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Binuclear Metal Complexes. XXIII.[1] Molecular Structure of a Hetero-metal Binuclear Complex, CuCo(fsaen)·$3H_2O(C_{18}H_{18}N_2O_9CoCu)$

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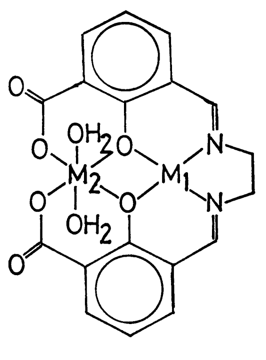
The crystal structure of hetero-metal binuclear complex, CuCo(fsaen)·$3H_2O$, with *N,N'*-bis(3-carboxysalicylidene)ethylenediamine (H_4fsaen) was determined by the single-crystal X-ray diffraction method. The crystals are trigonal, space group $P3_221$, $a=b=12.845(2)$, $c=9.962(1)$ Å, $V=1423.5(4)$ Å^3, and $Z=3$. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method to an *R* factor of 0.028. The copper atom is coordinated by two nitrogen atoms and two phenolic oxygen atoms in a square-planar manner. The cobalt atom is coordinated by two equatorial carboxyl oxygen atoms, two equatorial phenolic oxygen atoms and two axial water oxygen atoms in a distorted octahedral geometry. The detailed structure determined is in conformity with the magnetic and spectral properties previously reported.

In the previous papers of this series,[2,5] it was shown that the Schiff bases derived from 3-formylsalicylic acid and diamines are binucleating ligands with coordinative selectivity. By use of these ligands, many hetero-metal binuclear complexes have been synthesized and characterized on the basis of elemental analyses, IR, electronic spectra, and magnetic measurements over the temperature range.[1–4] However, no direct proof of the structure has been given yet. Therefore, it is desired to establish the basic structure of these hetero-metal binuclear complexes. In this study, the crystal structure of CuCo(fsaen)·$3H_2O$ which is one of those hetero-metal binuclear complexes was analyzed by the single-crystal X-ray diffraction method, where H_4fsaen represents *N,N'*-bis(3-carboxysalicylidene)ethylenediamine.

According to the previous paper,[3] the electronic spectrum of CuCo(fsaen)·$3H_2O$ was interpreted in terms of the planar copper(II) in the "inside" coordination site and the octahedral cobalt(II) in the "outside" coordination site. On the basis of the magnetic property, it was assumed that the ground state of the cobalt(II) is orbitally singlet and, hence, the geometry around the cobalt atom is slightly distorted from the regular octahedron. Hence, in view of this assumption, it is interesting to provide the detailed structural data of this complex obtained by the X-ray analysis.



Experimental

CuCo(fsaen)·$3H_2O$ was prepared by the method previously reported.[3] Crystals suitable for an X-ray study were obtained as red-purple prisms by crystallization from a dilute aqueous solution.

Preliminary Weissenberg photographs showed that the complex crystallizes in a trigonal system. The cell parameters and intensities were measured on a Syntex P$\bar{1}$ automated four-circle diffractometer with monochromated Mo *K*α radiation ($\lambda=0.71073$ Å). The crystal was ground to a sphere (radius 0.152 mm). The cell parameters were determined by the least-squares refinement based on the 15 reflections in the range of $17<2\theta<38°$. The values are $a=b=12.845$ (2), $c=9.962$ (1) Å, and $V=1423.5$ (4) Å^3. The density $D_m=1.84$ g/cm^3 obtained by floatation in hexane-1,2-dibromoethane solution agrees well with the density $D_C=1.85$ g/cm^3 calculated for three molecules per unit cell. The crystallographic data are given in Table 1.

TABLE 1. CRYSTAL DATA

Molecular formula	CuCo($C_{18}H_{12}N_2O_6$)·$3H_2O$
Molecular weight	528.8
Crystal system	Trigonal
Space group	$P3_121$ or $P3_221$
$a=b=12.845(2)$, $c=9.962(1)$ Å	
$V=1423.5(4)$ Å^3	
$Z=3$	
$D_m=1.84$ g/cm^3	
$D_c=1.85$ g/cm^3	
$\mu=21.1$ cm^{-1} (for Mo *K*α)	

Intensity data were collected by the θ-2θ scan technique with a variable scan rate of 4.0 to 24.0°/min. Three standard reflections were monitored every 50 reflections, and their intensities showed a good stability. A total of 4493 reflections with $2\theta<48°$ were collected. The intensities were corrected for the Lorentz and the polarization effects, but corrections for absorption were not applied on account of $\mu r=0.32$. 839 independent reflections with $|F_o|\geq 2.5\sigma(F_o)$ were considered as "observed" and were used for the structure analysis.

Solution and Refinement of the Structure

The observed Laue symmetry of the reflections is $\bar{3}$ml. The observed setting of the symmetry, $I(hkl)=I(kh\bar{l})$, and the systematic absences of $00l$ for $l\neq 3n$ indicate that either of the two enantiomorphous space groups $P3_121$ or $P3_221$ is possible.

The structure was solved by the heavy atom method. The positions of the copper and cobalt atoms were determined by a three-dimensional Patterson synthesis. The copper and cobalt atoms were located on the twofold axes in the special positions. The successive Fourier syntheses and the difference Fourier syntheses revealed all the nonhydrogen atoms. Refinement was carried out by the block-diagonal least-squares method. One of the water oxygens, O(5) was found to be positionally disordered, with a half-occupancy of the two positions related by the twofold axis. Being introduced anisotropic thermal parameters, the block-diagonal least-squares refinement yielded a discrepancy factor $R_1=\sum||F_o|-|F_c||/\sum|F_o|=0.046$. At this stage, a difference Fourier map revealed all the hydrogen atoms. The refinement was performed for both the enantiomorphous space groups $P3_121$ and $P3_221$. The final discrepancy factors were : $R_1=0.038$ and $R_2=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.059$ for space group $P3_121$; $R_1=0.028$ and $R_2=0.045$ for space group $P3_221$. As has been pointed out,[6,7] the best refinement should correspond to the correct configuration. Accordingly, the hypothesis of space group $P3_121$ can be rejected at a confidence level higher than 99.5%.[9] A further check on the $P3_221$ configuration was carried out in comparing the intensities of Friedel pairs. Table 2 lists observed and calculated intensity relations between some *hkl* and $\bar{h}\bar{\imath}l$ reflections. Inspecting these relations, one can confirm that $P3_221$ is the correct space group for the crystal studied here.

TABLE 2. OBSERVED AND CALCULATED INTENSITY RELATIONS BETWEEN SOME *hkl* AND $\bar{h}\bar{\imath}l$ REFLECTIONS

h	*k*	*l*	$F_c(hkl)$	Obsd	$F_c(\bar{h}\bar{\imath}l)$	$\bar{h}$	$\bar{\imath}$	*l*
4	7	1	20.2	>	16.2	$\bar{4}$	11	1
6	4	1	12.9	<	16.6	$\bar{6}$	10	1
6	5	1	15.3	>	10.7	$\bar{6}$	11	1
1	3	2	15.0	<	17.9	$\bar{1}$	4	2
1	10	2	9.3	<	11.9	$\bar{1}$	11	2
2	2	2	19.8	<	24.3	$\bar{2}$	4	2
2	8	2	13.9	<	15.4	$\bar{2}$	10	2
3	1	2	15.2	<	18.0	$\bar{3}$	4	2
3	2	2	17.8	<	20.9	$\bar{3}$	5	2
4	6	2	6.1	<	10.2	$\bar{4}$	10	2
7	4	2	21.0	>	17.1	$\bar{7}$	11	2
9	2	2	13.5	<	16.2	$\bar{9}$	11	2
1	1	3	29.8	<	36.2	$\bar{1}$	2	3
5	5	3	19.7	<	23.6	$\bar{5}$	10	3
4	7	4	10.3	>	6.5	$\bar{4}$	11	4
6	4	4	13.3	<	16.5	$\bar{6}$	10	4
6	5	4	16.8	>	12.8	$\bar{6}$	11	4
4	6	5	6.9	<	10.2	$\bar{4}$	10	5
5	6	5	11.8	>	8.9	$\bar{5}$	11	5
7	4	5	13.0	>	9.6	$\bar{7}$	11	5

In the least-squares refinement the function minimized was $\sum w(|F_o|-k|F_c|)^2$, and the weighting scheme was $w=(10+|F_o|+0.01|F_o|^2)^{-1}$.[8] The final shift in the atomic parameters of the nonhydrogen atoms averaged 0.05σ with the maximum of 0.26σ. Atomic scattering factors for Cu, Co, O, N, C_{val}, and H, and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$ for Cu

TABLE 4. FRACTIONAL POSITIONAL PARAMETERS ($\times 10^3$) AND ISOTROPIC TEMPERATURE FACTORS OF HYDROGEN ATOMS (The average of estimated standard deviations of the isotropic temperature factors is 1.4.)

Atom	*X*	*Y*	*Z*	*B*
H(O4)	169(7)	245(7)	−252(7)	4.5
H(O4)′	182(7)	157(7)	−243(7)	4.4
H(O5)	−58(11)	−17(17)	165(30)	3.1
H(O5)′	−143(10)	−63(11)	59(10)	1.9
H(C3)	−20(8)	460(8)	−32(7)	5.3
H(C4)	75(6)	656(6)	0(6)	2.8
H(C5)	276(5)	745(5)	−1(5)	1.3
H(C8)	461(6)	736(6)	2(5)	2.7
H(C9)	639(6)	730(6)	108(5)	3.1
H(C9)′	667(8)	766(8)	−54(7)	5.9

TABLE 3. FRACTIONAL POSITIONAL PARAMETERS AND ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$) OF NON-HYDROGEN ATOMS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

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

Atom	*X*	*Y*	*Z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	4520(1)	4520(1)	0	32(1)	32(1)	83(1)	5(1)	−2(1)	2(1)
Co	2165(2)	2165(2)	0	32(1)	32(1)	83(1)	17(1)	−1(1)	1(1)
O(1)	2844(3)	4000(3)	41(4)	36(3)	25(3)	113(5)	13(3)	13(3)	14(3)
O(2)	550(3)	2014(4)	211(4)	30(3)	32(3)	112(5)	10(3)	−1(3)	7(3)
O(3)	−891(4)	2403(4)	−240(4)	36(3)	51(4)	107(4)	20(3)	−8(3)	−4(4)
O(4)	2066(5)	2199(5)	−2139(5)	76(4)	79(5)	103(5)	50(4)	−17(4)	−1(4)
O(5)	−943(9)	−482(9)	807(9)	60(9)	78(10)	106(10)	20(8)	−18(8)	7(8)
N	5026(5)	6196(4)	77(4)	55(5)	36(4)	61(4)	11(3)	−5(4)	−3(3)
C(1)	174(5)	2747(5)	−36(5)	38(4)	46(5)	71(6)	29(4)	−4(4)	−4(4)
C(2)	1034(5)	4087(6)	−28(5)	63(6)	51(5)	56(5)	36(5)	1(5)	−13(4)
C(3)	521(7)	4807(6)	−58(6)	75(6)	63(6)	78(6)	49(5)	0(5)	−1(5)
C(4)	1169(6)	6045(6)	−38(7)	83(7)	41(5)	97(6)	34(5)	−8(5)	−10(5)
C(5)	2408(8)	6608(6)	16(6)	122(8)	34(5)	85(6)	42(5)	−15(6)	−11(5)
C(6)	2999(6)	5927(5)	29(5)	82(6)	42(5)	57(5)	34(5)	12(5)	11(4)
C(7)	2310(5)	4639(5)	−4(5)	43(5)	28(4)	62(5)	17(4)	−1(4)	−4(4)
C(8)	4262(6)	6585(5)	62(5)	60(5)	34(4)	59(6)	13(4)	5(5)	−1(4)
C(9)	6323(6)	7001(6)	171(7)	48(6)	54(6)	103(7)	5(5)	−9(5)	−2(5)

and Co, were taken from International Tables for X-Ray Crystallography.⁹⁾ The final difference Fourier map showed no important features, the highest peak being 0.3 e/Å^3.

The final positional and thermal parameters with their estimated standard deviations are given in Tables 3 and 4.***

The calculations were carried out at the Computer Center of Kyushu University, by the use of the UNICS-II program system.

Description of the Structure and Discussion

The molecular structure obtained is shown in Fig. 1. As has been expected, the molecule is a binuclear complex in which two metal atoms (M_1 and M_2) are coordinated by fsaen^{4-}. Metal atoms, M_1 and M_2, lie on the twofold axis. The molecule has the C_2 symmetry on this twofold axis. The "inside" metal atom, M_1, is coordinated by two nitrogen atoms of the ethylenediamine and two phenolic oxygen atoms in the typical square-planar manner. The "outside" metal atom, M_2, is octahedrally coordinated by two equatorial carboxyl oxygen atoms, two equatorial phenolic oxygen atoms, and two axial water oxygen atoms. Therefore, we can conclude that M_1=Cu and M_2=Co, since no alternative assignment is compatible with the magnetic and spectral properties as were already discussed in the previous paper.³⁾ The bond distances and angles with their estimated standard deviations are listed in Tables 5 and 6, respectively. Some least-squares planes with the deviations of atoms from the planes are given in Table 7. The Cu–O distance (1.909(5) Å) and the Cu–N distance (1.915(6) Å) are of the normal in-plane coordination. The Co–O distance (2.065(4) Å) of the bridging oxygen atom is slightly longer than that (1.995(5) Å) of the terminal oxygen atom. This relation had also been observed in the structures of some other binuclear complexes with Schiff bases.¹⁰⁻¹²⁾ As seen in Table 5, the Co–O(1) distance is considerably longer than the Cu–O(1) distance. This is consistent with a fact that Co–O distances are generally longer than Cu–O ones.¹³⁾ The axial Co–O distance (2.137(5) Å) is somewhat longer than that of the in-plane coordination. As seen in Table 6, the in-plane O–Co–O angles considerably deviate from right angle (77.1(2), 86.2(2), and 110.7(2)°), whereas the apical O–Co–basal O angles are 86.6(2), 89.5(2), and 92.2(2)°. As seen in Table 7, four coordinating atoms around the copper atom are almost coplanar with the deviations within ±0.02 Å. On the other hand, four equatorial atoms around the cobalt atom deviate from the mean plane by ±*ca.* 0.07 Å and show a slight distortion toward the tetrahedron. Accordingly the coordination geometry about

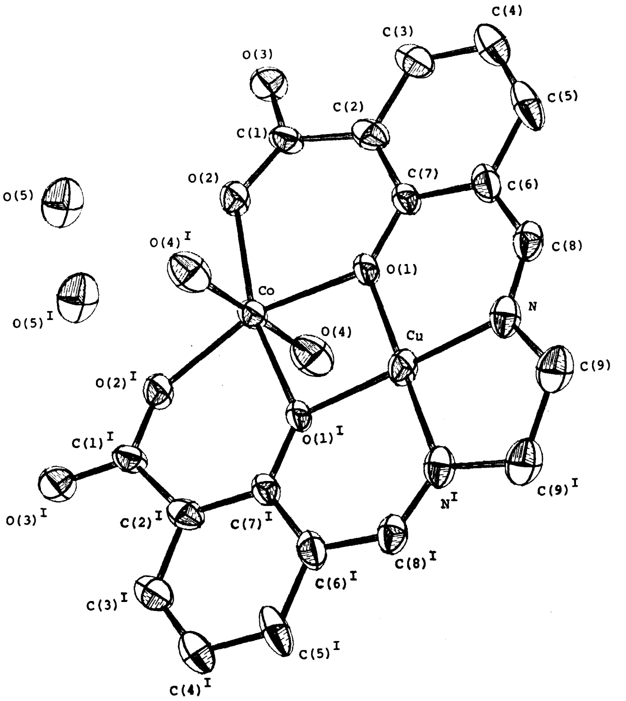


Fig. 1. Molecular structure of CuCO(fsaen)·3H_2O with thermal ellipsoids.

TABLE 5. INTERATOMIC DISTANCES (*l*/Å) IN THE MOLECULE OF CuCo(fsaen)·3H_2O
The standard deviations are given in parentheses.

Cu–Co	3.025(2)	N–C(9)	1.460(8)
Cu–O(1)	1.909(5)	C(1)–C(2)	1.511(8)
Cu–N	1.915(6)	C(2)–C(3)	1.378(13)
Co–O(1)	2.065(4)	C(3)–C(4)	1.378(10)
Co–O(2)	1.995(5)	C(4)–C(5)	1.381(11)
Co–O(4)	2.137(5)	C(5)–C(6)	1.414(14)
O(1)–C(7)	1.307(9)	C(6)–C(7)	1.435(8)
O(2)–C(1)	1.279(10)	C(2)–C(7)	1.424(9)
O(3)–C(1)	1.226(8)	C(6)–C(8)	1.406(10)
N–C(8)	1.305(11)	C(9)–C(9)^{I}	1.548(14)

I) y, x, −z.

TABLE 6. BOND ANGLES (*ψ*/°) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

O(1)–Cu–O(1)^{I}	84.7(2)	O(2)–C(1)–O(3)	122.1(5)
O(1)–Cu–N	94.7(2)	O(2)–C(1)–C(2)	120.5(5)
N–Cu–N^{I}	85.9(3)	O(3)–C(1)–C(2)	117.4(7)
O(1)–Co–O(1)^{I}	77.1(2)	C(1)–C(2)–C(3)	116.2(6)
O(1)–Co–O(2)	86.2(2)	C(1)–C(2)–C(7)	124.8(7)
O(2)–Co–O(2)^{I}	110.7(2)	C(3)–C(2)–C(7)	119.0(6)
O(1)–Co–O(4)	89.5(2)	C(2)–C(3)–C(4)	123.9(7)
O(1)^{I}–Co–O(4)	92.2(2)	C(3)–C(4)–C(5)	118.5(9)
O(2)–Co–O(4)	92.2(2)	C(4)–C(5)–C(6)	120.7(6)
O(2)^{I}–Co–O(4)	86.6(2)	C(5)–C(6)–C(7)	120.0(6)
O(4)–Co–O(4)^{I}	177.8(2)	C(5)–C(6)–C(8)	116.3(6)
Cu–O(1)–Co	99.1(2)	C(7)–C(6)–C(8)	123.7(8)
Cu–O(1)–C(7)	129.3(3)	O(1)–C(7)–C(2)	121.5(5)
Co–O(1)–C(7)	131.4(3)	O(1)–C(7)–C(6)	120.6(6)
Co–O(2)–C(1)	131.7(3)	C(2)–C(7)–C(6)	117.8(7)
Cu–N–C(8)	122.2(4)	C(6)–C(8)–N	129.3(6)
Cu–N–C(9)	115.1(6)	N–C(9)–C(9)^{I}	110.6(6)
C(8)–N–(C(9)	122.7(6)		

I) y, x, −z.

*** A list of structure factors has been deposited with the Chemical Society of Japan as a Document No. 7836.

TABLE 7. ANALYSIS OF MEAN PLANES
(Daviations from planes (l/Å))

I. Plane through O(1), N, $\mathrm{O(1)^{I}}$, and $\mathrm{N^{I}}$
(Copper coordination sphere)
$0.0228X-0.0395Y+0.9990Z=0.0000$ a)

Cu	0.000	$\mathrm{O(1)^{I}}$	0.018
O(1)	−0.018	$\mathrm{N^{I}}$	−0.017
N	0.017		

II. Plane through O(1), O(2), $\mathrm{O(1)^{I}}$, and $\mathrm{O(2)^{I}}$
(Cobalt coordination sphere)
$0.0459X-0.0795Y+0.9958Z=0.0000$ a)

Co	0.000	$\mathrm{O(1)^{I}}$	0.077
O(1)	−0.077	$\mathrm{O(2)^{I}}$	−0.060
O(2)	0.060		

III. Plane through C(2), C(3), C(4), C(5), C(6), and C(7)
(Benzene ring)
$-0.0302X-0.0005Y+0.9995Z=-0.0755$ a)

C(2)	0.010	C(5)	0.007
C(3)	−0.003	C(6)	0.000
C(4)	−0.005	C(7)	−0.009

IV. Plane through Cu, Co, O(1), O(2), O(3), N, C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), $\mathrm{O(1)^{I}}$, $\mathrm{O(2)^{I}}$, $\mathrm{O(3)^{I}}$, $\mathrm{N^{I}}$, $\mathrm{C(1)^{I}}$, $\mathrm{C(2)^{I}}$, $\mathrm{C(3)^{I}}$, $\mathrm{C(4)^{I}}$, $\mathrm{C(5)^{I}}$, $\mathrm{C(6)^{I}}$, $\mathrm{C(7)^{I}}$, $\mathrm{C(8)^{I}}$, and $\mathrm{C(9)^{I}}$
(CuCo(fsaen) moiety)
$-0.0022X+0.0039Y+1.0000Z=0.0000$ a)

Cu	0.000		
Co	0.000		
O(1)	0.047	$\mathrm{O(1)^{I}}$	−0.047
O(2)	0.218	$\mathrm{O(2)^{I}}$	−0.218
O(3)	−0.223	$\mathrm{O(3)^{I}}$	0.223
N	0.083	$\mathrm{N^{I}}$	−0.083
C(1)	−0.023	$\mathrm{C(1)^{I}}$	0.023
C(2)	−0.013	$\mathrm{C(2)^{I}}$	0.013
C(3)	−0.037	$\mathrm{C(3)^{I}}$	0.037
C(4)	−0.014	$\mathrm{C(4)^{I}}$	0.014
C(5)	0.037	$\mathrm{C(5)^{I}}$	−0.037
C(6)	0.043	$\mathrm{C(6)^{I}}$	−0.043
C(7)	0.008	$\mathrm{C(7)^{I}}$	−0.008
C(8)	0.073	$\mathrm{C(8)^{I}}$	−0.073
C(9)	0.174	$\mathrm{C(9)^{I}}$	−0.174
O(4)	−2.130	$\mathrm{O(4)^{I}}$	2.130
O(5)	0.807	$\mathrm{O(5)^{I}}$	−0.807

I) y, x, −z. a) Equations have the form $AX+BY+CZ=D$ where X, Y, and Z are Cartersian axes lying along $\boldsymbol{a}\times\boldsymbol{c}^*$, $\boldsymbol{b}$, and $\boldsymbol{c}^*$, respectively.

the cobalt atom evidently deviates from a regular octahedron, so that the orbital degeneracy of the ground state ($^4\mathrm{T}_{1g}$) in $\mathrm{O_h}$ symmetry is removed. The first excited state may possibly be thermally nonaccessible, thereby the cryomagnetic behavior of $\mathrm{CuCo(fsaen)\cdot 3H_2O}$ being expressed by the Van Vleck equation based on the Heisenberg model with $S_1=1/2$ and $S_2=3/2$.

The unit cell contains three binuclear molecules and three uncoordinated crystal water molecules. The carboxyl oxygen O(3) and the water oxygen O(4) coordinated to the cobalt atom of the adjacent molecule are hydrogen-bonded and the O(3)···O(4) distance is 2.699(8) Å. The crystal water is in the vicinity of the carboxyl oxygen O(2) by hydrogen bonding with the O(5)···O(2) distance of 2.86(1) Å. The absolute configuration of the packing is that of a left-handed helical sequence of molecules, the axis of the helix being the c axis. Each binuclear molecule points its "outside" moiety toward the inside of the helix in which the crystal water molecules are housed.

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