C′(11)–N′(6)–C′(12)	108.6(15)
C″(11)–N″(6)–C″(12)	111.0(13)	C‴(11)–N‴(6)–C‴(12)	109.2(13)
O(4)–Cl–O(5)	110.1(8)	O′(4)–Cl′–O′(5)	107.8(8)
O″(4)–Cl″–O″(5)	106.0(13)	O‴(4)–Cl‴–O‴(5)	112.3(14)
O(4)–Cl–O(6)	111.1(8)	O′(4)–Cl′–O′(6)	112.6(10)
O″(4)–Cl″–O″(6)	103.0(13)	O‴(4)–Cl‴–O‴(6)	112.3(14)
O(4)–Cl–O(7)	109.2(9)	O′(4)–Cl′–O′(7)	108.4(8)
O″(4)–Cl″–O″(7)	101.4(13)	O‴(4)–Cl‴–O‴(7)	108.9(15)
O(5)–Cl–O(6)	108.6(8)	O′(5)–Cl′–O′(6)	115.1(10)
O″(5)–Cl″–O″(6)	112.3(14)	O‴(5)–Cl‴–O‴(6)	98.5(12)
O(5)–Cl–O(7)	108.8(9)	O′(5)–Cl′–O′(7)	107.9(9)
O″(5)–Cl″–O″(7)	113.3(13)	O‴(5)–Cl‴–O‴(7)	112.3(15)
O(6)–Cl–O(7)	109.0(8)	O′(6)–Cl′–O′(7)	104.8(9)
O″(6)–Cl″–O″(7)	118.7(13)	O‴(6)–Cl‴–O‴(7)	112.3(13)

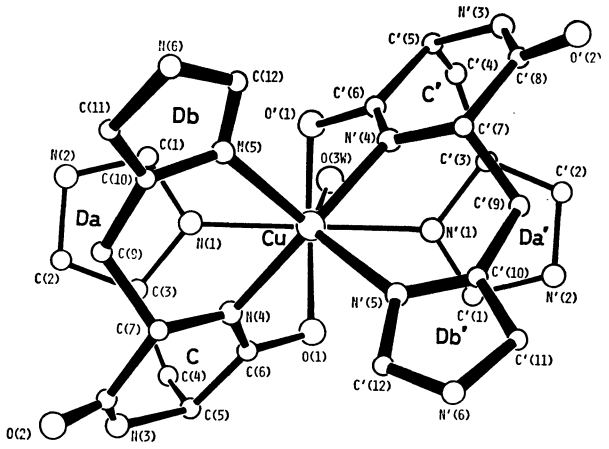
structure, but the values of a number of bond angles in one complex are somewhat different from those of the corresponding ones in the other. Furthermore, some of the corresponding bonds show a slight but, in view of a statistical significant test, significant differences in length. However, the "significant differences" may be ascribed to the underestimation of standard deviation. On the other hand, the bond angle will vary with the packing. Therefore, the two complex cations should be considered to be chemically identical. Since the difference between the equivalent structural parameters including the equivalent bond angles is small, we will use the mean values of the respective parameters in the following description, unless we state otherwise, and make use of one of the two complex cations for illustration.

Figures 3(a) and (b) show the elevation perpendicular to a plane through Cu(A), Cu(B), N(1), and N′(1), and the projection along the Cu(A)···Cu(B) axis, respectively. The complex cation is dimeric, with two Cu atoms of different coordination modes. In case the ligating water molecule [O(3W)] is excluded from the complex, the remaining part has a pseudo twofold axis which passes through the two Cu atoms. The structural parameters related by this axis are almost identical except for the Cu(A)–O(1) and Cu(A)–O′(1) bond lengths. The average bond lengths are shown in Fig. 4.

The Cu(B) atom has a flattened tetrahedral coordination by the N(5) atom of the Im group and the anionic N(4) atom of the $DKPH^-$ moiety of one ligand, and the chemically equivalent N′(5) and N′(4) atoms of the other [Cu–N=1.97 Å]. The average value of the chelate bite angles at the Cu(B) is 91.7°. The dihedral angle between the N(4), Cu(B), and N(5) plane and the N′(4), Cu(B), N′(5) plane is 50.0°, which is comparable to the value (53.6°) in bis(*N*-*t*-butylsalicylideneaminato)copper(II).[8] The tetrahedral coordination of bivalent copper is rather unusual. The dimerization



(a)



(b)

Fig. 3. Projection of aquabis(cyclo-L-histidyl-L-histidyl-ato)dicopper(II).
(a) On the plane through Cu(A), Cu(B), N(1), and N'(1), (b) along the Cu(A)···Cu(B) axis.

and strong affinity of Cu(II) for N atoms may be responsible for such a coordination in the present complex.

The coordination geometry of Cu(A) atom seems to be intermediate between the square pyramid and the trigonal bipyramid (Fig. 3). From the square-pyramidal viewpoint, the apical position is occupied by the O(1) atom, whereas the basal plane is defined by the O(3W) (oxygen of ligating water molecule), N(1), O'(1), and N'(1) atoms. The disposition of the four basal atoms is not planar, the maximum deviation of the atom from the plane being 0.38 Å. The Cu–O(1) apical bond is longer than the four basal bonds ($Cu–O(1)_{apex}=2.21$, $Cu–O_{base}=2.04$, $Cu–N_{base}=1.97$ Å). The N(1)–Cu(A)–N'(1) angle is close to 180°, which is suggestive of the trigonal-bipyramidal coordination. In the trigonal bipyramidal approximation, the N(1) and N'(1) atoms occupy the axial positions. The Cu(A) atom is displaced 0.13 Å toward N'(1) from the equatorial

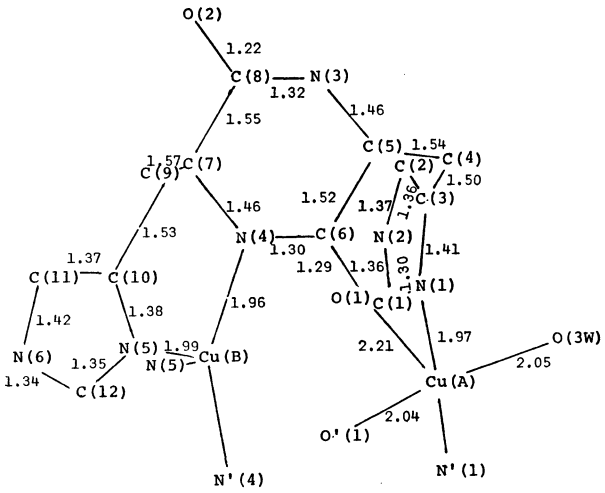


Fig. 4. The average bond lengths of aquabis(cyclo-L-histidyl-L-histidylato)dicopper(II).

TABLE 4. DEVIATIONS OF THE ATOMS FROM LEAST-SQUARES PLANES (d/Å) AND THE DIHEDRAL ANGLES BETWEEN THEM

(B) plane through C(9), C(10), N(4), N(5), and Cu(B) (Plane B)							
C(7)	−0.65	C(9)	0.08	C(10)	−0.13	N(4)	−0.03
N(5)	0.09	Cu(B)	−0.01				
(B') plane through C'(9), C'(10),N'(4), N'(5), and Cu(B) (Palne B')							
C'(7)	−0.66	C'(9)	0.08	C'(10)	−0.08	N'(4)	−0.06
N'(5)	0.02	Cu(B)	0.04				
(B'') plane through C''(9), C''(10), N''(4), N''(5), and Cu'(B) (Plane B'')							
C''(7)	0.74	C''(9)	−0.05	C''(10)	0.01	N''(4)	0.06
N''(5)	0.05	Cu'(B)	−0.07				
(B''') plane through C'''(9), C'''(10), N'''(4), N'''(5), and Cu'(B) (Plane B''')							
C'''(7)	0.66	C'''(9)	−0.04	C'''(10)	0.06	N'''(4)	0.02
N'''(5)	−0.04	Cu'(B)	0.00				
(C) plane through C(5), C(6), C(7), C(8), N(3), and N(4) (Plane C)							
C(4)	−1.22	C(5)	−0.03	C(6)	0.05	C(7)	−0.06
C(8)	0.10	C(9)	−1.50	N(3)	−0.05	N(4)	−0.01
O(1)	0.09	O(2)	0.31	Cu(B)	−0.23		
(C') plane through C'(5), C'(6), C'(7), C'(8), N'(3), and N'(4) (Plane C')							
C'(4)	1.12	C'(5)	−0.05	C'(6)	0.02	C'(7)	0.15
C'(8)	−0.07	C'(9)	1.59	N'(3)	−0.08	N'(4)	−0.06
O'(1)	0.04	O'(2)	−0.17	Cu(B)	0.31		

TABLE 4. (Continued)

(C″) plane through C″(5), C″(6), C″(7), C″(8), N″(3), and N″(4) (Plane C″)							
C″(4)	1.35	C″(5)	0.08	C″(6)	−0.04	C″(7)	0.08
C″(8)	−0.04	C″(9)	1.49	N″(3)	0.01	N″(4)	−0.08
O″(1)	−0.04	O″(2)	−0.18	Cu′(B)	−0.05		
(C‴) plane through C‴ (5), C‴(6), C‴(7), C‴(8), N‴(3), and N‴ (4) (Plane C‴)							
C‴(4)	1.32	C‴(5)	0.03	C‴(6)	0.02	C‴(7)	0.06
C‴(8)	−0.03	C‴(9)	1.48	N‴(3)	−0.03	N‴(4)	−0.05
O‴(1)	0.09	O‴(2)	−0.11	Cu′(B)	0.04		
(Da) plane through C(1), C(2), C(3), N(1), and N(2) (Plane Da)							
C(1)	0.00	C(2)	0.00	C(3)	0.00	C(4)	−0.08
N(1)	0.00	N(2)	0.00	Cu(A)	−0.04		
(Db) plane through C(10), C(11), C(12), N(5), and N(6) (Plane Db)							
C(9)	0.07	C(10)	0.01	C(11)	−0.01	C(12)	0.00
N(5)	0.00	N(6)	0.01	Cu(B)	−0.71		
(Da′) plane through C′(1), C′(2), C′(3), N′(1), and N′(2) (Plane Da′)							
C′(1)	0.02	C′(2)	0.00	C′(3)	0.02	C′(4)	−0.06
N′(1)	−0.02	N′(2)	−0.01	Cu(A)	−0.15		
(Db′) plane througA C′(10), C′(11), C′(12), N′(5), and N′(6) (Plane Db′)							
C′(9)	0.10	C′(10)	−0.02	C′(11)	0.02	C′(12)	0.00
N′(5)	0.01	N′(6)	−0.02	Cu(B)	−0.15		
(Da″) plane through C″(1), C″(2), C″(3), N″(1), and N″(2) (Plane Da″)							
C″(1)	0.00	C″(2)	0.01	C″(3)	−0.02	C″(4)	0.13
N″(1)	0.01	N″(2)	−0.01	Cu′(A)	−0.12		
(Db″) plane through C″(10), C″(11), C″(12), N″(5), and N″(6) (Plane Db″)							
C″(9)	0.02	C″(10)	0.00	C″(11)	0.01	C″(12)	0.01
N″(5)	−0.01	N″(6)	−0.01	Cu′(B)	−0.12		
(Da‴) plane through C‴(1), C‴(2), C‴(3), N‴(1), and N‴(2) (Plane Da‴)							
C‴(1)	0.00	C‴(2)	0.00	C‴(3)	0.00	C‴(4)	−0.01
N‴(1)	0.00	N‴(2)	0.00	Cu′(A)	0.03		
(Db‴) plane through C‴ (10), C‴(11), C‴(12), N‴(5), and N‴(6) (Plane Db‴)							
C‴(9)	−0.12	C‴(10)	0.01	C‴(11)	0.00	C‴(12)	0.01
N‴(5)	−0.01	N‴(6)	−0.01	Cu′(B)	0.15		

Dihedral angles between the planes (ϕ/°):

B and B′	54.9	B″ and B‴	49.7	Da and Da′	11.2
Db and Db′	75.6	Da″ and Da‴	8.3	Db″ and Db‴	52.7

Equations of planes:

(B)	$0.131X+0.790Y+0.599Z-9.868=0$	(Da)	$0.041X+0.953Y+0.300Z-12.190=0$
(B′)	$0.131X-0.954Y+0.269Z+4.098=0$	(Db)	$0.052X+0.582Y+0.811Z-9.708=0$
(B″)	$0.204X+0.607Y-0.768Z-2.373=0$	(Da′)	$0.037X+0.993Y+0.109Z-11.494=0$
(B‴)	$0.847X+0.127Y-0.516Z-13.310=0$	(Db′)	$0.111X-0.929Y+0.354Z+3.794=0$
(C)	$-0.024X-0.267Y-0.963Z+7.206=0$	(Da″)	$0.513X+0.443Y-0.736Z-3.889=0$
(C′)	$-0.032X+0.596Y-0.802Z+0.892=0$	(Db″)	$0.162X+0.594Y-0.788Z-1.312=0$
(C″)	$-0.112X-0.942Y+0.315Z+2.557=0$	(Da‴)	$0.614X+0.468Y-0.636Z-6.769=0$
(C‴)	$-0.739X+0.522Y+0.426Z+6.810=0$	(Db‴)	$0.835X+0.068Y-0.547Z-12.185=0$

where X, Y, and Z are coordinates in Å units relative to the a, b, and c^* axes respectively.

plane defined by the O(1), O′(1), and O(3W) atoms. One of the equatorial bonds is longer than the other two, and the O–Cu–O angles in the equatorial plane are 103.6, 106.5, and 149.7°. The Cu(B) atom is distant from O(1) and O′(1) by 2.81(1) and 2.80(1) Å respectively, and the interatomic distance, Cu(A)··· Cu(B), is 3.570(3) Å.

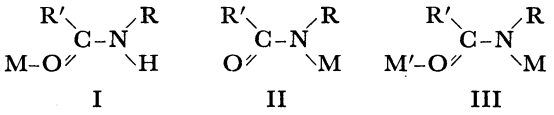
All the $HISH^-$ ligands assume a similar, asymmetric conformation; the C(4)–Im and C(9)–Im fragments are rotated respectively about the C(4)–C(5) and C(7)–C(9) bonds in such a way that the donor atoms in the Im groups are favorably located for coordination to the Cu(A) and Cu(B) atoms. The average bond lengths in the $HISH^-$ ligand are also shown in Fig. 4. Each Im group is planar within 0.02 Å, and the bond lengths and angles are in agreement with the corresponding ones in the bis(histidino)-nickel(II) and -cobalt(II).[9] The leastsquares planes of various parts of the complex and the dihedral angles between them are listed in Table 4. The $DKPH^-$ ring is nearly planar, and the torsional angles in the ring (IUPAC-IUB conventions)[10] are presented in Table 5. In the two C=O bonds, the one whose O atom participates in the coordination is longer than the other. In the peptide-bondings, N(4)–C(6)–O(1) and N(3)–C(8)–O(2), a short N–C bond length indicated the delocalization of π electrons over this bonding.

The $DKPH_2$ can be regarded as a kind of secondary

TABLE 5. TORSIONAL ANGLES (deg.) IN DKPH$^-$ [a]

Angle		Angle	
ϕ[C(5), N(3)]	−4.2	ϕ[C(7), N(4)]	5.1
ϕ[C(6), C(5)]	−6.5	ϕ[C(8), C(7)]	−14.9
ω[N(4), C(6)]	5.4	ω[N(3), C(8)]	14.9
ϕ[C′(5), N′(3)]	−1.1	ϕ[C′(7), N′(4)]	11.0
ϕ[C′(6), C′(5)]	0.2	ϕ[C′(8), C′(7)]	−11.9
ω[N′(4), C′(6)]	−5.4	ω[N′(3), C′(8)]	7.3
ϕ[C″(5), N″(3)]	5.4	ϕ[C″(7), N″(4)]	14.1
ϕ[C″(6), C″(5)]	−5.2	ϕ[C″(8), C″(7)]	−13.2
ω[N″(4), C″(6)]	−5.0	ω[N″(3), C″(8)]	4.0
ϕ[C‴(5), N‴(3)]	2.9	ϕ[C‴(7), N‴(4)]	12.8
ϕ[C‴(6), C‴(5)]	0.7	ϕ[C‴(8), C‴(7)]	−9.0
ω[N‴(4), C‴(6)]	−9.2	ω[N‴(3), C‴(8)]	1.5
χ[C(4), C(5)]	73.1	χ[C(9), C(7)]	−63.1
χ[C′(4), C′(5)]	74.1	χ[C′(9), C′(7)]	−62.9
χ[C″(4), C″(5)]	74.4	χ[C″(9), C″(7)]	−65.8
χ[C‴(4), C‴(5)]	76.5	χ[C‴(9), C‴(7)]	−61.0

a) The conventions of the IUPAC-IVB Commission are followed.[b] b) See also Ref. 10.



I II III

amide group which is capable of ligating in three ways:[11] I is most usual, whereas II and III are uncommon and deprotonation is necessary prior to complex formation. The coordination mode of the "amide group" in the present DKPH$^-$ group can be classified as III. In μ-formamide-bis[pentaamminecobalt(III)] pentachloride monohydrate, which is known as the sole example of III, the M′–O bond is nearly coplanar with the plane of the amide group, the M′–O–C bond angle being 126°.[12] However, in the present complex the Cu(A)–O′(1) bond is not coplanar with the [N′(4), C′(6), O′(1)] "amide plane," but makes an angle of 59.3° with this plane. Similarly, the Cu(A)–O(1) bond intersects the [N(4), C(6), O(1)] "amide plane" in an angles of 61.7°.

TABLE 6. DATA OF THE HYDROGEN BONDS

A–H–B		A–B	Positions[a] of A	Positions[a] of B
N(3)	O′(5)	3.03	1	1
N(6)	O(11W)	2.96	1	1
N′(3)	O″(5)	3.12	1	1
N″(3)	O′(2)	2.85	1	1
N‴(6)	O(6)	2.96	1	1
O(10W)	O(2)	2.67	1	1
O‴(6)	O(3)	2.98	1	1
O(8W)	O″(1)	2.78	1	1
O(8W)	O(9W)	2.90	1	1
O(12W)	O(8W)	2.98	1	1
O(12W)	O(5)	3.08	1	1
O′(3)	O″(2)	2.53	2	1
N(3)	O‴(2)	2.97	1	3
N‴(3)	O(2)	3.02	3	1
O(3)	O′(2)	2.74	4	1
N′(2)	O(11W)	2.86	4	1
O(13W)	O(1)	2.98	1	4
N(2)	O(7)	3.03	1	5
N‴(2)	O(10W)	2.73	5	1
O(11W)	O‴(5)	2.92	1	5
O(13W)	N(2)	2.78	1	5
N″(2)	O‴(2)	2.78	1	6

a) Numerals refer to the following equivalent positions: 1 (x,y,z), 2 $(x,y,-1+z)$, 3 $(-1+x,y,-1+z)$, 4 $(1-x,-1/2+y,1-z)$, 5 $(1-x,-1/2+y,2-z)$, 6 $(2-x,-1/2+y,2-z)$.

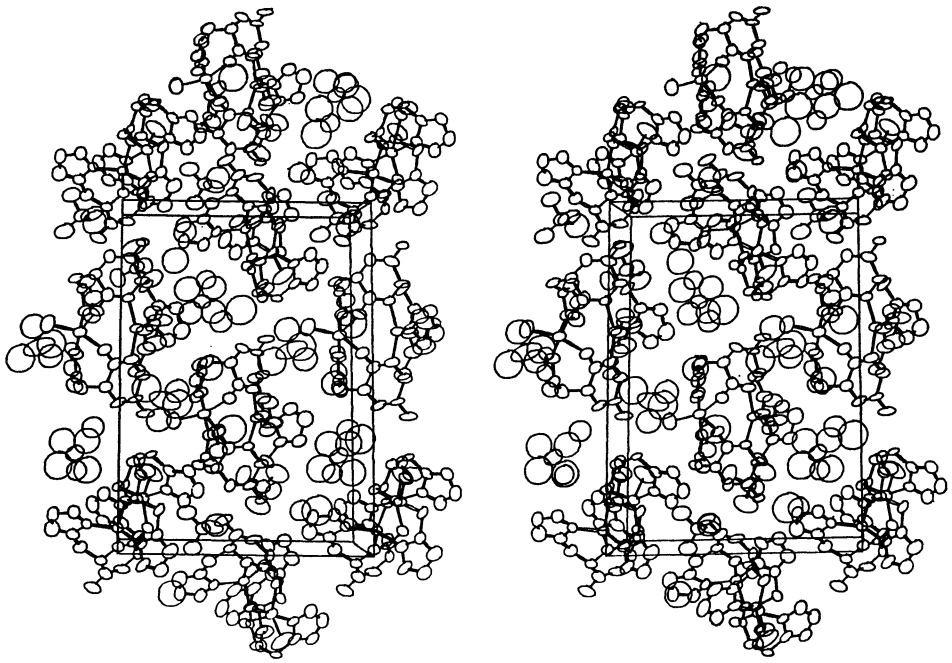


Fig. 5. Stereoview of crystal structure of aquabis(cyclo-L-histidyl-L-histidylato)dicopper(II) perchlorate hydrate along the c axis.

Both of the 6-membered chelate rings, B[N(4), Cu(B), N(5), C(10), C(9), C(7)] and B'[N'(4), Cu(B), N'(5), C'(10), C'(9), C'(7)], which are related mutually by the pseudo twofold axis, assume an envelope form; the five atoms in each chelate ring are planar within 0.13 Å, whereas C(7) in B and C'(7) in B' deviate by 0.65 and 0.66 Å from the respective least-squares planes defined by the five atoms. The 7-membered ring A[Cu(A), O(1), C(6), C(5), C(3), C(4), N(1)] and the A' related with A by the pseudo twofold axis have a boat form. Although the 7-membered ring has been thought generally to be unstable compared with 5- and 6- membered ones, and although, moreover, the ligating ability of the oxygen in an amide group toward metal is not strong, the formation of the 7-membered ring in the present complex presumably results from the dimerization and migration of the negative charge to the O atom from the adjacent "anionic" N atom.

Figure 5 shows the stereoview of the crystal structure along the c axis. The data concerning hydrogen bonds are presented in Table 6. The perchlorate anions and uncoordinated water molecules participate in the O–H···O, N–H···O, and O–H···N hydrogen bonds. The N(3) atom in the complex which involves unprimed Cu atoms has short contacts of N(3)···O'(5) (3.03 Å) and N(3)—O''(2)(2.97 Å). These contacts suggest that the H atom linked to N(3) takes part in the bifurcated hydrogen bonding.

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