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Registry No. $[Cu(cyclops)CN]^{-}\cdot CH_3OH$, 74282-49-8; $[Cu(cyclops)H_2O](ClO_4)$, 70178-69-7.

Supplementary Material Available: Table V, a listing of structure factor amplitudes (×10) for $[Cu(cyclops)CN]\cdot CH_3OH$ (7 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of $CuCo(fsa)_2en\cdot 6H_2O$ ($H_4(fsa)_2en$ = *N*,*N'*-Bis(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane): An Example of Close-Packed Association of Two Heterobinuclear Units through the Formation of a Water Molecule Network

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The crystal structure of $CuCo(fsa)_2en\cdot 6H_2O$, one member of the wide series $MM'L\cdot X$ (M, M' = transition element, L = $H_4(fsa)_2en$, X = H_2O, CH_3OH) was determined by the X-ray single-crystal diffraction method. It crystallizes in the orthorhombic space group *Pbca* with a = 20.549 (5) Å, b = 15.948 (4) Å, c = 13.307 (5) Å, V = 4.360.9 (1) Å^3, ρ_{exptl} = 1.76 (1) g/cm^3, and Z = 8. The structure was solved by direct methods and refined by full-matrix least squares to a conventional R of 0.050 for 3623 reflections with $I > 2.5\sigma(I)$. The copper atom, coordinated by two nitrogen atoms and two phenolic oxygen atoms in a square-planar manner, occupies the "inside" site of the molecule, a water molecule being above at 2.784 Å; the cobalt atom in the "outside" site, coordinated to four oxygen atoms and one water molecule, has square-pyramidal coordination. Two molecules related by a symmetry center are packed together, forming a tetramer $[CuCo(fsa)_2en\cdot H_2O]_2$ in which the two transition metals occupy the center of octahedra sharing edges and corners. Such units are encapsulated in a three-dimensional network of water molecules. The title complex exhibits some unusual structural features in the series $MM'L\cdot X$.

Introduction

Whereas the study of homobinuclear complexes with paramagnetic metallic centers is still a very active field in inorganic chemistry, the study of heterobinuclear complexes takes on increasing importance. Such complexes have already led to a more advanced understanding of the mechanism of exchange interaction. In this respect, the most striking result is likely the strict orthogonality of the magnetic orbitals centered on the metallic centers, which was realized in a $Cu^{II}VO^{II}$ complex.[2] An identical situation was obtained in a $Co^{II}Cu^{II}$ complex.[3] Among the bichelating ligands used to obtain heterobinuclear complexes,[4-6] the ligand noted $(fsa)_2en^{4-}$ derived from the Schiff base *N*,*N'*-bis(2-hydroxy-3-carbobenzylidene)-1,2-diaminoethane seems to be the one having the greatest versatility. This ligand was used for the first time by Okawa et al.[7] and was used since by several groups.[8-16]

The synthesis of new heterobinuclear complexes, the determination of their crystal and molecular structure, and then the investigation of their magnetic properties are the three cornerstones of the study of the *interaction in heterobinuclear complexes*. The knowledge of the structure is often necessary and always useful to interpret the magnetic properties; it can also sometimes have a great importance in itself when this structure reveals some quite unusual features. Such is the case for the structure described in this paper. Attempting to recrystallize from a methanolic solution the complex $CoCu(fsa)_2en\cdot 3H_2O$, the structure of which was recently published,[17] we noticed that in some specific conditions, in addition to the starting material, a new compound of formula $CuCo(fsa)_2en\cdot 6H_2O$ was obtained. It was of interest to compare its structure to that of $CuCo(fsa)_2en\cdot 3H_2O$. These two structures appeared to be very different. The Co(II) ion in the outside site of the new complex has a fivefold coordination

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Table I

1. Physical and Crystallographic Data

formula: $CuCoN_2O_6C_{18}H_{12}\cdot 6H_2O$
mol wt: 582.88
cryst system: orthorhombic
space group: *Pbca*
$a = 20.549$ (5) Å
$V = 4360.9$ (1) Å^3
$b = 15.948$ (4) Å
$Z = 8$
$c = 13.307$ (5) Å
$F(000) = 2384$

$\rho_{\text{exptl}} = 1.76$ (1) g/cm^3, $\rho_X = 1.77$ g/cm^3
abs factor: $\mu_{\lambda(\text{Mo})} = 18.75$ cm^{-1}
morphology: parallelepiped 0.0048 × 0.0107 × 0.0155 cm
min and max abs cor: 0.585 and 0.839

2. Data Collection

temp: 293 K
radiatn: molybdenum, $\lambda(K\overline{\alpha}) = 0.710\ 69$ Å
monochromatizatn: oriented graphite cryst
cryst–detector dist: 208 mm
detector window: height* = 4 mm, width* = 4 mm
takeoff angle*: 4.5°
scan mode: θ,θ
max Bragg angle: 25°
scan angle: $\Delta\theta = (\Delta\theta_0 + B \tan\theta)°$, $\Delta\theta_0{}^* = 1.10°$, $B^* = 0.347$
values determining the scan speed: SIGPRE* = 0.66, SIGMA* = 0.018, VPRE* = 6.7°/min, TMAX* = 80 s
controls (reflctns) periodicity: intensity (800, 006, 562) 3600 s; orientation (325, 453) 100 reflctns

3. Conditions for Refinement

reflctns for the refinement of the cell dimens: 25
recorded reflctns: 4287
independent reflctns: 3623
utilized reflctns: 1552 with $I > 2.5\sigma(I)$
refined parameters: 308
reliability factors: $R = \Sigma \lvert k\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma k\lvert F_o\rvert = 0.0504$; $R_w = [\Sigma w^2(k\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w^2k^2F_o{}^2]^{1/2} = 0.0593$ (with $w = 4F_o{}^2/\sigma^2(F_o)^2$.

instead of a sixfold coordination in the previously investigated complex. Moreover, and this is not the least difference, the packing of molecules in $CuCo(fsa)_2en\cdot 6H_2O$ reveals a rather unusual situation: the molecules $CuCo(fsa)_2en\cdot H_2O$ are very closely packed two by two through the operation of the symmetry center in such a way that they form tetrameric entities, the planes of the organic skeletons remaining essentially parallel. This seems to be correlated with a squeezing effect of the three-dimensional network developed by the noncoordinated water molecules.

Experimental Section

Synthesis. $CuCo(fsa)_2en\cdot 3H_2O$ was synthesized according to ref 8 under the form of a polycrystalline powder. The X-ray powder diagram confirmed that this compound crystallizes with the structure recently determined.[17] $CuCo(fsa)_2en\cdot 3H_2O$ was then dissolved in methanol containing a few drops of water. The very slow evaporation of the solvent led to a large majority of well-formed single crystals of $CuCo(fsa)_2en\cdot 3H_2O$ and a few percent of well-formed crystals of $CuCo(fsa)_2en\cdot 6H_2O$.

Analysis. A direct analysis on the crystal which served for the present structural determination was performed by microprobe analysis. The simultaneous presence of copper and cobalt was unambiguously determined.

A blue-black single crystal of $CuCo(fsa)_2en\cdot 6H_2O$ having prismatic shape has been selected (Table I). The preliminary X-ray study was conducted by photographic methods using a Weissenberg camera and Ni-filtered Cu Kα radiation. Approximate unit cell parameters and systematic absences for the reflections were derived from *hk*0, *hk*1, and *hk*2 sets of photographic data.

The density calculated for eight molecules agrees well with the value obtained by the flotation method. Experimental data are tabulated in Table I.

The specimen was then mounted on a CAD4 Enraf-Nonius PDP8/M computer controlled single-crystal diffractometer, and the unit cell was refined by optimizing the settings of 25 reflections (Mo Kα radiation).

The intensities of selected reflections ($I > 2.5\sigma(I)$) were corrected for Lorentz and polarization factors, and absorption corrections were applied.

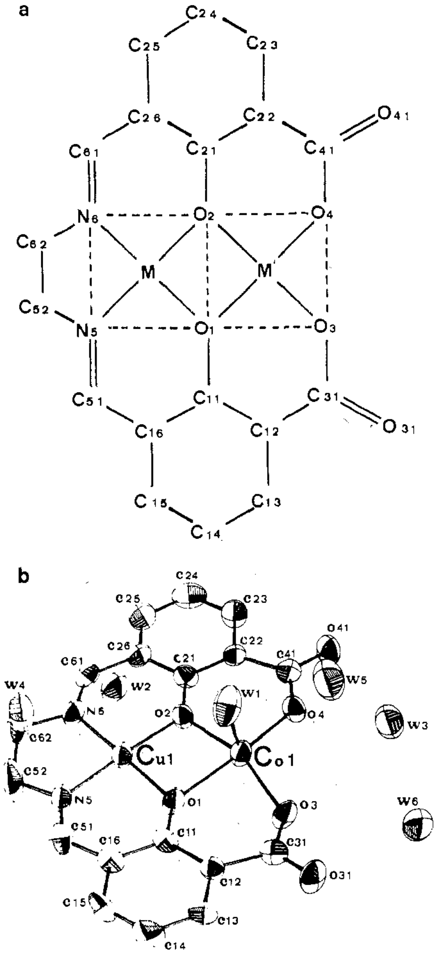

Figure 1.

Atomic scattering factors of Cromer and Waber for the nonhydrogen atoms and those of Stewart, Davidson, and Simpson for the spherical hydrogen atoms were used. Real and imaginary dispersion corrections given by Cromer were applied for copper and cobalt atoms.

Direct methods were used to solve the structure (MULTAN 72). In a first step, the program yielded the positions of Cu, Co, and their immediate environment; the carbon and oxygen atoms of the ligand were located by Fourier synthesis. The structure was then refined by full-matrix least-squares techniques. A difference Fourier map and a priori calculations made it possible for the positions of the hydrogen atoms to be determined. All nonhydrogen atoms were then allowed to refine with anisotropic thermal parameters and a fixed, isotropic thermal parameter of $B_H = 1.2B_{eq}(C)$ Å^2 as assigned to the hydrogen atoms ($B_{eq}(C)$ is the isotropic equivalent temperature factor of the carbon to which the hydrogen is bonded; $B_{eq}(C) = {}^4/_3\sum_{ij}(\vec{a}_i\cdot\vec{a}_i)\beta_{ij}$). A difference Fourier map showed then no peaks greater than 0.2 e Å^{-3} even around the oxygen atoms of the water molecules.

In addition to local programs CAD4-CICT10 LEGROS and AUSSOLEIL, the following ones were used on the CICT CII Iris 80 system: Zalkin's FOURIER; Germain's MULTAN; Ibers and Doeden's NUCLS; Busing, Martin and Levy's ORFFE; Johnson's ORTEP.

Results and Discussion of the Structure

Final atomic coordinates and anisotropic temperature factors corresponding to the factor $R = 0.0504$ are given in Table II. The interatomic distances and angles are listed in Table III. In Table IV, the system for convenient labeling of atoms following symmetry rules of the space group is indicated.

The asymmetric unit cell contains one molecule of the compound $CuCo(fsa)_2en\cdot H_2O$ and five water molecules of crystallization (Table V).

Figure 1 shows a perspective view of the whole molecule (without hydrogen atoms) and labeled schematic representa-

Table II. Positional and Thermal Parameters for the Atoms of $CuCo(fsa)_2en{\cdot}6H_2O$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	0.425 777 (73)	0.592 999 (93)	0.100 52 (13)	14.13 (38)	24.99 (69)	83.6 (15)	1.77 (48)	−0.84 (72)	−0.82 (97)
Co(1)	0.556 768 (77)	0.522 00 (10)	0.133 82 (15)	13.19 (41)	21.34 (75)	85.7 (17)	−0.08 (51)	4.74 (76)	1.6 (11)
O(1)	0.464 08 (35)	0.485 27 (46)	0.108 16 (71)	15.5 (21)	15.7 (34)	104.7 (92)	−0.8 (23)	6.9 (36)	5.8 (50)
O(2)	0.512 86 (35)	0.629 40 (45)	0.103 43 (70)	13.4 (22)	21.7 (36)	70.8 (83)	−0.8 (23)	−3.2 (38)	4.8 (46)
O(3)	0.579 76 (36)	0.404 48 (47)	0.120 42 (66)	17.6 (22)	18.6 (35)	94.0 (86)	−0.8 (25)	13.4 (40)	4.0 (53)
O(4)	0.640 68 (34)	0.578 40 (49)	0.119 96 (66)	13.5 (21)	29.4 (41)	64.2 (78)	−5.5 (23)	0.7 (34)	7.8 (47)
O(31)	0.575 67 (42)	0.272 87 (48)	0.165 73 (72)	21.3 (25)	22.0 (40)	106.3 (97)	4.8 (27)	2.4 (43)	19.2 (50)
O(41)	0.713 43 (38)	0.677 34 (52)	0.099 35 (74)	13.6 (23)	41.3 (47)	102.0 (10)	−4.8 (26)	4.3 (44)	2.8 (57)
N(5)	0.340 28 (45)	0.550 92 (64)	0.095 82 (95)	13.4 (28)	26.8 (51)	79.0 (11)	3.1 (30)	2.9 (48)	2.9 (64)
N(6)	0.389 88 (49)	0.701 32 (61)	0.086 02 (86)	18.8 (31)	21.5 (51)	71.0 (11)	5.6 (32)	0.6 (48)	1.1 (62)
C(11)	0.436 38 (55)	0.413 87 (76)	0.129 11 (78)	16.3 (34)	37.4 (63)	5.6 (77)	−4.8 (41)	0.1 (44)	3.1 (68)
C(12)	0.474 04 (56)	0.340 64 (73)	0.146 9 (10)	15.5 (34)	23.7 (58)	41.0 (11)	−3.1 (36)	0.3 (54)	0.8 (68)
C(13)	0.443 24 (63)	0.265 92 (74)	0.166 1 (10)	21.0 (39)	25.1 (61)	63.0 (13)	−3.5 (39)	−0.3 (59)	−3.2 (66)
C(14)	0.377 39 (68)	0.259 15 (84)	0.166 5 (12)	25.0 (44)	25.3 (66)	82.0 (14)	−9.2 (44)	−3.8 (67)	14.8 (77)
C(15)	0.339 44 (58)	0.328 27 (89)	0.147 2 (11)	14.0 (37)	46.5 (81)	61.0 (13)	−10.9 (42)	−0.2 (56)	8.0 (85)
C(16)	0.368 56 (57)	0.407 55 (79)	0.128 97 (80)	18.3 (34)	38.6 (65)	9.2 (86)	−4.0 (40)	0.0 (44)	5.1 (73)
C(21)	0.536 25 (59)	0.705 93 (78)	0.093 6 (11)	18.6 (38)	23.8 (60)	51.0 (12)	−3.2 (38)	−3.5 (55)	6.1 (76)
C(22)	0.603 30 (59)	0.720 71 (76)	0.092 5 (11)	16.1 (34)	20.7 (55)	66.0 (12)	−1.0 (35)	0.2 (56)	−5.6 (73)
C(23)	0.625 62 (62)	0.804 89 (80)	0.082 3 (12)	20.7 (40)	24.4 (65)	101.0 (16)	−4.9 (39)	2.2 (64)	7.5 (84)
C(24)	0.582 73 (80)	0.869 50 (82)	0.071 6 (13)	37.8 (59)	24.9 (63)	103.0 (17)	−10.7 (52)	−1.1 (81)	−2.3 (77)
C(25)	0.516 36 (72)	0.855 23 (85)	0.069 1 (13)	26.2 (46)	30.8 (66)	97.0 (17)	1.8 (44)	−5.6 (69)	−3.1 (81)
C(26)	0.492 83 (62)	0.774 56 (73)	0.082 3 (11)	20.3 (38)	22.0 (57)	74.0 (14)	2.2 (39)	−0.7 (60)	−6.4 (71)
C(31)	0.547 89 (62)	0.338 99 (81)	0.143 6 (10)	19.4 (39)	28.9 (61)	36.0 (11)	−5.2 (40)	5.5 (57)	2.3 (73)
C(41)	0.655 60 (63)	0.655 61 (81)	0.107 3 (11)	18.7 (37)	30.2 (65)	57.0 (13)	−2.2 (40)	−0.3 (61)	−4.3 (77)
C(51)	0.323 73 (58)	0.476 21 (91)	0.108 51 (98)	17.0 (34)	44.1 (74)	48.0 (12)	1.1 (46)	1.6 (53)	10.0 (95)
C(52)	0.293 66 (65)	0.617 2 (10)	0.070 5 (17)	14.3 (39)	48.6 (96)	247.0 (27)	9.9 (47)	−10.2 (83)	20.0 (13)
C(61)	0.422 32 (70)	0.766 68 (77)	0.079 4 (11)	23.0 (41)	22.1 (59)	72.0 (14)	7.2 (43)	−4.3 (64)	−6.6 (69)
C(62)	0.318 72 (67)	0.699 67 (92)	0.087 3 (13)	16.5 (37)	39.0 (78)	127.0 (18)	11.6 (44)	−18.4 (71)	−4.0 (10)
W(1)	0.541 87 (40)	0.531 20 (63)	0.287 43 (67)	27.0 (29)	64.3 (56)	60.8 (77)	14.0 (32)	10.6 (39)	16.6 (57)
W(2)	0.424 68 (40)	0.604 91 (50)	0.309 24 (73)	21.0 (25)	29.9 (41)	111.3 (91)	−0.2 (28)	7.7 (44)	−8.5 (52)
W(3)	0.721 64 (40)	0.462 30 (59)	0.219 23 (72)	23.2 (27)	52.5 (54)	89.1 (91)	1.1 (31)	−8.1 (42)	3.7 (56)
W(4)	0.307 26 (37)	0.554 66 (56)	0.403 97 (75)	15.1 (24)	49.5 (49)	109.0 (10)	2.8 (27)	2.6 (42)	14.7 (57)
W(5)	0.643 30 (43)	0.471 20 (66)	0.396 48 (75)	25.6 (28)	86.9 (68)	83.0 (10)	6.6 (38)	−8.1 (42)	−2.9 (72)
W(6)	0.706 43 (42)	0.296 18 (56)	0.190 78 (80)	23.8 (29)	44.9 (53)	111.0 (10)	0.7 (30)	1.8 (45)	−9.0 (60)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(113)	0.469	0.216	0.179	4.2	H(151)	0.277	0.463	0.105	4.2
H(114)	0.357	0.205	0.179	5.1	H(152)	0.279	0.611	0.003	6.5
H(115)	0.292	0.324	0.144	4.6	H(252)	0.255	0.609	0.116	6.5
H(123)	0.673	0.814	0.082	5.2	H(161)	0.400	0.819	0.072	4.5
H(124)	0.599	0.928	0.068	5.8	H(162)	0.302	0.735	0.037	6.3
H(125)	0.487	0.900	0.058	5.5	H(262)	0.304	0.718	0.154	6.3

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. The form of the anisotropic thermal ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^4$.

Table III. Notation of Equivalent Positions in the Space Group *Pbca*[a]

(1) x, y, z	55501	(5) $\bar{x}, \bar{y}, \bar{z}$	55505
(2) $^1/_2 + x, {}^1/_2 - y, \bar{z}$	55502	(6) $^1/_2 - x, {}^1/_2 + y, z$	55506
(3) $\bar{x}, {}^1/_2 + y, {}^1/_2 - z$	55503	(7) $x, {}^1/_2 - y, {}^1/_2 + z$	55507
(4) $^1/_2 - x, \bar{y}, {}^1/_2 + z$	55504	(8) $^1/_2 + x, y, {}^1/_2 - z$	55508

[a] The two last numbers in the five-digit number specify the symmetry operations (1-8). The three first digits specify unit cell translation along *a*, *b*, and *c* with 5 added to each digit.

tion of $MM'(fsa)_2en$ (MM' being possibly Mg, VO, Mn, Fe, Co, Ni, Cu, Zn, Cd, and UO_2).[2,3,7-17]

The ligand part of this binuclear complex exhibits features very similar to those of $CuVO(fsa)_2en{\cdot}CH_3OH$[2] and $Cu_2(fsa)_2en{\cdot}CH_3OH$[16] studied by Galy, Kahn, et al., $CuCo(fsa)_2en{\cdot}3H_2O$ studied by Mikurita et al.,[17] and $CuMg(fsa)_2en$ determined by Beale et al.[15]

In the present compound $CuCo(fsa)_2en{\cdot}6H_2O$, the copper atom, in square-planar coordination, occupies the "inside" M site; there is a water molecule W(2), above the square-planar N(5)N(6)O(1)O(2), but the distance Cu–W(2) = 2.784 Å, rather important, does not imply a Cu–O bond, such a fact being also supported by the negligible displacement of the copper out of the plane (0.031 Å) and the value of the sum of the four bond angles around Cu, i.e., 359.9° (Table VI). Such a coordination for Cu is very close to the one found in $Cu_2(fsa)_2en{\cdot}CH_3OH$ for the copper atom occupying the M′ site (Cu(2)).[16]

The cobalt atoms in the "outside" M′ site has a fivefold coordination, the atoms O(1)O(2)O(3)O(4) and W(1) being at the apex; such a coordination occurs also for copper in the site Cu(1) in $Cu_2(fsa)_2en{\cdot}CH_5OH$. The bond length Co–W(1) = 2.072 Å is only slightly longer than the other Co–O bonds, and it should be noticed that Co is 0.268 Å above the square plane of oxygens.

Finally, the part of the structure directly concerned with the metal atoms consists of a planar square CuN_2O_2 and a square pyramid CoO_4W sharing an edge O(1)O(2). The short O(1)O(2) interatomic distance and the O(1)CuO(2) and O(1)CoO(2) angles (<90°) indicate that there is no direct metal–metal interaction.

At the level of copper coordination, it can be noticed that this structure exhibits Cu–O and Cu–N bond lengths slightly smaller than the ones found in $CuCo(fsa)_2en{\cdot}3H_2O$[17] and $CuMg(fsa)_2en{\cdot}3H_2O$[15] but very similar to the ones already determined in our compound $CuCu(fsa)_2en{\cdot}CH_3OH$.[16] Such a fact (a shortening of the bond length) could be related with the presence of a close water molecule above the copper atom in the compounds. For the cobalt atom which is fivefold coordinated in the title compound, bond lengths are similar with sixfold coordinated cobalt in $CuCo(fsa)_2en{\cdot}3H_2O$, the biggest change affecting the bond angle O(3)CoO(4).

Table IV[a]

Bond Lengths (Å)			
Cu(1)-O(1)	1.893 (4)	Cu(1)-O(2)	1.882 (4)
Cu(1)-N(5)	1.882 (5)	Cu(1)-N(6)	1.888 (5)
Cu(1)-W(2)	2.784 (5)	Cu(1)-O(3′)	2.942 (5)
Co(1)-O(1)	2.022 (4)	Co(1)-O(2)	1.978 (4)
Co(1)-O(3)	1.941 (4)	Co(1)-O(4)	1.954 (4)
Co(1)-W(1)	2.072 (5)	Co(1)-O(1′)	3.250 (5)
O(1)-O(2)	2.508 (5)	O(1)-O(3)	2.709 (5)
O(1)-N(5)	2.756 (4)	O(1)-C(11)	1.303 (8)
O(2)-O(4)	2.758 (5)	O(2)-N(6)	2.785 (8)
O(2)-C(21)	1.318 (8)	O(3)-O(4)	3.043 (6)
N(5)-N(6)	2.609 (7)	C(11)-C(12)	1.421 (7)
C(12)-C(13)	1.373 (6)	C(13)-C(14)	1.357 (8)
C(14)-C(15)	1.374 (7)	C(15)-C(16)	1.419 (8)
C(16)-C(11)	1.397 (7)	C(21)-C(22)	1.398 (8)
C(22)-C(23)	1.425 (7)	C(23)-C(24)	1.364 (9)
C(24)-C(25)	1.383 (7)	C(25)-C(26)	1.386 (9)
C(26)-C(21)	1.420 (7)	O(3)-C(31)	1.271 (7)
C(12)-C(31)	1.518 (7)	C(31)-O(31)	1.234 (8)
O(4)-C(41)	1.280 (7)	C(22)-C(41)	1.507 (8)
C(41)-O(41)	1.242 (8)	C(16)-C(51)	1.457 (8)
C(26)-C(61)	1.455 (7)	C(51)-N(5)	1.251 (9)
C(61)-N(6)	1.241 (8)	N(5)-C(52)	1.466 (9)
N(6)-C(62)	1.463 (7)	C(52)-C(62)	1.430 (8)
Bond Angles (Deg)			
N(5)-Cu(1)-O(2)	176.9 (4)	O(2)-Cu(1)-N(6)	95.2 (4)
O(2)-Cu(1)-O(1)	83.3 (3)	O(2)-Cu(1)-W(2)	88.0 (3)
O(2)-Cu(1)-O(3)	93.0 (3)	N(5)-Cu(1)-N(6)	87.6 (4)
N(5)-Cu(1)-O(1)	93.8 (4)	N(5)-Cu(1)-W(2)	92.9 (4)
N(5)-Cu(1)-O(3′)	86.3 (4)	N(6)-Cu(1)-O(1)	176.8 (4)
N(6)-Cu(1)-W(2)	92.1 (4)	N(6)-Cu(1)-O(3′)	82.5 (4)
O(1)-Cu(1)-W(2)	90.7 (3)	O(1)-Cu(1)-O(3′)	94.7 (3)
W(2)-Cu(1)-O(3)	174.6 (2)	O(3)-Co(1)-O(4)	102.8 (3)
O(3)-Co(1)-O(2)	158.2 (3)	O(3)-Co(1)-O(1)	86.2 (3)
O(3)-Co(1)-W(1)	101.2 (4)	O(3)-Co(1)-O(1′)	84.6 (3)
O(4)-Co(1)-O(2)	89.1 (3)	O(4)-Co(1)-O(1)	161.6 (4)
O(4)-Co(1)-W(1)	101.0 (4)	O(4)-Co(1)-O(1′)	92.2 (3)
O(2)-Co(1)-O(1)	77.7 (3)	O(2)-Co(1)-W(1)	94.2 (4)
O(2)-Co(1)-O(1′)	76.6 (3)	O(1)-Co(1)-W(1)	92.7 (4)
O(1)-Co(1)-O(1′)	72.4 (3)	W(1)-Co(1)-O(1′)	163.8 (3)
Cu(1)-O(1)-Co(1)	100.2 (4)	Cu(1)-O(2)-Co(1)	99.8 (3)

[a] In this table, the atoms O(1′) and O(3′) are deduced from O(1) and O(3) by the operation 66505.

Table V. Selected Interatomic Distances between Oxygen Atoms and Water Molecules[a]

O(31)[55501]-W(2)[64503]	2.670 (9)
O(31)[55501]-W(6)[55501]	2.733 (9)
O(41)[55501]-W(4)[55501]	2.747 (8)
O(41)[55501]-W(6)[65506]	2.790 (9)
W(1)[55501]-W(2)[55501]	2.695 (8)
W(1)[55501]-W(5)[55501]	2.714 (9)
W(2)[55501]-W(4)[55501]	2.838 (9)
W(3)[55501]-W(6)[55501]	2.694 (8)
W(3)[55501]-W(4)[55508]	2.820 (9)
W(3)[55501]-W(5)[55501]	2.859 (8)
W(4)[55501]-W(5)[66605]	2.873 (9)

[a] Each atom is notated following the code indicated in Table III.

The main differences in interatomic distances affect the basal edges of the square-pyramid CoO$_4$W, all of them being diminished by 0.03 Å for O(2)O(4) to 0.24 Å for O(3)O(4).

As far as the packing of molecules is concerned, the cell reveals very important features. Two molecules are directly packed together through the operation of a symmetry center. The main result is schematized by Figure 2. If the association of two square pyramids CuN(5)N(6)O(1)O(2)W(2) and CoO(1)O(2)O(3)O(4)W(1) sharing the O(1)O(2) edge is considered, a kind of tetramer is created, each metal atom completing its coordination sphere to six, giving rise to an entity of four octahedra sharing edges (O(1)O(2), O(1′)O(2′), O(2)O(4′), O(2)O(2′), O(2′)O(4)). The sixth distance is rather long for both copper and cobalt atoms: Cu–O(4′) = 2.942 Å and Co–O(2′) = 3.25 Å.

Table VI[a]

Mean Planes		
1	O(1)-O(2)-N(5)-N(6)	$0.049\,76x - 0.064\,11y - 0.996\,70z + 1.472\,82 = 0$
2	O(1)-O(2)-O(3)-O(4)	$0.058\,88x - 0.040\,27y - 0.997\,45z + 1.169\,44 = 0$
3	Cu(1)-Co(1)-W(2)	$-0.395\,38x - 0.916\,59y + 0.059\,52z + 12.047\,82 = 0$
4	Cu(1)-Co(1)-W(1)	$-0.388\,85x - 0.921\,27y + 0.007\,88z + 12.104\,00 = 0$

Angles between Planes (Deg)

1–2	181.5	2–3	92.6
1–3	91.2	3–4	183.0
1–4	88.2		

Deviations of the Atoms from Mean Planes (Å)

	1	2	3	
Cu(1)	−0.031	−0.030	0	0
Co(1)	−0.266	−0.268	0	0
O(1)	0.016	−0.016	1.269	1.278
O(2)	−0.018	0.012	−1.237	−1.230
O(3)	0.055	0.012	1.520	1.541
O(4)	−0.055	−0.019	−1.517	−1.500
N(5)	−0.013	−0.044	1.306	1.300
N(6)	0.013	0.049	−1.303	−1.306
W(1)	−2.328	−2.331	0.108	0
W(2)	−2.812	−2.809	0.0	−0.144

[a] The chosen reference *x*, *y*, *z* for the calculation of the plane equation is such that 0*Y* ∥ *b* axis, 0*Z* ∥ *c* axis, and 0*X* ⊥ *bc* plane.

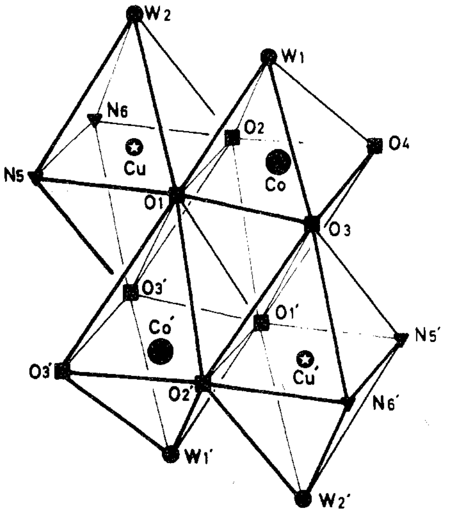

Figure 2.

This structure shows the first example of a close packing of two planar molecules of the MM′(fsa)$_2$en type, the two molecules remaining parallel. Such an association could justify tetramer formulation for this compound, i.e., [CuCo(fsa)$_2$en·H$_2$O]$_2$.

To the best of our knowledge, such a weak interaction between two binuclear units related by inversion centers was only found once before, namely, in the complex Cu$_2$(DTFACP)$_2$·2H$_2$O containing the dianion 2,5-bis(trifluoroacetyl)cyclopentanone.[18]

The tetramolecular units sit on a face-centered orthorhombic prism, the uncoordinated water molecules building a three-dimensional network encapsulating these units.

Registry No. CuCo(fsa)$_2$en·6H$_2$O, 73940-58-6; CuCo(fsa)$_2$en·2H$_2$O, 62109-46-0.

Supplementary Material Available: A listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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(18) Lintvedt, R. L.; Glick, M. D.; Tomlonovic, B. K.; Gavel, D. P.; Kuszas, J. M. *Inorg. Chem.* **1976**, *15*, 1633.