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The Crystal Structure of the Copper(II) Chelate of N,N'-Ethylenebis(l-ephedrine)

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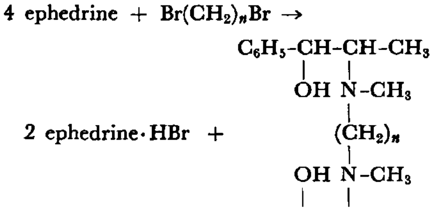
The crystal structure of the copper(II) chelate of N,N'-ethylenebis(l-ephedrine), where two molecules of l-ephedrine are connected through an ethylene group, has been determined by three dimensional X-ray analysis. The dimensions of the orthorhombic unit cell with the space group $P2_12_12_1$-D_2^4 are $a=8.431$, $b=15.92$, $c=16.70$ Å, $Z=4$ and $\rho_0=1.34$ g/cm^3. The intensity data were collected by multiple film technique, and the structure was determined by the heavy atom method. The positions of the copper atom simulated the symmetry of a higher space group than that of $P2_12_12_1$ and the phases calculated from them gave two pseudo mirrors in the Fourier map based on the copper atom only. The structural determination was made with the use of the methods of successive approximations and diagonal and block diagonal least-squares. The problems concerning the pseudo mirrors were solved mainly from the behaviors of the thermal parameters. The final results were obtained by correcting some unsuitable positional and thermal parameters found by the block diagonal least-squares refinement. The final R-factor is 13.0%. The structure shows that two crystalline water molecules do not coordinate to the copper atom and that the N–C–C–N bridge causes distortion of the square planar coordination around the copper atom.

In a previous paper,[1] we reported that the *trans*-bis(l-ephedrine)copper(II)[2] chelate reacted with carbon tetrachloride and chloroform. Considering that this peculiar reaction might be concerned with the structure of the chelate, we attempted synthesis of some N,N'-polymethylenebis(ephedrine) by combining two molecules of ephedrine with a polymethylene group and preparation of their copper(II) chelates in order to investigate their properties from the structural point of view.



$$
\begin{array}{l}
4\ \text{ephedrine} + \text{Br}(\text{CH}_2)_n\text{Br} \rightarrow \\
\qquad\qquad \begin{array}{c}
\text{C}_6\text{H}_5\text{-CH-CH-CH}_3 \\
\quad|\qquad| \\
\quad\text{OH}\ \ \text{N-CH}_3 \\
\qquad| \\
\qquad(\text{CH}_2)_n \\
\qquad| \\
\quad\text{OH}\ \ \text{N-CH}_3 \\
\quad|\qquad| \\
\text{C}_6\text{H}_5\text{-CH-CH-CH}_3
\end{array} + 2\ \text{ephedrine}\cdot\text{HBr}
\end{array}
$$

When n is equal to one, the corresponding substance could not be obtained, and oxazolidine was obtained instead.[3] When n is equal to three, neither N,N'-trimethylenebis(l-ephedrine) nor its hydrochloride was obtained in the pure state. N,N'-Hexamethylenebis(l-ephedrine) hydrochloride[*1] with $n=6$ was isolated, but its copper(II) chelate could not be prepared because of its instability. When n is equal to two, the copper(II) chelate of

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[1] Y. Amano and T. Uno, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 1105 (1965).

[2] Y. Amano, K. Osaki and T. Watanabe, This Bulletin, **37**, 1363 (1964).

[3] H. Williams, *J. Pharm. Pharmacol.*, **16**, *Suppl.*, 166 T (1964).

[*1] Anal., Found: C, 64.22; H, 8.88; N, 5.99; Cl, 14.64%. Calcd for $C_{26}H_{42}O_2Cl_2$: C, 64,31; H, 8.72; N, 5.77; Cl, 14.60% mp: 249°C.

meso-*N*,*N′*-ethylenebis(ephedrine),[4] where one molecule of *l*-ephedrine is connected with one molecule of *d*-ephedrine through an ethylene group, was obtained as a green crystalline powder, but the purification was not feasible. On the other hand, *N*,*N′*-ethylenebis(*l*-ephedrine)[4] reacted with copper sulfate in the presence of sodium hydroxide to give *N*,*N′*-ethylenebis(*l*-ephedrinato) copper(II) chelate (abbreviated as EBECu hereafter). From the results of the elemental analysis and the continuous variations, it became clear that this chelate has a ligand in the ratio of 1 : 1 to copper(II) and that one molecule of this chelate has two water molecules.

The IR spectrum of this chelate shows two absorption bands at 1670 and 1710 cm^{-1}. On recrystallization from deuterium oxide, two new absorption bands appear at 1170 and 1210 cm^{-1} with the decrease of the intensities of the original bands, so we assigned the original two absorption bands to the bending vibrations of water, but there seemed to be some ambiguities about the assignment, because the frequency (1710 cm^{-1}) was higher than the frequencies found for ordinary H_2O bending vibrations. The existence of two different absorption bands was supposed to show either that there were two water molecules in the different states in the crystal or that two molecules of water approached so near that they had influence on each other with consequent splitting of the bands.

It was reported that the copper(II) chelate coordinated by oxygen and nitrogen were blue or blue violet (trans coordination)[5,6] or green (cis coordination).[7,8] From the chemical structure of the ligand, EBECu was presumed to have cis coordination structure for oxygen and nitrogen, but it was blue. When it was dissolved in acetone and some of acetone was distilled, the color turned green but changed to original blue on addition of water. From this fact it was presumed that the blue chelate had two molecules of water which coordinated to the copper atom and that the chelate had an octahedral structure around the copper atom. In order to make clear the state of the water molecules in the chelate and to compare the structure with that of *trans*-bis(*l*-ephedrine) copper (II) chelate, we carried out three dimensional X-ray crystal structure analysis.

Experimental

***N*,*N′*-Ethylenebis(*l*-ephedrianto) Copper(II) Chelate.** Sixty milliliters of 20% aqueous solution of sodium hydroxide was slowly added under cooling in ice to a mixture of 3.6 g of *N*,*N′*-ethylene bis(*l*-ephedrine) in dilute hydrochloric acid and 2.4 g of $Cu(SO_4)_2 \cdot 5H_2O$ in water. At this time light blue precipitates were once formed and they turned deep blue gradually. The blue precipitates were filtered and washed with small volumes of water and diethyl ether and dried well in a desiccator under reduced pressure. The blue precipitates were dissolved in dry pyridine, and the blue solution was filtered, concentrated *in vacuo*, and water was added, when blue needles separated. This reprecipitation procedure was repeated two more times (mp 156—157°C, decomp.). Found: C, 58.45; H, 7.66; N, 6.19; Cu, 14.27%. Calcd for $C_{22}H_{30}O_2N_2Cu \cdot 2H_2O$: C, 58.19; H, 7.55; N, 6.17; Cu, 13.99%;

Continuous Variations. An aqueous solution of copper sulfate (10^{-2} M) was mixed at various ratios with a solution of *N*,*N′*-ethylenebis(*l*-ephedrine) in dilute hydrochloric acid (10^{-2} M) to make the total volume 10 m*l*. After 10 min the blue substance was extracted with 15 m*l* of isoamyl alcohol, dried with anhydrous sodium sulfate, and the absorbance was measured at 620 mμ. The results are shown in Fig. 1.

Intensity Data. From the precession and Weissenberg photographs of the crystals prepared by the method described above, the unit cell dimensions were determined and are shown in Table 1. The reflection data were collected by multiple film technique. They

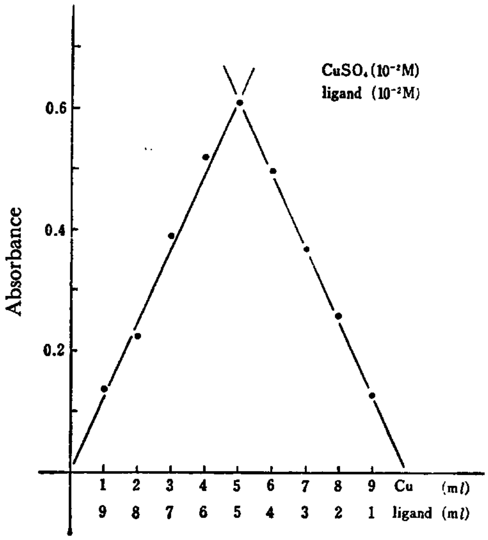

Fig. 1. Continuous variations.

TABLE 1. CRYSTALLOGRAPHIC DATA

Space group: $P2_12_12_1$-D_2^4

$a = 8.431 \pm 0.005$ Å

$b = 15.92 \pm 0.03$

$c = 16.70 \pm 0.03$

$V = 2241.5$ Å^3

$Z = 4$

$\rho_{\text{calcd.}} = 1.345$ g/cm^3

$\rho_{\text{obs.}} = 1.34$ g/cm^3

$M_{\text{calcd.}} = 454.1$

$M_{\text{obs.}} = 452.3$

μ(for Cu$K\alpha$) = 16.78 cm^{-1}

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[4] H. Nishimura, O. Yamauchi and H. Takamatsu, *Chem. Pharm. Bull.*, **12**, 1004 (1964).

[5] K. Tomita, This Bulletin, **34**, 297 (1961).

[6] R. F. Bryan, R. J. Poljak and K. Tomita, *Acta Cryst.*, **14**, 1125 (1961).

[7] F. J. Lewellyn and T. N. Waters, *J. Chem. Soc.*, **1960**, 2639.

[8] D. Hall and T. N. Waters, *ibid.*, **1960**, 2644.

were recorded on equi-inclination Weissenberg photographs around a axis ($(0kl)$—$(5kl)$) and 30° precession photographs ($(hk0)$, $(hk1)$, $(h0l)$). The copper $K\alpha$ radiation with a nickel filter was used for the Weissenberg and the precession photographs, and 1968 independent reflections were observed. For 1752 reflections the intensities were measured by visual comparison with the standard intensity scale prepared from the same crystal. The intensities ranged from 0.5 to 10^4 for 1752 reflections. The 216 reflections, which had too weak intensities, to be measured were given the intensities 0.2. The Lorentz and polarization corrections and calculations of Wilson's scaling were made in the usual way by the program which was written by the author. No corrections were made for the absorptions because the crystal size was small ($\mu R=0.166$). The overall thermal parameter of the crystal was 5.0 Å^2. The computations in the present study were carried on the electronic computer KDC-II (Hitachi, HITAC 5020) of the Kyoto University Computation Center and on the HITAC 5020E of the Tokyo University Computation Center.

Structure Determination

The ordinary heavy atom method was applied to phase determination. From Haker sections, the positional parameters of copper atom were determined: $x/a=0.250, y/b=0.075$ and $z/c=0.000$. The structure amplitudes were calculated on the basis

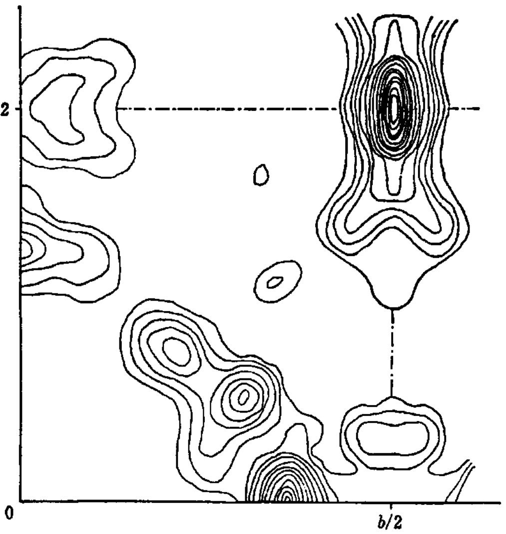


Fig. 2. Patterson map.

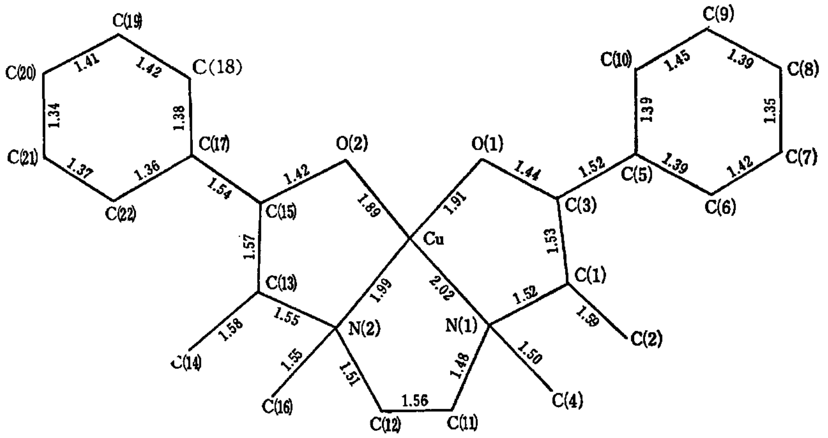
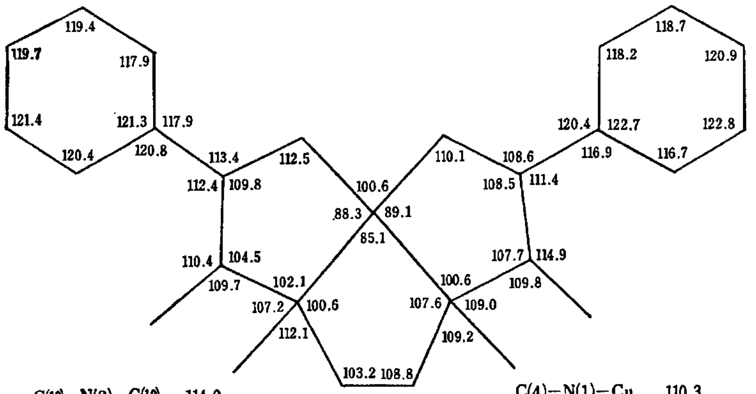


Fig. 3(a). Bond lengths of EBECu (in Å).



C(13)–N(2)–C(12) 114.0
C(16)–N(2)–Cu 110.4

C(4)–N(1)–Cu 110.3
C(1)–N(1)–Cu 119.6

Fig. 3(b). Bond angles of EBECu (in °).

of this atom only, and the R-factor

$$R=\sum||F_o|-|F_c||/\sum|F_o|$$

was found to be 74%. The atomic scattering factors were taken from the International Tables for X-ray Crystallography, and no dispersion corrections for atomic scattering factors were applied. As the copper atom, the only heavy atom in an asymmetric unit, had the positional parameters $x/a=1/4$ and $z/c=0$, two pseudo mirrors were found in the Fourier synthesis using the phases calculated on the basis of the copper atom only, and there were four peaks having the same height for one atom. Accordingly it was very difficult to discriminate the correct peaks out of them. From the copper-copper peaks in the Haker sections somewhat extended along b axis as shown in Fig. 2 for example, it was supposed that two or more copper-copper peaks overlapped one another. Therefore, the positional parameters of copper atom x and z were shifted by 1/60 of the unit cell dimensions and the structure amplitudes were calculated. The R-factor was 45%. After the Fourier synthesis the four peaks, which had shown the same peak height when copper had the positional parameters $x/a=1/4$ and $z/c=0$, gained different positions and different peak heights. So the method of successive approximations was applied.

First, as the results of the Fourier synthesis with phases calculated on the basis of the copper atom only, 15 peaks of light atoms were found, and then the Fourier synthesis based on 16 atoms, namely, copper and 15 light atoms, gave additional six peaks. This process was repeated once more, giving

TABLE 2. FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS

The anisotropic temperature factors are expressed in the form of

$$\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$$

Atom	x $\sigma(x)$	y $\sigma(y)$	z $\sigma(z)$	B_{11} $\sigma(B_{11})$	B_{22} $\sigma(B_{22})$	B_{33} $\sigma(B_{33})$	B_{12} $\sigma(B_{12})$	B_{13} $\sigma(B_{13})$	B_{23} $\sigma(B_{23})$
Cu	0.2219 2	0.0719 2	0.0119 2	1387 47	376 7	391 7	13 32	147 31	−41 13

(B_{11} *etc.*: $\times10^{-5}$, $\sigma(B_{11})$ *etc.*: $\times10^{-5}$, $\sigma(x)$ *etc.*: $\times10^{-3}$ Å)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
O(1)	0.0145	12	0.0255	10	−0.0054	10	5.26	0.22
O(2)	0.1952	12	0.1182	10	0.1150	10	5.10	0.22
W(1)	0.1389	18	0.6088	16	0.3841	16	9.82	0.44
W(2)	0.1157	18	0.9589	16	0.1616	16	9.82*	0.45
N(1)	0.2286	15	0.9488	11	0.3951	11	4.38	0.24
N(2)	0.4542	13	0.0856	10	0.0249	10	4.00	0.22
C(1)	0.3452	19	0.0192	15	0.3761	15	4.97	0.33
C(2)	0.2767	21	0.1063	16	0.4071	16	6.12	0.39
C(3)	0.5068	19	0.9945	15	0.4113	15	4.74	0.32
C(4)	0.2703	20	0.8729	15	0.3459	15	5.33	0.33
C(5)	0.3762	18	0.5659	15	0.0954	14	4.76	0.31
C(6)	0.2936	20	0.5736	17	0.1679	16	6.05	0.37
C(7)	0.1872	25	0.6421	20	0.1749	20	7.68	0.51
C(8)	0.1591	24	0.6965	19	0.1145	20	7.25	0.49
C(9)	0.2362	24	0.6880	19	0.0414	18	7.52	0.48
C(10)	0.3480	21	0.6195	17	0.0311	17	6.22	0.41
C(11)	0.0565	19	0.9646	15	0.3889	15	4.73	0.31
C(12)	0.0329	20	0.4015	17	0.0554	16	5.70	0.38
C(13)	0.4648	18	0.1629	14	0.0814	14	4.21	0.29
C(14)	0.4168	19	0.2448	14	0.0343	14	4.55	0.31
C(15)	0.3414	19	0.1441	15	0.1494	15	4.81	0.32
C(16)	0.5247	21	0.0099	17	0.0707	17	5.88	0.39
C(17)	0.3233*	17	0.2183*	13	0.2081*	13	4.02	0.27
C(18)	0.1722	20	0.2570	15	0.2131	15	5.00	0.33
C(19)	0.1609	22	0.3260	17	0.2667	18	6.34	0.42
C(20)	0.2925	21	0.3519	16	0.3122	16	5.59	0.36
C(21)	0.4318*	22	0.3109*	19	0.3051*	18	6.45	0.43
C(22)	0.4481	20	0.2448	16	0.2529	16	5.33	0.36

($\sigma(x)$ *etc.*: $\times10^{-3}$ Å, $\sigma(B)$: Å^2)

Table 3. Observed and calculated structure factors (×10)

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FB	H	FO	FC	H	FC	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	TO	FC
K,L=	1	0	1	20	40	2	33	49	1	417	310	K,L=	10	3	5	211	197	5	316	307	K,L=	1	6	4	47	61	0	27	29
1	(A)	1154	2	64	77	3	108	122	2	114	138	0	164	194	K,L=	7	4	K,L=	4	5	0	576	551	5	25	40	1	70	62
2	560	591	3	8	9	4	45	49	3	186	213	1	450	412	0	56	57	0	287	306	1	554	520	K,L=	18	6	2	50	49
3	654	663	K,L=	20	0	5	49	62	4	127	139	2	11	42	1	853	865	1	555	506	2	144	183	0	114	107	3	68	74
4	389	439	0	77	63	K,L=	17	1	5	94	101	3	374	398	2	303	316	2	196	170	3	28	25	1	20	19	4	9	29
5	644	520	2	49	69	0	135	111	K,L=	14	2	4	78	74	3	289	327	3	436	441	4	214	246	2	8	14	5	31	45
K,L=	2	0	K,L=	0	1	1	51	44	0	205	184	5	237	218	4	121	129	4	156	83	5	109	150	3	37	44	K,L=	16	7
1	562	526	1	373	347	2	97	103	1	124	100	K,L=	11	3	5	155	149	5	208	220	K,L=	2	6	4	26	42	0	69	53
2	129	64	2	44	64	3	12	41	2	163	156	0	506	456	K,L=	8	4	K,L=	5	5	0	503	474	K,L=	19	6	1	95	94
3	466	465	3	359	386	4	73	87	3	60	54	1	102	100	0	409	478	0	(G)	1067	1	381	349	0	27	20	2	11	22
4	624	583	4	693	697	5	8	24	4	85	109	2	418	445	1	458	438	1	491	492	2	273	291	1	66	65	3	37	52
5	298	369	5	46	45	K,L=	18	1	5	11	18	3	39	31	2	470	519	2	345	404	3	99	137	2	6	24	4	50	56
K,L=	3	0	K,L=	1	1	0	12	22	K,L=	15	2	4	170	179	3	132	99	3	162	150	4	186	188	K,L=	0	7	5	43	49
1	853	939	1	493	557	1	159	123	0	15	23	5	104	88	4	317	321	4	181	195	5	336	331	1	251	227	K,L=	17	7
2	473	398	2	329	188	2	10	11	1	169	147	K,L=	12	3	5	55	50	5	179	154	K,L=	3	6	2	242	233	0	145	121
3	64	3	3	707	824	3	76	84	2	73	59	0	103	54	K,L=	9	4	K,L=	6	5	0	373	366	3	236	181	1	53	29
4	358	321	4	303	315	4	13	36	3	134	149	1	210	196	0	12	48	0	272	316	1	223	237	4	313	321	2	53	68
5	16	27	5	424	386	5	23	39	4	83	112	2	68	99	1	291	259	1	126	74	2	109	151	5	51	34	3	33	27
K,L=	4	0	K,L=	2	1	K,L=	19	1	5	58	76	3	110	101	2	10	17	2	108	143	3	28	71	K,L=	1	7	4	47	62
0	424	423	0	487	536	0	65	50	K,L=	16	2	4	163	171	3	267	284	3	158	172	4	440	413	0	351	336	K,L=	18	7
1	365	364	2	393	384	1	10	14	0	87	81	5	109	138	4	200	197	4	386	366	5	164	155	1	453	427	0	85	32
2	(B)	1110	3	686	820	2	65	72	1	51	46	K,L=	13	3	5	67	68	5	215	182	K,L=	4	6	2	287	372	1	93	88
3	67	136	4	260	157	3	18	20	2	126	151	0	68	54	K,L=	10	4	K,L=	7	5	0	384	397	3	218	209	2	42	43
4	44	73	5	345	348	K,L=	20	1	3	44	41	1	40	43	0	81	85	0	347	212	1	255	200	4	295	289	3	52	75
5	432	372	K,L=	3	1	0	40	37	4	9	20	2	149	142	1	54	43	1	153	97	2	203	214	5	393	331	K,L=	19	7
K,L=	5	0	1	814	882	2	16	25	5	46	64	3	191	208	2	96	71	2	183	175	3	222	180	K,L=	2	7	0	32	22
1	660	656	2	499	713	K,L=	0	2	K,L=	17	2	4	71	50	3	295	300	3	329	344	4	228	205	0	31	76	2	30	52
2	85	49	3	230	245	1	494	520	0	13	16	5	127	143	4	82	53	4	97	119	5	302	260	1	583	571	K,L=	0	8
3	643	648	4	864	811	2	174	64	1	32	22	K,L=	14	3	5	223	189	5	303	338	K,L=	5	6	2	315	300	0	750	736
4	473	441	5	227	163	3	169	157	2	33	35	0	64	22	K,L=	11	4	K,L=	8	5	0	465	367	3	512	504	1	704	698
5	359	365	K,L=	4	1	4	767	842	3	19	43	1	77	102	0	13	41	0	97	67	1	281	300	4	283	246	2	440	457
K,L=	6	0	0	115	55	5	177	197	4	8	30	2	144	136	1	195	196	1	347	326	2	208	229	5	171	204	3	187	127
0	685	712	1	548	667	K,L=	1	2	5	7	18	3	79	101	2	27	26	2	206	251	3	146	138	K,L=	3	7	4	153	148
1	106	141	2	184	197	0	423	440	K,L=	18	2	4	139	148	3	69	68	3	117	95	4	423	416	0	852	863	5	235	242
2	755	723	3	530	567	1	875	965	0	53	33	5	37	49	4	254	257	4	161	140	5	219	204	1	174	183	K,L=	1	8
3	404	374	4	198	148	2	320	286	1	12	36	K,L=	15	3	5	33	71	5	205	195	K,L=	6	6	2	571	641	0	489	467
4	279	215	5	443	367	3	666	658	2	10	12	0	198	193	K,L=	12	4	K,L=	9	5	0	524	438	3	141	115	1	794	775
5	56	67	K,L=	5	1	4	271	259	3	35	48	1	83	73	0	391	402	0	497	438	1	491	498	4	292	301	2	184	168
K,L=	7	0	0	940	984	5	434	438	4	7	20	2	96	118	1	118	81	1	269	243	2	270	264	5	266	257	3	380	329
1	547	553	1	229	212	K,L=	2	2	5	41	72	3	66	94	2	189	224	2	341	341	3	11	22	K,L=	4	7	4	254	238
2	204	233	2	360	398	1	566	502	K,L=	19	2	4	107	109	3	167	187	3	222	227	4	318	302	0	336	371	5	296	293
3	514	464	3	748	735	2	416	414	0	10	3	5	46	57	4	142	151	4	167	178	5	128	158	1	573	597	K,L=	2	8
4	237	188	4	678	619	3	485	461	1	80	70	K,L=	16	3	5	101	113	5	261	240	K,L=	7	6	2	171	189	0	555	558
5	337	312	5	252	204	4	569	539	2	21	36	0	20	36	K,L=	13	4	K,L=	10	5	0	411	435	3	341	370	1	447	446
K,L=	8	0	K,L=	6	1	5	332	270	3	46	55	1	106	87	0	179	187	0	97	106	1	499	447	4	288	319	2	355	346
0	132	174	0	245	313	K,L=	3	2	K,L=	20	2	2	12	19	1	381	362	1	317	314	2	259	246	5	338	318	3	287	249
1	23	2	1	358	372	0	570	654	0	74	69	3	73	81	2	12	20	2	188	213	3	211	230	K,L=	5	7	4	189	179
2	468	497	2	156	135	1	472	471	2	41	50	4	30	43	3	182	175	3	263	289	4	101	88	0	117	99	5	261	233
3	217	265	3	185	173	2	542	492	K,L=	0	3	5	67	76	4	48	65	4	147	164	5	105	131	1	502	462	K,L=	3	8
4	207	214	4	344	330	3	584	553	1	330	247	K,L=	17	3	5	130	154	5	169	197	K,L=	8	6	2	110	85	0	642	584
5	28	32	5	278	272	4	527	475	2	279	234	0	183	178	K,L=	14	4	K,L=	11	5	0	410	386	3	255	252	1	168	150
K,L=	9	0	K,L=	7	1	5	208	185	3	265	234	1	13	32	0	171	153	0	336	306	1	209	174	4	274	296	2	168	148
1	111	134	0	201	225	K,L=	4	2	4	312	348	2	96	109	1	55	36	1	258	209	2	181	164	5	198	189	3	84	69
2	237	281	1	249	195	0	223	272	5	97	73	3	32	39	2	220	222	2	234	223	3	348	334	K,L=	6	7	4	261	279
3	118	50	2	186	208	1	88	102	K,L=	1	3	4	70	69	3	77	78	3	144	155	4	245	269	0	305	320	5	70	78
4	189	180	3	300	326	2	268	265	0	535	573	5	7	12	4	142	138	4	89	73	5	178	181	1	76	94	K,L=	4	8
5	155	178	4	200	201	3	150	184	1	538	542	K,L=	18	3	5	41	45	5	72	97	K,L=	9	6	2	316	305	0	15	12
K,L=	10	0	5	261	212	4	96	51	2	231	202	0	116	79	K,L=	15	4	K,L=	12	5	0	257	272	3	112	119	1	11	274
0	167	140	K,L=	8	1	5	338	302	3	145	149	1	155	117	0	33	36	0	116	113	1	248	236	4	301	343	2	223	232
1	12	6	0	358	737	K,L=	5	2	4	272	238	2	9	38	1	187	181	1	185	155	2	201	179	5	118	123	3	181	186
2	157	184	1	216	221	0	145	147	5	435	435	3	73	76	2	89	86	2	102	77	3	159	138	K,L=	7	7	4	145	167
3	268	266	2	213	218	1	554	580	K,L=	2	3	4	9	18	3	90	103	3	208	250	4	290	309	0	12	26	5	263	254
4	72	24	3	129	151	2	148	150	0	(C)	1331	K,L=	19	3	4	45	60	4	156	179	5	11	45	1	136	111	K,L=	5	8
5	93	90	4	196	165	3	570	541	1	421	363	0	53	40	5	44	51	5	80	68	K,L=	10	6	2	71	77	0	191	186
K,L=	11	0	5	42	32	4	138	150	2	630	517	1	9	22	K,L=	16	4	K,L=	13	5	0	157	157	3	312	314	1	410	399
1	141	129	K,L=	9	1	5	278	263	3	225	202	2	54	58	0	88	63	0	43	46	1	83	53	4	182	150	2	159	144
2	102	161	0	96	102	K,L=	6	2	4	178	145	3	7	23	1	92	86	1	48	44	2	199	206	5	238	198	3	329	316
3	67	92	1	126	104	0	736	720	5	737	216	K,L=	20	3	2	65	63	2	13	24	3	254	223	K,L=	8	7	4	148	164
4	250	295	2	338	396	1	486	412	K,L=	3	3	0	29	26	3	84	101	3	130	148	4	177	184	0	91	38	5	178	184
5	42	3	3	18	40	2	597	628	0	(D)	1158	K,L=	0	4	4	20	16	4	49	42	5	116	89	1	226	218	K,L=	6	8
K,L=	12	0	4	169	141	3	251	242	1	497	433	0	101	1	5	58	59	5	77	88	K,L=	11	6	2	199	201	0	477	447
0	342	251	5	115	101	4	159	159	2	645	613	1	169	187	K,L=	17	4	K,L=	14	5	0	48	35	3	224	205	1	211	203
1	42	73	K,L=	10	1	5	360	290	3	537	461	2	89	40	0	26	21	0	15	20	1	108	99	4	195	182	2	256	246
2	45	44	0	104	48	K,L=	7	2	4	646	592	3	167	101	1	23	41	1	107	105	2	56	49	5	118	109	3	113	108
3	14	64	1	487	459	0	174	170	5	188	177	4	590	529	2	37	30	2	96	89	3	151	143	K,L=	9	7	4	301	305
4	158	156	2	84	92	1	552	600	K,L=	4	3	5	370	317	3	11	22	3	50	67	4	64	85	0	250	264	5	298	283
5	93	109	3	258	260	2	59	85	0	298	270	K,L=	1	4	4	78	94	4	103	123	5	112	154	1	202	188	K,L=	7	8
K,L=	13	0	4	114	114	3	75	408	1	(E)	1037	0	320	298	5	7	4	5	10	18	K,L=	12	6	2	204	214	0	466	408
1	231	184	5	169	182	4	98	94	2	185	198	1	187	194	K,L=	18	4	K,L=	15	5	0	82	60	3	21	38	1	262	227
2	62	62	K,L=	11	1	5	330	295	3	196	211	2	417	382	0	97	79	0	160	156	1	70	63	4	98	91	2	255	201
3	79	78	0	426	354	K,L=	8	2	4	77	92	3	422	404	1	11	18	1	14	47	2	238	244	5	28	70	3	197	215
4	35	56	1	104	65	0	449	462	5	188	189	4	429	437	2	9	6	2	112	119	3	89	129	K,L=	10	7	4	143	181
5	80	72	2	365	392	1	247	214	K,L=	5	3	5	313	267	3	9	38	3	110	131	4	54	62	0	260	267	5	171	206
K,L=	14	0	3	143	138	2	586	600	0	(F)	1077	K,L=	2	4	4	40	56	4	10	41	5	69	78	1	231	225	K,L=	8	8
0	160	165	4	151	136	3	267	291	1	368	370	0	577	492	K,L=	19	4	5	62	72	K,L=	13	6	2	237	250	0	266	212
1	182	120	5	79	69	4	322	322	2	347	308	1	176	128	0	68	50	K,L=	16	5	0	175	159	3	246	216	1	305	285
2	239	267	K,L=	12	1	5	114	140	3	306	297	2	201	210	1	72	56	0	14	7	1	235	202	4	162	175	2	242	256
3	14	18	0	15	54	K,L=	9	2	4	279	270	3	216	217	2	23	36	1	158	160	2	96	87	5	57	54	3	389	409
4	106	128	1	390	378	0	11	2	5	96	91	4	506	501	3	42	55	2	39	46	3	117	114	K,L=	11	7	4	189	195
5	22	25	2	78	82	1	483	448	K,L=	6	3	5	301	236	K,L=	20	4	3	77	90	4	90	79	0	226	216	5	167	187
K,L=	15	0	3	177	195	2	72	120	0	343	273	K,L=	3	4	0	80	71	4	51	71	5	55	68	1	263	247	K,L=	9	8
1	156	121	4	148	145	3	190	196	1	659	606	0	281	195	K,L=	0	5	5	72	78	K,L=	14	6	2	210	226	0	186	211
2	12	42	5	69	77	4	193	183	2	211	228	1	610	537	1	580	605	K,L=	17	5	0	289	252	3	153	153	1	214	192
3	155	206	K,L=	13	1	5	98	112	3	354	332	2	550	557	2	405	364	0	171	151	1	86	61	4	79	89	2	241	227
4	51	66	0	14	16	K,L=	10	2	4	440	426	3	422	387	3	421	351	1	47	47	2	216	245	5	11	32	3	242	250
5	10	24	1	108	100	0	168	167	5	243	230	4	191	193	4	41	81	2	73	85	3	77	97	K,L=	12	7	4	47	58
K,L=	16	0	2	312	316	1	105	98	K,L=	7	3	5	117	116	5	221	210	3	35	46	4	94	109	0	207	186	5	90	106
0	142	148	3	85	86	2	113	96	0	367	410	K,L=	4	4	K,L=	1	5	4	52	57	5	29	30	1	187	179	K,L=	10	8
1	50	66	4	47	54	3	315	336	1	355	290	0	483	412	0	64	76	5	6	29	K,L=	15	6	2	133	139	0	122	65
2	121	146	5	75	87	4	68	74	2	171	144	1	546	544	1	492	446	K,L=	18	5	0	58	74	3	97	129	1	96	71
3	36	41	K,L=	14	1	5	204	174	3	225	265	2	127	84	2	274	274	0	82	45	1	168	148	4	55	64	2	114	118
4	9	40	0	66	46	K,L=	11	2	4	202	184	3	529	549	3	232	184	1	100	80	2	55	53	5	78	81	3	105	117
5	61	85	1	102	118	0	13	1	5	301	259	4	144	126	4	234	260	2	9	26	3	75	78	K,L=	13	7	4	50	65
K,L=	17	0	2	47	58	1	142	153	K,L=	8	3	5	457	359	5	398	339	3	47	58	4	61	55	0	130	110	5	71	77
1	13	18	3	92	118	2	64	13	0	37	110	K,L=	5	4	K,L=	2	5	4	36	46	5	48	67	1	111	97	K,L=	11	8
2	46	61	4	70	75	3	13	14	1	337	334	0	439	431	0	248	223	K,L=	19	5	K,L=	16	6	2	58	61	0	15	8
3	51	82	5	46	66	4	191	187	2	333	316	1	360	379	1	948	880	0	61	55	0	48	30	3	115	115	1	43	27
4	80	105	K,L=	15	1	5	29	32	3	163	193	2	216	268	2	382	319	1	8	20	1	13	30	4	66	73	2	67	92
5	31	33	0	155	134	K,L=	12	2	4	402	424	3	140	95	3	380	409	2	59	63	2	72	86	5	88	93	3	14	7
K,L=	18	0	1	140	99	0	272	254	5	174	175	4	311	319	4	304	311	3	30	48	3	54	76	K,L=	14	7	4	98	109
0	62	57	2	40	49	1	108	76	K,L=	9	3	5	130	127	5	183	196	K,L=	0	6	4	38	46	0	14	10	5	83	104
1	12	29	3	49	51	2	166	159	0	505	469	K,L=	6	4	K,L=	3	5	0	599	561	5	22	35	1	57	59	K,L=	12	8
2	10	5	4	67	80	3	105	119	1	122	97	0	794	799	0	76	135	1	793	797	K,L=	17	6	2	58	71	0	56	37
3	20	11	5	60	77	4	179	160	2	349	389	1	433	436	1	456	437	2	788	799	0	12	17	3	13	46	1	116	96
4	7	5	K,L=	16	1	5	194	166	3	88	94	2	293	332	2	159	168	3	177	185	1	12	14	4	68	86	2	151	138
5	45	72	0	75	68	K,L=	13	2	4	186	198	3	205	222	3	352	312	4	305	249	2	10	19	5	16	26	3	97	105
K,L=	19	0	1	141	144	0	134	90	5	273	228	4	276	276	4	363	413	5	229	228	3	33	48	K,L=	15	7	4	44	58

TABLE 3. (Continued)

H	FO	FC
5*	51	54
K,L=13	8	
0*	185	160
1*	174	149
2*	81	95
3*	105	122
4*	59	54
5*	10	31
K,L=14	8	
0*	79	44
1*	78	57
2*	105	111
3*	102	117
4*	68	76
5*	9	29
K,L=15	8	
0*	89	70
1*	129	116
2*	11	25
3*	71	98
4*	28	41
5*	32	48
K,L=16	8	
0*	101	63
1*	46	37
2*	56	81
3*	27	36
4*	29	42
5*	19	40
K,L=17	8	
0*	11	4
1*	11	22
2*	9	17
3*	9	25
4*	15	30
K,L=18	8	
0*	53	44
1*	23	21
2*	7	26
3*	22	43
K,L= 0	9	
1*	76	81
2*	100	46
3*	151	99
4*	254	314
5*	168	205
K,L= 1	9	
0*	384	360
1*	359	292
2*	362	337
3*	166	144
4*	228	210
5*	277	264
K,L= 2	9	
0*	367	390
1*	306	313
2*	244	228
3*	140	103
4*	237	241
5*	160	134
K,L= 3	9	
0*	631	628
1*	408	335
2*	375	356
3*	254	256
4*	197	219
5*	96	86
K,L= 4	9	
0*	249	278
1*	439	425
2*	242	199
3*	238	205
4*	200	206
5*	237	250
K,L= 5	9	
0*	514	515
1*	392	353
2*	271	262
3*	209	251
4*	243	233
5*	236	247
K,L= 6	9	
0*	65	83
1*	431	409
2*	168	158
3*	256	269
4*	219	253
5*	76	78
K,L= 7	9	
0*	38	46
1*	93	107
2*	161	155
3*	120	147
4*	264	258
5*	98	128
K,L= 8	9	
0*	139	138
1*	223	186
2*	103	100
3*	264	220
4*	132	109
5*	12	22
K,L= 9	9	
0*	79	74
1*	111	131
2*	228	229
3*	193	172
4*	125	111
5*	76	71
K,L=10	9	
0*	162	146
1*	234	223
2*	145	143
3*	112	141
4*	153	169
5*	11	21
K,L=11	9	
0*	176	142
1*	209	233
2*	228	229
3*	86	67
4*	105	123
5*	66	82
K,L=12	9	
0*	103	90
1*	139	103
2*	111	127
3*	108	111
4*	81	105
5*	53	70
K,L=13	9	
0*	109	96
1*	57	58
2*	65	75
3*	70	76
4*	10	54
5*	31	34
K,L=14	9	
0*	20	4
1*	80	71
2*	12	28
3*	13	29
4*	29	35
5*	47	54
K,L=15	9	
0*	37	33
1*	51	43
2*	11	18
3*	37	49
4*	8	41
5*	7	29
K,L=16	9	
0*	104	77
1*	56	33
2*	44	58
3*	22	30
4*	32	47
5*	13	30
K,L=17	9	
0*	81	47
1*	90	75
2*	47	53
3*	8	14
K,L=18	9	
0*	77	56
1*	80	65
2*	38	40
K,L= 0	10	
0*	718	645
1*	377	375
2*	332	319
3*	302	291
4*	212	247
5*	166	159
K,L= 1	10	
0*	346	300
1*	418	360
2*	276	330
3*	274	300
4*	191	188
5*	254	241
K,L= 2	10	
0*	449	407
1*	231	199
2*	10	132
3*	209	223
4*	233	266
5*	215	194
K,L= 3	10	
0*	93	92
1*	184	160
2*	73	84
3*	246	251
4*	185	208
5*	129	112
K,L= 4	10	
0*	132	49
1*	135	126
2*	118	119
3*	108	105
4*	180	185
5*	213	193
K,L= 5	10	
0*	512	504
1*	169	179
2*	251	214
3*	195	162
4*	109	148
5*	81	119
K,L= 6	10	
0*	188	203
1*	333	292
2*	463	470
3*	155	117
4*	78	63
5*	105	95
K,L= 7	10	
0*	355	347
1*	371	342
2*	174	144
3*	318	326
4*	128	139
5*	91	101
K,L= 8	10	
0*	268	277
1*	80	70
2*	148	159
3*	106	116
4*	90	85
5*	61	74
K,L= 9	10	
0*	14	25
1*	155	147
2*	126	119
3*	107	016
4*	77	92
5*	63	94
K,L=10	10	
0*	15	0
1*	14	20
2*	114	97
3*	108	127
4*	101	112
5*	66	99
K,L=11	10	
0*	103	79
1*	111	78
2*	146	142
3*	27	40
4*	80	67
5*	48	68
K,L=12	10	
0*	15	32
1*	68	68
2*	68	87
3*	60	64
4*	39	48
5*	47	76
K,L=13	10	
0*	181	144
1*	74	54
2*	47	63
3*	58	72
4*	37	46
5*	21	31
K,L=14	10	
0*	124	108
1*	78	81
2*	68	70
3*	47	53
4*	34	40
5*	41	59
K,L=15	10	
0*	135	94
1*	12	40
2*	37	52
3*	42	68
4*	41	58
5*	6	17
K,L=16	10	
0*	24	68
1*	89	64
2*	22	37
3*	29	35
4*	37	47
K,L=17	10	
0*	50	24
1*	9	18
2*	48	56
3*	25	48
K,L= 0	11	
1*	57	44
2*	145	146
3*	159	161
4*	133	166
5*	183	229
K,L= 1	11	
0*	12	14
1*	328	274
2*	111	86
3*	189	163
4*	130	186
5*	148	155
K,L= 2	11	
0*	442	419
1*	215	210
2*	271	255
3*	111	109
4*	90	96
5*	126	147
K,L= 3	11	
0*	230	202
1*	340	313
2*	195	179
3*	232	249
4*	109	117
5*	173	188
K,L= 4	11	
0*	293	294
1*	378	346
2*	180	138
3*	242	251
4*	187	188
5*	56	48
K,L= 5	11	
0*	208	211
1*	249	227
2*	211	230
3*	146	131
4*	254	262
5*	40	48
K,L= 6	11	
0*	45	30
1*	210	157
2*	126	96
3*	211	199
4*	61	63
5*	89	112
K,L= 7	11	
0*	242	230
1*	140	130
2*	87	49
3*	154	201
4*	81	75
5*	89	112
K,L= 8	11	
0*	335	301
1*	117	40
2*	36	22
3*	67	80
4*	114	117
5*	47	54
K,L= 9	11	
0*	124	103
1*	145	103
2*	237	239
3*	114	99
4*	43	56
5*	97	119
K,L=10	11	
0*	110	98
1*	181	171
2*	13	24
3*	40	88
4*	103	104
5*	35	70
K,L=11	11	
0*	63	45
1*	122	106
2*	108	111
3*	83	79
4*	74	92
5*	50	77
K,L=12	11	
0*	56	22
1*	156	135
2*	12	23
3*	90	108
4*	44	69
5*	37	51
K,L=13	11	
0*	27	21
1*	63	54
2*	11	40
3*	53	75
4*	31	44
5*	35	47
K,L=14	11	
0*	53	18
1*	29	19
2*	10	26
3*	11	22
4*	50	58
5*	18	28
K,L=15	11	
0*	41	39
1*	73	58
2*	30	29
3*	17	37
4*	37	59
K,L=16	11	
0*	54	55
1*	99	68
2*	29	34
3*	37	52
K,L=17	11	
0*	66	39
1*	64	68
2*	33	44
K,L= 0	12	
0*	727	220
1*	269	259
2*	11	25
3*	159	153
4*	209	252
5*	57	63
K,L= 1	12	
0*	170	112
1*	187	164
2*	222	213
3*	228	206
4*	123	157
5*	113	127
K,L= 2	12	
0*	332	338
1*	128	109
2*	108	125
3*	81	102
4*	172	181
5*	76	86
K,L= 3	12	
0*	141	98
1*	71	93
2*	112	124
3*	280	279
4*	79	101
5*	104	125
K,L= 4	12	
0*	14	58
1*	146	149
2*	219	216
3*	86	79
4*	125	121
5*	87	104
K,L= 5	12	
0*	266	306
1*	162	133
2*	148	145
3*	84	82
4*	141	163
5*	40	34
K,L= 6	12	
0*	43	45
1*	228	216
2*	232	247
3*	107	80
4*	11	48
5*	100	130
K,L= 7	12	
0*	217	237
1*	156	160
2*	97	79
3*	103	121
4*	100	121
5*	11	50
K,L= 8	12	
0*	189	146
1*	155	136
2*	181	169
3*	86	101
4*	55	80
5*	24	25
K,L= 9	12	
0*	15	9
1*	106	77
2*	105	103
3*	39	50
4*	111	123
5*	21	34
K,L=10	12	
0*	83	81
1*	73	76
2*	12	32
3*	14	19
4*	33	55
5*	25	26
K,L=11	12	
0*	109	70
1*	51	51
2*	12	13
3*	54	62
4*	58	63
5*	47	60
K,L=12	12	
0*	124	125
1*	62	78
2*	52	47
3*	47	71
4*	53	67
5*	57	72
K,L=13	12	
0*	150	103
1*	60	59
2*	59	76
3*	34	53
4*	55	66
5*	20	42
K,L=14	12	
0*	154	106
1*	117	85
2*	46	61
3*	49	52
4*	9	30
5*	35	62
K,L=15	12	
0*	73	53
1*	50	38
2*	71	76
3*	31	42
4*	47	65
K,L=16	12	
0*	30	28
1*	78	67
2*	16	21
3*	15	24
K,L= 0	13	
1*	101	115
2*	35	40
3*	167	194
4*	11	35
5*	68	77
K,L= 1	13	
0*	106	109
1*	117	104
2*	153	167
3*	42	42
4*	141	165
5*	116	166
K,L= 2	13	
0*	315	302
1*	96	64
2*	161	150
3*	87	101
4*	101	121
5*	32	37
K,L= 3	13	
0*	139	110
1*	219	197
2*	139	104
3*	199	214
4*	49	58
5*	68	77
K,L= 4	13	
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1*	170	142
2*	221	214
3*	88	124
4*	85	107
5*	11	23
K,L= 5	13	
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1*	90	81
2*	51	74
3*	71	71
4*	11	44
5*	77	98
K,L= 6	13	
0*	30	35
1*	94	78
2*	159	171
3*	67	66
4*	65	68
5*	55	85
K,L= 7	13	
0*	173	114
1*	106	103
2*	100	115
3*	117	107
4*	105	131
5*	62	78
K,L= 8	13	
0*	222	203
1*	29	59
2*	12	27
3*	71	75
4*	107	119
5*	69	97
K,L= 9	13	
0*	15	37
1*	168	143
2*	60	61
3*	111	139
4*	30	34
5*	10	51
K,L=10	13	
0*	226	222
1*	125	107
2*	76	85
3*	52	48
4*	75	79
5*	21	41
K,L=11	13	
0*	47	41
1*	130	97
2*	75	89
3*	50	49
4*	28	38
5*	40	66
K,L=12	13	
0*	157	96
1*	66	82
2*	50	48
3*	18	36
4*	21	36
5*	7	22
K,L=13	13	
0*	34	17
1*	12	8
2*	37	42
3*	46	61
4*	56	72
5*	22	35
K,L=14	13	
0*	11	14
1*	73	41
2*	9	6
3*	39	44
4*	31	41
K,L=15	13	
0*	97	75
1*	25	21
2*	28	36
3*	15	26
K,L=16	13	
0*	53	38
1*	53	52
K,L= 0	14	
0*	15	27
1*	242	228
2*	34	25
3*	71	31
4*	89	81
5*	51	77
K,L= 1	14	
0*	135	144
1*	172	150
2*	141	116
3*	79	96
4*	44	57
5*	11	42
K,L= 2	14	
0*	55	58
1*	225	208
2*	54	47
3*	79	74
4*	63	97
5*	11	18
K,L= 3	14	
0*	64	47
1*	110	113
2*	137	131
3*	79	105
4*	39	52
5*	48	51
K,L= 4	14	
0*	60	43
1*	126	134
2*	33	39
3*	95	95
4*	51	74
5*	75	108
K,L= 5	14	
0*	88	76
1*	95	67
2*	113	126
3*	110	122
4*	87	115
5*	53	93
K,L= 6	14	
0*	15	17
1*	160	153
2*	165	178
3*	106	112
4*	60	54
5*	34	59
K,L= 7	14	
0*	183	172
1*	77	73
2*	99	109
3*	59	62
4*	120	157
5*	10	0
K,L= 8	14	
0*	40	32
1*	179	153
2*	49	56
3*	75	89
4*	10	19
5*	69	94
K,L= 9	14	
0*	171	150
1*	56	54
2*	87	80
3*	79	102
4*	75	88
5*	63	75
K,L=10	14	
0*	30	21
1*	74	65
2*	41	49
3*	78	92
4*	47	72
5*	45	58
K,L=11	14	
0*	73	61
1*	30	42
2*	24	56
3*	26	49
4*	45	58
5*	34	52
K,L=12	14	
0*	105	92
1*	111	87
2*	39	53
3*	41	51
4*	48	58
5*	20	46
K,L=13	14	
0*	116	82
1*	96	86
2*	70	72
3*	42	48
4*	47	51
K,L=14	14	
0*	110	75
1*	137	94
2*	14	30
3*	48	59
K,L=15	14	
1*	63	58
2*	45	64
K,L= 0	15	
1*	94	124
2*	138	154
3*	76	89
4*	10	1
5*	11	6
K,L= 1	15	
0*	97	92
1*	110	121
2*	87	92
3*	57	57
4*	60	72
5*	11	44
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0*	175	200
1*	74	69
2*	84	75
3*	104	136
4*	86	105
5*	28	37
K,L= 3	15	
0*	112	112
1*	156	131
2*	71	82
3*	83	92
4*	48	57
5*	76	126
K,L= 4	15	
0*	167	179
1*	71	56
2*	127	147
3*	87	98
4*	97	111
5*	10	5
K,L= 5	15	
0*	73	44
1*	173	160
2*	64	44
3*	134	156
4*	10	29
5*	37	71
K,L= 6	15	
0*	103	76
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2*	86	101
3*	13	19
4*	47	51
5*	51	79
K,L= 7	15	
0*	14	4
1*	14	26
2*	65	74
3*	13	10
4*	50	71
5*	43	63
K,L= 8	15	
0*	42	44
1*	63	58
2*	31	47
3*	87	67
4*	42	59
5*	63	78
K,L= 9	15	
0*	101	70
1*	94	114
2*	81	94
3*	80	82
4*	54	77
5*	64	75
K,L=10	15	
0*	207	164
1*	37	46
2*	69	77
3*	11	29
4*	62	81
5*	7	39
K,L=11	15	
0*	63	28
1*	133	110
2*	43	59
3*	80	76
4*	7	42
5*	25	37
K,L=12	15	
0*	119	102
1*	11	18
2*	92	91
3*	52	74
4*	25	33
K,L=13	15	
0*	9	12
1*	45	32
2*	7	10
3*	18	24
K,L=14	15	
0*	49	21
2*	5	1
K,L= 0	16	
0*	15	19
1*	205	176
2*	12	7
3*	94	88
4*	23	43
5*	28	68
K,L= 1	16	
0*	224	236
1*	68	46
2*	126	117
3*	14	47
4*	80	105
5*	10	37
K,L= 2	16	
0*	65	60
1*	120	126
2*	47	53
3*	93	117
4*	10	37
5*	65	88
K,L= 3	16	
0*	15	2
1*	88	92
2*	66	66
3*	36	55
4*	10	18
5*	10	42
K,L= 4	16	
0*	15	16
10	14	22
2*	95	98
3*	21	26
4*	71	95
5*	9	30
K,L= 5	16	
0*	81	57
1*	14	24
2*	47	45
3*	28	46
4*	46	60
5*	9	40
K,L= 6	16	
0*	14	32
1*	128	117
2*	12	16
3*	93	97
4*	39	55
5*	27	54
K,L= 7	16	
0*	197	177
1*	71	62
2*	106	133
3*	64	61
4*	78	86
5*	8	5
K,L= 8	16	
0*	13	30
1*	115	110
2*	41	47
3*	94	88
4*	8	13
5*	36	61
K,L= 9	16	
0*	142	106
1*	38	37
2*	61	66
3*	11	25
4*	54	69
K,L=10	16	
0*	12	21
1*	51	54
2*	23	42
3*	19	18
4*	59	75
K,L=11	16	
0*	11	9
1*	50	38
2*	8	13
3*	50	56
4*	20	18
K,L=12	16	
0*	9	6
1*	55	48
2*	14	48
3*	36	44
K,L=13	16	
0*	91	75
2*	42	53
K,L= 0	17	
1*	78	76
2*	82	119
3*	55	89
4*	21	19
5*	9	25
K,L= 1	17	
0*	43	68
1*	109	91
2*	12	5
3*	51	58
4*	35	65
5*	46	70
K,L= 2	17	
0*	94	99
1*	14	28
2*	57	56
3*	68	91
4*	60	82
5*	9	33
K,L= 3	17	
0*	128	133
1*	194	189
2*	56	56
3*	109	101
4*	9	13
5*	8	48
K,L= 4	17	
0*	167	164
1*	58	53
2*	103	123
3*	24	44
4*	64	84
5*	33	39
K,L= 5	17	
0*	27	35
1*	103	104
2*	11	11
3*	67	63
4*	16	40
5*	8	42
K,L= 6	17	
0*	105	68
1*	46	43
2*	56	67
3*	48	48
4*	16	33
5*	35	51
K,L= 7	17	
0*	29	4
1*	42	49
2*	42	42
3*	11	7
4*	15	40
5*	25	39
K,L= 8	17	
0*	35	17
1*	33	23
2*	42	31
3*	45	53
4*	7	28
5*	16	47
K,L= 9	17	
0*	67	40
1*	78	69
2*	38	42
3*	39	49
4*	21	28
K,L=10	17	
0*	78	63
1*	54	38
2*	51	54
3*	8	33
K,L=11	17	
0*		
1*	77	74
3*	34	51
K,L=12	17	
0*	41	44
K,L= 0	18	
0*	13	73
1*	62	61
2*	59	84
3*	118	133
4*	8	14
5*	67	94
K,L= 1	18	
0*	183	154
1*	49	44
2*	94	112
3*	11	41
4*	67	90
5*	7	26
K,L= 2	18	
0*	97	75
1*	107	109
2*	58	67
3*	69	77
4*	53	69
5*	7	39
K,L= 3	18	
0*	13	13
1*	13	20
2*	10	1
3*	49	59
4*	8	30
5*	37	59
K,L= 4	18	
0*	13	0
1*	68	69
2*	10	20
3*	11	17
4*	18	30
K,L= 5	18	
0*	127	103
1*	19	19
2*	80	82
3*	35	39
4*	17	22
K,L= 6	18	
0*	65	22
1*	109	94
2*	35	46
3*	86	81
4*	6	33
K,L= 7	18	
0*	120	84
1*	11	17
2*	80	85
3*	9	17
4*	11	28
K,L= 8	18	
0*	40	33
1*	81	73
2*	8	17
3*	40	42
K,L= 9	18	
0*	59	57
1*	9	11
2*	40	51
K,L= 0	19	
1*	93	81
2*	10	16
3*	97	70
4*	6	20
K,L= 1	19	
0*	63	54
1*	11	30
2*	92	59
3*	47	56
4*	28	45
K,L= 2	19	
0*	99	69
1*	22	31
2*	76	79
3*	18	41
4*	38	51
K,L= 3	19	
0*	11	22
1*	117	97
2*	9	22
3*	38	38
4*	8	18
K,L= 4	19	
0*	116	83
1*	37	31
2*	88	91
3*	25	44
4*	34	55
K,L= 5	19	
0*	11	17
1*	77	64
2*	8	23
3*	47	64
4*	22	49
K,L= 6	19	
0*	10	17
1*	28	37
2*	11	34
3*	15	34
K,L= 7	19	
0*	9	0
1*	9	2
K,L= 8	19	
0*	67	30
1*	8	7
K,L= 9	19	
1*	40	52
K,L= 0	20	
0*	54	22
1*	110	96
2*	8	22
3*	59	86
K,L= 1	20	
0*	68	57
1*	10	27
2*	52	62
K,L= 2	20	
0*	10	3
1*	9	22
2*	8	32
K,L= 3	20	
0*	10	25
1*	9	24
2*	7	23
K,L= 4	20	
0*	9	4
1*	9	23
2*	28	35
K,L= 5	20	
0*	67	52
1*	8	15
2*	34	45
K,L= 6	20	
1*	53	63
K,L= 0	21	
1*	17	36
K,L= 1	21	
0*	10	39
1*	37	40
K,L= 2	21	
0*	14	20
1*	18	20
K,L= 3	21	
1*	35	45

	FO
(A)	967
(B)	1119
(C)	1128
(D)	984
(E)	954
(F)	942
(G)	1118

all 29 peaks except the peaks for hydrogen atoms. At this stage the R-factor was found to be 33%. The validity of the determined positional parameters of all the atoms except hydrogen atoms was examined by refining them by the method of diagonal least squares using 655 reflection data ($0.1 \leqq \sin\theta \leqq 0.6$). Only the real part of dispersion corrections were taken into account at this stage. After five cycles, there was one atom whose thermal parameter diverged, so that the new positional parameters were determined from the Fourier map obtained by the structure amplitude from 28 atoms except that atom with the use of all reflection data. After four cycles there was no atom with diverging thermal parameter. At this stage the thermal parameters of the atoms were generally small owing to the use of only a part of the observed reflection data in the least-squares treatment, but some of them were exceptionally small. By considering the bond lengths and angles, the positions of some atoms were found to be opposite to the correct ones with respect to the pseudo mirrors. We revised these erroneous positions and carried out five cycles of diagonal least-squares treatment using all reflection data. After this calculation, all the thermal parameters, bond lengths and angles were found to be nearly satisfactory, the R-factor being 16.4%. The data were then refined by the block diagonal least-squares method by using all the reflection data and the isotropic temperature factors for all the atoms. For this stage we used the computer program which was written by Dr. T. Ashida and is reserved at the Tokyo University Computation Center. As described in the diagonal least-squares method, only the real part of the dispersion corrections was considered. All reflection data were weighted equally. After four cycles, the R-factor was found to be 14.4%. However, two unreasonable results were obtained; the thermal factor of one crystal water W(2) was 12.3 Å^2 and the C(21)–C(22) bond length was 1.26 Å. Using the anisotropic temperature factor for the copper atom and excluding seven reflection data supposed to have the extinction effects, we attempted the refinement by the block diagonal least-squares method but failed to obtain better results. The R-factor was 12.8%. Considering the fact that the thermal parameter of W(2) remained large, we supposed that the correct position of this atom might be on the opposite side of the pseudo mirrors, and without changing the parameters of the other 28 atoms, we calculated the atomic distances by assuming the three positions on the opposite side of the pseudo mirrors. However, the results were not satisfactory because the three positions calculated were unreasonably close to the chelating molecules.

Taking account of these facts, we set thermal parameter of W(2) equal to that of W(1) and corrected the positional parameters of C(17) and of C(21) so as to have a reasonable atomic distance between C(21) and C(22). The final parameters thus obtained are shown in Table 2, where the values with asterisk refer to the corrected parameters. The bond lengths and angles calculated from these parameters are shown in Fig. 3. The R-factor calculated from these corrected parameters was found to be 13.0%. The observed and calculated structure factors computed from corrected parameters are listed in Table 3.

Results and Discussion

Figure 4 shows one molecule of the copper chelate and the two nearest crystallization water. As described in the previous section, the copper atom has the position near $x/a = 1/4$ and $z/c = 0$, and the distances from copper atom to this position along a

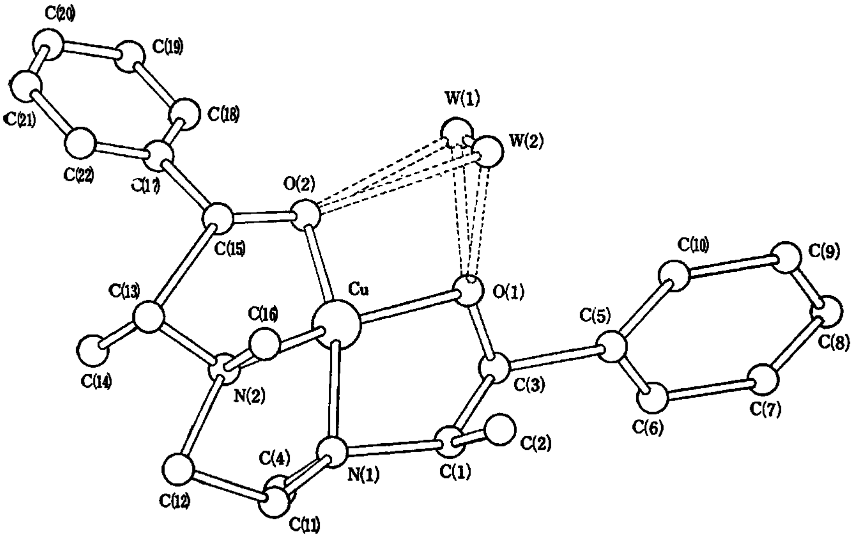

Fig. 4. The molecular structure of EBECu.

TABLE 4. BEST PLANE

[a] Each plane is represented by $Z=AX+BY+D$, where X, Y and Z are coordinates in Å. For this calculation the positional parameters are translated from Table 2 by symmetric codes.

Plane	*A*	*B*	*D*	Atoms
Benzene ring (I)	2.1874	1.7764	−23.089	C(3), C(5)-C(10)
Benzene ring (II)	0.3690	−0.8694	12.716	C(15), C(17)-C(22)
Chelate ring (III)	−1.5472	−4.3636	57.953	Cu, O(1), C(3), N(1)
Chelate ring (IV)	−0.1654	−2.1405	28.679	Cu, O(2), C(15), N(2)

[b] Displacement of atoms from the planes (in Å).

Plane(I)		Plane(II)		Plane(III)		Plane(IV)	
C(3)	−0.019	C(15)	−0.005	Cu	−0.018	Cu	−0.020
C(5)	0.002	C(17)**	0.003	O(1)	0.032	O(2)	0.026
C(6)	0.023	C(18)	0.005	C(3)	−0.026	C(15)	−0.019
C(7)	−0.009	C(19)	−0.001	N(1)	0.013	N(2)	0.013
C(8)	−0.013	C(20)	−0.007	C(1)*	0.657	C(13)*	−0.695
C(9)	0.000	C(21)**	0.006				
C(10)	0.016	C(22)	−0.002				

* shows that the atom was not included in the evalution of the equation of the plane.
** shows corrected positional parameters (see Text).

and *c* axis are 0.028 (0.239 Å) and 0.021 (0.191 Å), respectively, whereas the distance along *b* axis is 0.072 (1.144 Å).

The copper atom is situated at the center of a distorted square plane where the two oxygen atoms O(1), O(2) and two nitrogen atoms N(1), N(2) assume the cis configuration. The bond lengths of Cu–O(1), Cu–O(2), Cu–N(1) and Cu–N(2) are 1.91, 1.89, 2.02 and 1.99 A, respectively, which are in good agreement with those of *trans*-bis(*l*-ephedrine)-copper(II) chelate (Cu–O: 1.88, Cu–N: 2.05 Å). These five-atom system is non-planar. The oxygen atom, O(1), is −0.516 Å from the plane through N(1), Cu and N(2), and O(2) is +0.423 Å from this plane. The fact that the O(1)–Cu–N(2) and O(2)–Cu–N(1) angles are 163.3 and 165.5°, respectively, indicates the probable distortion of the square-planar structure owing to the N(1)–C(11)–C(12)–N(2) bridge formation. This bridge is in the *gauche* form with the internal rotation angle of 53.8°, and C(11) is −0.354 Å from the plane through N(1), Cu and N(2), and C(12) is +0.392 Å from this plane (Table 4).

As to the five membered chelate ring formed by Cu, O(2), C(15), C(13) and N(2), the atom C(13) deviates from the least-square plane through the other four atoms; C(13) is 0.695 Å apart from this plane, while the distances between each of the four atoms and the plane is in the range 0.013—0.026 Å. Similary, in the system formed by Cu, O(1), C(3), C(1) and N(1), the atom C(1) is 0.657 Å apart from the least-square plane through the other four atoms, while the distances from this plane are between 0.013 and 0.032 Å with respect to the other four atoms. In these chelate rings the carbon atoms adjacent to the nitrogen atoms are far from the plane., These results also coincide well with the *trans*-bis(*l*-ephedrine)copper(II) chelate.

The thermal parameters of N(1) and N(2) are small as compared with those of the other atoms. This fact may be interpreted in terms of the distortion of the tetrahedral structure around the nitrogen atoms and the restriction of the movements caused by the N–C–C–N bridge. Some of C–N bond lengths, 1.55 Å for C(16)–N(2) or C(13)–N(2), appear to be somewhat longer than he mean value for C–N single bond (1.47 Å). We can find, however, the cases such as quaternary ammonium salts. where C–N bonds are between 1.50 and 1.55 Å.[9] Therefore our results are not unreasonable.

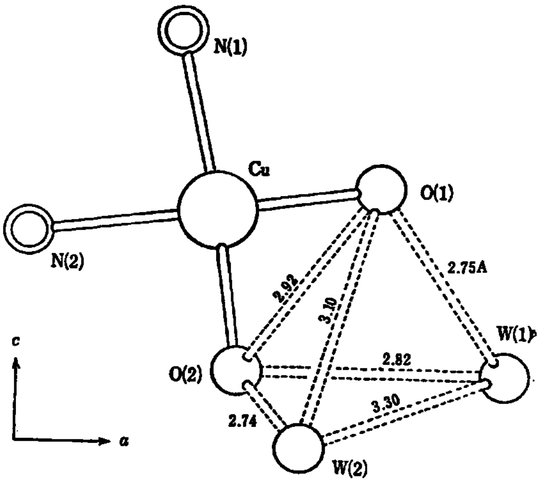

Fig. 5. Interatomic distances of oxygen atoms.

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9) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965).

Four oxygen atoms projected on *ac* are shown in Fig. 5. As shown in the figure, the interatomic distances of these four atoms are between 2.74 and 3.30 Å, and the interatomic angles are 50—73° (Table 5). Accordingly the four atoms are nearly at the corners of a tetrahedron, and it is impossible to consider that one atom has the hydrogen bond with other special oxygen atom. However, because the thermal parameters of W(1) and W(2) are larger than the corresponding values of the other atoms, we consider that, as Bryan *et al.* reported about bis(β-aminobuthyrato)-copper(II) dihydrate,[6] a water molecule forms a hydrogen bond with each of the two oxygen atoms alternately. It is improbable that the two hydrogen atoms of a water molecule are hydrogen-bonded with the oxygen atoms at the same time. As there is no obvious difference between W(1) and W(2) and the two water molecules approach each other, the splitting of the absorption bands near 1700 cm^{-1} may be ascribed to the interaction between the two water molecules.

TABLE 5. INTERATOMIC ANGLES OF OXYGEN ATOMS

O(2)-O(1)-W(1)	59.6°
O(2)-O(1)-W(2)	53.9
W(1)-O(1)-W(2)	68.4
O(1)-O(2)-W(1)	57.1
O(1)-O(2)-W(2)	66.4
W(1)-O(2)-W(2)	72.8
O(1)-W(1)-W(2)	61.0
O(1)-W(1)-O(2)	63.3
O(2)-W(1)-W(2)	52.4
O(1)-W(2)-W(1)	50.7
O(1)-W(2)-O(2)	60.0
W(1)-W(2)-O(2)	54.8

About the reversible color change of EBECu, it was presumed first that the octahedral chelate of EBECu containing two molecules of water would be blue and that the anhydrous square planar chelate would be green, but on the contrary the present X-ray studies show that the blue chelate has the square planar structure. This phenomenon may be

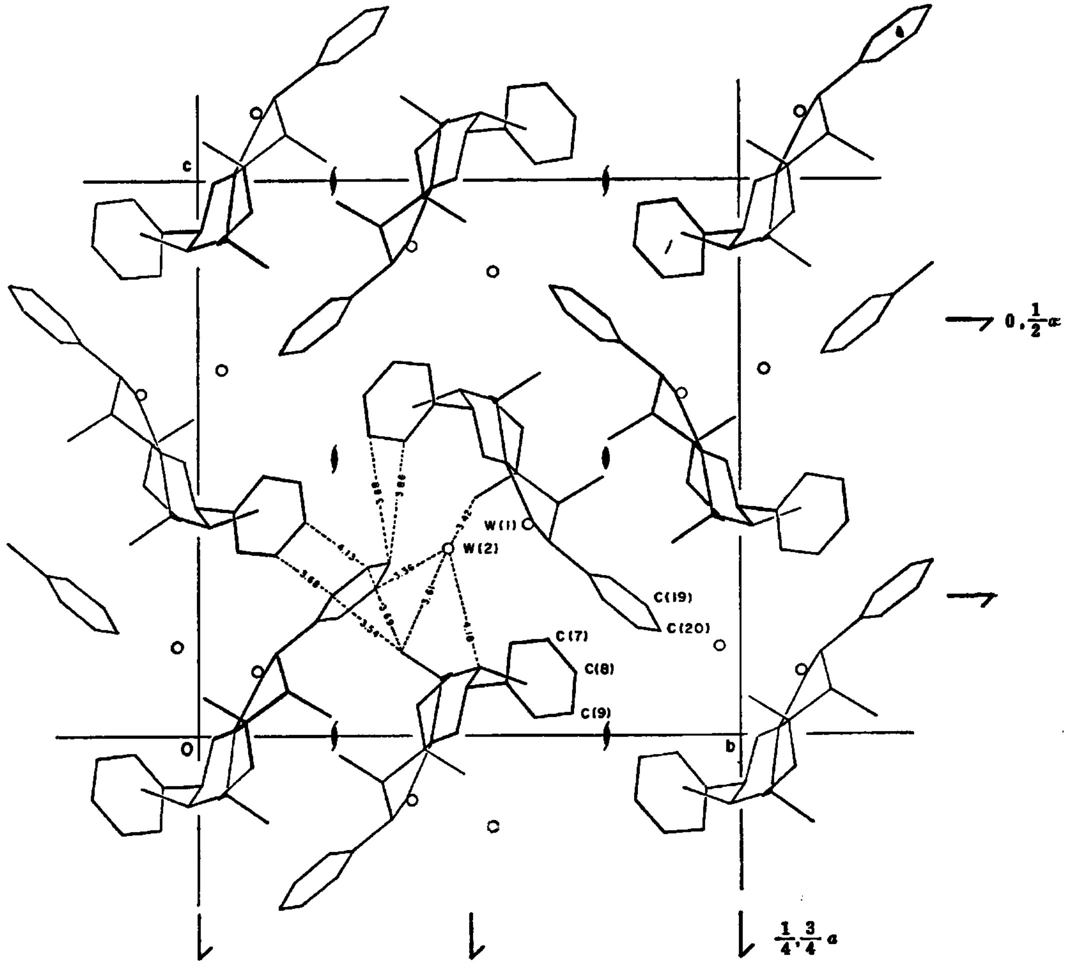

Fig. 6(a). Projection of the structure along the *a* axis.

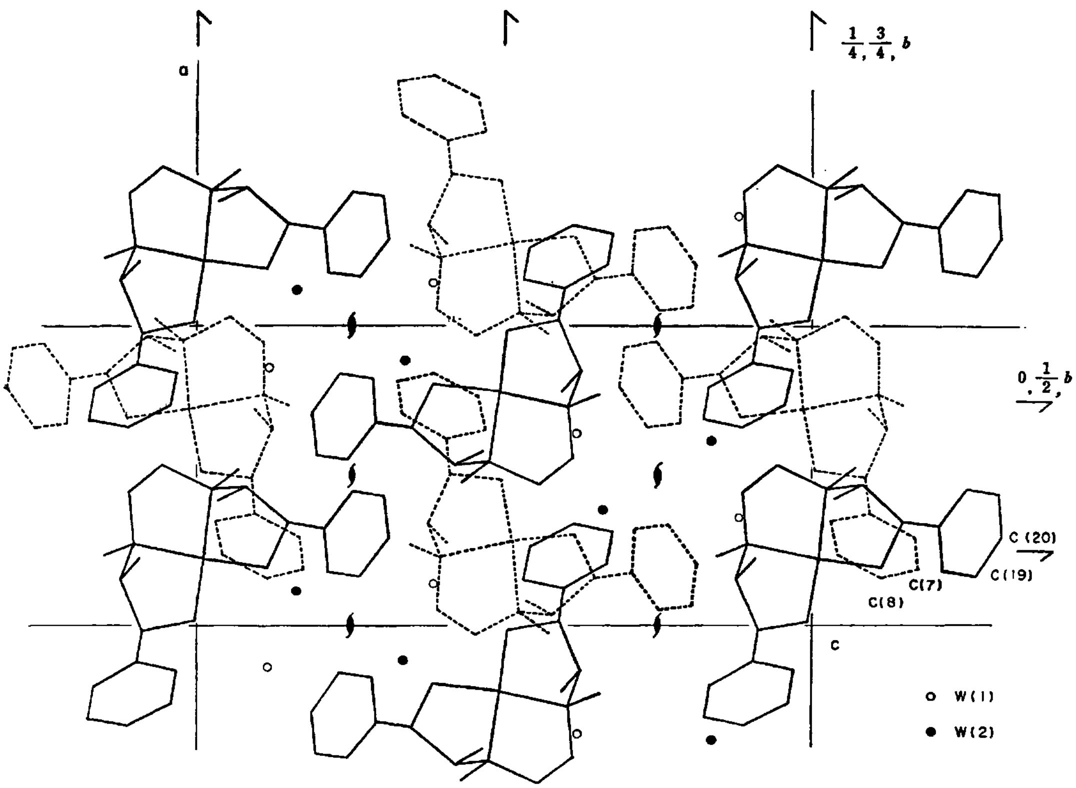

Fig. 6(b). Projection of the structure along the *b* axis.

TABLE 6. INTERMOLECULAR ATOMIC DISTANCES

[a] from benzene carbon atoms (less than 3.9Å)				
C(22)	C(4)	$[-1+x,\ 1+y,\ 1+z]^{*}$	3**	3.54Å
C(20)	C(16)	$[1+x,\ y,\ z]$	4	3.54
C(7)	C(11)	$[1+x,\ y,\ z]$	1	3.65
C(22)	C(7)	$[1+x,\ 1+y,\ -1+z]$	2	3.69
C(22)	C(2)	$[1+x,\ 1+y,\ -1+z]$	2	3.69
C(21)	C(4)	$[-1+x,\ 1+y,\ 1+z]$	3	3.70
C(18)	C(12)	$[x,\ 1+y,\ 1+z]$	3	3.70
C(22)	C(6)	$[1+x,\ 1+y,\ -1+z]$	2	3.73
C(17)	C(2)	$[1+x,\ 1+y,\ -1+z]$	2	3.79
C(21)	C(16)	$[1+x,\ y,\ z]$	4	3.80
C(19)	C(11)	$[x,\ 1+y,\ 1+z]$	3	3.87
C(19)	C(12)	$[x,\ 1+y,\ 1+z]$	3	3.88
C(21)	C(2)	$[1+x,\ 1+\mathrm{y},\ -1+z]$	2	3.90

[b] from other atoms (less than 4.0Å)				
W(1)	C(16)	$[1+x,\ y,\ x]$	1	3.33
W(1)	C(14)	$[x,\ 1+y,\ 1+z]$	3	3.46
W(1)	C(13)	$[1+x,\ y,\ z]$	1	3.50
C(6)	C(11)	$[1+x,\ y,\ z]$	1	3.55
W(2)	C(4)	$[1+x,\ 1+y,\ -1+z]$	2	3.61
W(1)	N(2)	$[1+x,\ y,\ z]$	1	3.77
O(1)	C(14)	$[x,\ 1+y,\ 1+z]$	3	3.78
W(2)	C(11)	$[1+x,\ 1+y,\ -1+z]$	2	3.83
C(14)	C(4)	$[-1+x,\ 1+y,\ 1+z]$	3	3.89
Cu	C(14)	$[x,\ 1+y,\ 1+z]$	3	3.96
C(6)	C(12)	$[1+x,\ y,\ z]$	1	3.98
W(1)	C(12)	$[1+x,\ y,\ z]$	1	3.98

* lattice translation

** symmetry translation in the unit cell

1 $+x,\ +y,\ +z$, 2 $\frac{1}{2}-x,\ -y,\ \frac{1}{2}+z$, 3 $\frac{1}{2}+x,\ \frac{1}{2}-y,\ -z$, 4 $-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$

explained as follows; on dissolving the chelate in acetone the hydrogen bonds connecting the crystal water with the oxygen atoms in the chelate are cleaved, affecting the coordinating abilities of the oxygen atoms of the chelate and consequently the color of the chelate. The orientation of molecules in the crystal projected on *bc* and *ac* are shown in Fig. 6. Table 6 shows the intermolecular atomic distances which are less than 3.9 Å from one of the carbon atoms of benzene ring and less than 4.0 Å from one of the other atoms. The distances are considered to be reasonable. The benzene rings in four different molecules fairly approach one another, and if this state is projected on *bc* the twofold screw axis along *b* axis is found at the center of the four benzene rings. There are hydrogen bonds between the two water molecules and the nearest chelate molecule, but the atomic distances from these water molecules to the oxygen atoms of the other chelate molecules are more than 5.0 Å, so that there are no intermolecular hydrogen bonds.

For *trans*-bis(*l*-ephedrine)copper(II) chelate, we presumed in earlier publiciation[1] that the hydrogen bonds were cleaved in polar solvents and that halogenated hydrocarbons could easily approach the copper atom and react with it. There are active hydrogen atoms on the nitrogen coordinating to the copper atom, but it is not clear whether they are concerned with this reaction or not. EBECu chelate dissolved in ethyl alcohol also reacts with carbon tetrachloride. It is probable that the cleavage of the hydrogen bonds due to solvation results in the formation of a vacant space near the copper atom, allowing carbon tetrachloride molecules to approach the copper atom. Although EBECu has no active hydrogen, it reacts with carbon tetrachloride. It seems therefore that in the case of *trans*-bis(*l*-ephedrine)copper(II) chelate, the existence of active hydrogen is not an important factor for these reactions.

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