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Bis[1,1,1,5,5,5-hexafluoro-2,4-pentanedionato-μ-(*N*-methyl-2-hydroxybenzylideneiminato)-μ-*O*]-dicopper(II). A Mixed-Ligand Binuclear Cu^{II} Complex

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Abstract. $C_{26}H_{18}Cu_2F_{12}N_2O_6$, monoclinic, $C2/c$, a = 23·414 (2), b = 7·727 (1), c = 16·430 (1) Å, β = 91·33 (1)°, Z = 4, D_m = 1·807, D_x = 1·809 Mg m^{-3}. The structure has a centre of symmetry. Each Cu atom has square-pyramidal coordination geometry. The bridging CuO_2Cu unit is nearly rectangular (Cu–O, 1·897, 2·450, Cu···Cu, 3·181 Å, Cu–O–Cu, 93·2°).

Introduction. Yokoi & Chikira (1975) reported that an equimolar mixture of bis(hexafluoroacetylacetonato)-copper(II), $Cu(hfa)_2$, and bis(*N*-salicylidenealkylaminato)copper(II), $Cu(RSal)_2$, in toluene gives a new series of binuclear mixed-ligand chelates, $[Cu(RSal)hfa]_2$, where the number of C atoms in the alkyl group (R) is from 0 to 5. The magnetic properties and electronic spectra of their crystals vary delicately with the alkyl group; particularly drastic changes are observed between the complex (1) where R is *tert*-butyl and the other members. In order to furnish a structural basis for these properties, we have determined the crystal structure of (1) and the complex (2) where R is methyl as a representative of the latter group (Shimanouchi, Sasada, Koyano & Yokoi, 1976). Since Sinn (1976) has published the structure of (1) as well as some related complexes $[Cu(RSal)hfa]_2$ where R is C_6H_5, iso-C_3H_7 or C_2H_5, the present paper deals with only the structure of (2).

Crystals of (2) (green needles) are monoclinic, the space group being $C2/c$ from systematic absences (hkl with $h + k = 2n + 1$ and $h0l$ with $l = 2n + 1$).

Intensity data of 1816 independent reflexions were collected on a Rigaku automatic four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation up to 2θ = 44° using a crystal, 0·40 × 0·30 × 0·30 mm in size. Of these, 1423 were considered as observed according to the criterion $|F_o| \geq 3\sigma(F_o)$. The data were corrected for Lorentz and polarization effects, but no absorption correction was applied (μ = 1·62 mm^{-1} for Mo $K\alpha$ radiation).

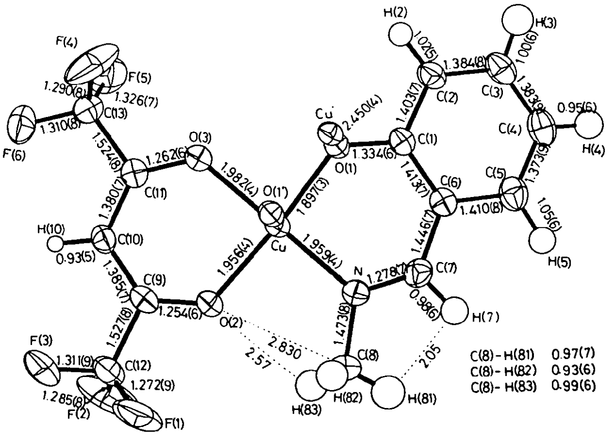

Fig. 1. Interatomic distances (Å), their e.s.d.'s (in parentheses) and thermal ellipsoids at the 30% probability level, viewed along the vector perpendicular to the least-squares plane of N, O(1), O(2), and O(3). Primed atoms, Cu′ and O(1′), are related to unprimed ones (at x,y,z) by a centre of symmetry at ($\frac{1}{4}$,$\frac{1}{4}$,0). The other symmetry-related atoms in the molecule are omitted.

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Table 1. *Final atomic coordinates* ($\times 10^4$ *for non-hydrogen atoms except* Cu $\times 10^5$; $\times 10^3$ *for hydrogen atoms*) *and their standard deviations* (*in parentheses*)

	x	*y*	*z*
Cu	20149 (2)	12141 (8)	2897 (3)
F(1)	658 (2)	2980 (8)	2039 (2)
F(2)	197 (2)	985 (6)	1509 (5)
F(3)	17 (2)	3489 (8)	1177 (3)
F(4)	1116 (2)	3807 (7)	−1980 (2)
F(5)	887 (2)	1177 (6)	−2044 (2)
F(6)	290 (2)	2987 (7)	−1661 (2)
O(1)	2632 (1)	810 (4)	−414 (2)
O(2)	1349 (1)	1742 (5)	942 (2)
O(3)	1571 (1)	1846 (5)	−708 (2)
N	2394 (2)	103 (5)	1228 (2)
C(1)	3032 (2)	−406 (6)	−318 (3)
C(2)	3370 (2)	−835 (7)	−983 (3)
C(3)	3808 (2)	−2030 (7)	−901 (4)
C(4)	3925 (2)	−2815 (7)	−159 (4)
C(5)	3598 (2)	−2439 (7)	501 (4)
C(6)	3144 (2)	−1243 (6)	433 (3)
C(7)	2832 (2)	−869 (7)	1162 (3)
C(8)	2163 (3)	313 (9)	2049 (3)
C(9)	870 (2)	2267 (6)	689 (3)
C(10)	693 (2)	2597 (7)	−106 (3)
C(11)	1057 (2)	2337 (6)	−742 (3)
C(12)	440 (2)	2443 (9)	1370 (4)
C(13)	836 (2)	2616 (8)	−1612 (3)
H(2)	328 (2)	−21 (7)	−151 (3)
H(3)	402 (2)	−229 (8)	−141 (4)
H(4)	421 (2)	−367 (7)	−9 (3)
H(5)	367 (2)	−299 (7)	108 (3)
H(7)	299 (2)	−135 (7)	167 (3)
H(10)	32 (2)	295 (6)	−21 (3)
H(81)	239 (3)	−38 (9)	243 (4)
H(82)	219 (2)	147 (8)	219 (3)
H(83)	178 (2)	−20 (8)	207 (3)

The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. After several anisotropic refinement cycles, all the H atoms were located on a difference Fourier map. Further refinement, including the coordinates and isotropic temperature factors of all the H atoms, led to convergence with an *R* value of 0·036 for the observed reflexions. A weighting scheme used in the later stage was $w = 1/[\sigma^2(F_o) + 0{\cdot}00628|F_o| + 0{\cdot}00004|F_o|^2]$ and $w = 0$ for the observed and unobserved reflexions respectively. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968). Positional parameters are given in Table 1.* Bond distances and angles are given in Fig. 1 and Table 2, respectively. Fig. 1 was drawn by use of the program *DEAM* (Takenaka, 1972).

Table 2. *Bond angles* (°)

O(1)—Cu—N	94·0 (2)	C(10)—C(11)—C(13)	119·1 (5)
O(2)—Cu—O(3)	89·6 (1)	O(3)—C(11)—C(13)	112·7 (5)
O(1)—Cu—O(3)	85·9 (1)	Cu—O(3)—C(11)	126·2 (3)
N—Cu—O(2)	90·7 (2)	C(9)—C(12)—F(1)	113·8 (6)
O(1)—Cu—O(2)	175·2 (1)	C(9)—C(12)—F(2)	110·7 (5)
O(3)—Cu—N	168·1 (2)	C(9)—C(12)—F(3)	112·6 (6)
O(1)—Cu—O(1′)	86·8 (1)	F(1)—C(12)—F(2)	107·7 (6)
O(2)—Cu—O(1′)	91·8 (1)	F(2)—C(12)—F(3)	104·4 (6)
O(3)—Cu—O(1′)	90·4 (1)	F(1)—C(12)—F(3)	107·1 (6)
N—Cu—O(1′)	101·5 (2)	C(11)—C(13)—F(4)	112·1 (5)
Cu—O(1)—C(1)	125·9 (3)	C(11)—C(13)—F(5)	110·5 (5)
C(1)—O(1)—Cu′	114·6 (3)	C(11)—C(13)—F(6)	113·5 (5)
Cu—O(1)—Cu′	93·2 (1)	F(4)—C(13)—F(5)	107·2 (5)
O(1)—C(1)—C(2)	118·8 (4)	F(5)—C(13)—F(6)	104·4 (5)
O(1)—C(1)—C(6)	122·8 (4)	F(4)—C(13)—F(6)	108·7 (6)
C(2)—C(1)—C(6)	118·4 (5)	C(1)—C(2)—H(2)	116 (3)
C(1)—C(2)—C(3)	120·7 (5)	C(3)—C(2)—H(2)	123 (3)
C(2)—C(3)—C(4)	120·7 (5)	C(2)—C(3)—H(3)	116 (3)
C(3)—C(4)—C(5)	120·0 (6)	C(4)—C(3)—H(3)	124 (3)
C(4)—C(5)—C(6)	120·6 (5)	C(3)—C(4)—H(4)	122 (3)
C(5)—C(6)—C(1)	119·5 (5)	C(5)—C(4)—H(4)	117 (3)
C(5)—C(6)—C(7)	117·4 (5)	C(4)—C(5)—H(5)	123 (3)
C(1)—C(6)—C(7)	123·0 (5)	C(6)—C(5)—H(5)	116 (3)
C(6)—C(7)—N	127·6 (5)	C(6)—C(7)—H(7)	116 (3)
C(7)—N—Cu	117·4 (5)	N—C(7)—H(7)	116 (3)
C(7)—N—C(8)	117·0 (5)	C(9)—C(10)—H(10)	119 (3)
Cu—N—C(8)	120·3 (4)	C(11)—C(10)—H(10)	120 (3)
Cu—O(2)—C(9)	127·2 (3)	N—C(8)—H(81)	109 (4)
O(2)—C(9)—C(10)	128·1 (5)	N—C(8)—H(82)	109 (4)
O(2)—C(9)—C(12)	112·7 (5)	N—C(8)—H(83)	110 (4)
C(10)—C(9)—C(12)	119·1 (5)	H(81)—C(8)—H(82)	110 (6)
C(9)—C(10)—C(11)	120·7 (5)	H(82)—C(8)—H(83)	116 (5)
C(10)—C(11)—O(3)	128·1 (5)	H(81)—C(8)—H(83)	104 (5)

Discussion. As shown in Fig. 1, the coordination geometry around the Cu atom is square-pyramidal. Dimerization occurs through the sharing of the MeSal ligand O atoms; the bridging O atoms occupy the apical sites of the square pyramids. The Cu atom is displaced 0·095 Å out of the basal plane towards the bridging O atom. Although the hfa ligand is nearly planar, the MeSal ligand deviates from the basal plane owing to the participation of O(1) in bridging. The planes of Cu, O(1), N and Cu, O(2), O(3) are inclined at an angle of 12·0° to each other. In the coordination of hfa, the Cu—O distances are longer than those in the complex bis(acetylacetonato)copper(II), Cu(acac)$_2$ (Lingafelter & Braun, 1966). The electron-withdrawing CF$_3$ groups probably decrease the electron density at O(2) and O(3) so that the smaller electron donation to Cu allows it to form the bridging bond, Cu—O(1′). This argument is compatible with the observation that Cu(acac)$_2$ and Cu(*R*Sal)$_2$ do not give the present type of dimer complexes.

It is noted that in the hfa ligand the Cu—O(2) length is significantly shorter than the Cu—O(3) bond which is situated *trans* to the Cu—N.

The above features are also observed in the related complexes reported by Sinn (1976).

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33900 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(ethylenediamine)(2-selenoacetato-*O*,*Se*)cobalt(III) Perchlorate

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Abstract. $[Co(C_2H_8N_2)_2(C_2H_2O_2Se)]ClO_4$, $P2_1/n$, $a = 11{\cdot}183\,(2)$, $b = 10{\cdot}171\,(2)$, $c = 12{\cdot}168\,(3)$ Å, $\beta = 96{\cdot}22\,(2)°$, $U = 1375{\cdot}9$ Å^3, $Z = 4$, $\mu(\text{Mo } K\alpha) = 4{\cdot}33$ mm^{-1}. The structure contains octahedral Co^{III} complex cations and perchlorate anions. The Co coordination is effected by four N atoms from the ethylenediamine ligands and O and Se atoms of the 2-selenoacetic acid ligand. The Co—N bond length for N *trans* to Se is 2·006 (7) Å whereas the mean for the three Co—N bonds *cis* to Se is 1·966 (7) Å, yielding a structural *trans* effect for the selenolato ligand in this complex of 0·040 (10) Å. This value is similar to that previously found for thiolato ligands in analogous Co^{III} complexes. The anisotropic thermal parameters for the perchlorate O atoms indicate that this ion undergoes significant librational motion or is rotationally disordered in the crystal. The structure was refined to an *R* of 0·046 for 1551 independent observed reflections.

Introduction. The structure of $[(en)_2Co(SeCH_2CO_2)]ClO_4$ has been determined as part of our program concerned with the structural *trans* effect in Co^{III} complexes (Elder, Heeg, Payne, Trkula & Deutsch, 1978). Specifically we wished to check our earlier observation that Se appears to cause a larger *trans* effect than S in such complexes (Stein, Ellis, Elder & Deutsch, 1976).

The synthesis and recrystallization of the title compound has been given elsewhere (Stein *et al.*, 1976). Preliminary precession photographs indicated the monoclinic space group $P2_1/n$. A lath-like brown-red crystal (0·06 × 0·11 × 0·72 mm) was mounted on a glass fiber with the long dimension coincident with the fiber axis. Intensity data were measured for 2354 reflections ($3 < 2\theta < 47°$) using Mo $K\alpha$ radiation on a Syntex $P\bar{1}$ diffractometer equipped with a graphite monochromator. From these, 1551 unique, observed reflections [$I > 2\sigma(I)$] were obtained by averaging after application of analytical absorption corrections. Calculated transmission coefficients ranged from 0·50 to 0·76.

The non-hydrogen atoms were located from Patterson and electron density syntheses, H atoms were placed at calculated positions and given fixed isotropic temperature parameters ($U = 0{\cdot}05$ Å^2). Refinement of non-hydrogen positional and anisotropic thermal parameters and H positional parameters converged to $R = 0{\cdot}046$ and $R' = [\sum w\Delta^2/\sum w(F_o)^2]^{1/2} = 0{\cdot}039$. The unweighted residual for all reflections was 0·048. Refinement of H positional parameters resulted in significant (0·005 level) improvement of the model (Hamilton, 1965). Mean values of $w\Delta^2$ varied only slightly with $\sin\theta$ or $|F_o|$. A final difference map was essentially featureless, the highest peaks (0·7 e Å^{-3}) occurring in the vicinity of the perchlorate anion. Complex neutral-atom scattering factors were used. Final non-hydrogen atomic coordinates are given in Table 1, with bond lengths and angles in Tables 2 and 3.*

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* Lists of structure factors, anisotropic thermal parameters, H coordinates and H bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33914 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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