Monodentate Hexafluoroacetylacetone. The Synthesis and Crystal Structure of Bis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)bis-(*NN*-dimethylethylenediamine)-copper(II)

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Summary The complex $(CF_3{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}CF_3)_2(Me_2NCH_2{\cdot}CH_2NH_2)_2Cu$ has been synthesised and shown by *X*-ray analysis to consist of copper centrosymmetrically six-co-ordinated by two chelate amines and one oxygen atom from each of two monodentate β-diketonates.

BIS-(1,1,1,5,5,5-HEXAFLUOROPENTANE-2,4-DIONATO)BIS-*NN*-DIMETHYLETHYLENEDIAMINE)COPPER(II), $[Cu(hfac)_2(asym\text{-}DMED)_2]$, is readily prepared by the stoicheiometric reaction of $Cu(hfac)_2$ and (asym-DMED) in benzene.[1] The complex is isolated as purple crystals and may be recrystallised from benzene or methanol. It gives a satisfactory chemical analysis. The molecular weight in benzene (osmometry) is 655 compared with 654 for a monomeric molecule. However, in nitromethane the conductivity, 61 cm^2 ohm^{-1} $mole^{-1}$, is between that of a non-conductor and a 1 : 1 electrolyte.[2] The colour and maximum absorption at 18·6 kK in the diffuse reflectance spectrum indicate that copper is co-ordinated by four nitrogen atoms. Chelation by both molecules of asym-DMED is confirmed by the i.r. spectrum. Absence of bands between 2760 and 2820 cm^{-1} indicates[3] co-ordination by the NMe_2 group while the triplet at 3180, 3280, and 3350 cm^{-1} is consistent[4] with a co-ordinated and hydrogen-bonded NH_2 group.

For the β-diketone the i.r. spectrum showed a strong band at 1675 cm^{-1}, a weak one at 1615 cm^{-1}, and a broad one at 1540 cm^{-1}. This suggested that the ligand was different from that in $Cu(hfac)_2$,[5] which has bands at 1644, 1614, 1565, and 1540 cm^{-1}; a more ionic form[6] or a carbon-bonded form[7] seemed possible. In fact, as shown by crystal structure analysis, the β-diketone is bonded through oxygen in a novel monodentate form. *Crystal data*: $C_{18}H_{22}CuF_{12}N_4O_4$. M = 654. Triclinic, a = 8·174, b = 8·495, c = 11·910 Å, α = 120·32°, β = 109·02°, γ = 94·65°, U = 643·7 Å^3. D_m (flotation) = 1·70, Z = 1, D_c = 1·69 g cm^{-3}. Space group $P\bar{1}(C_i^1)$. Molecular symmetry, centre. Mo-K_α radiation [λ = 0·7107 Å (10^{-10} m)].

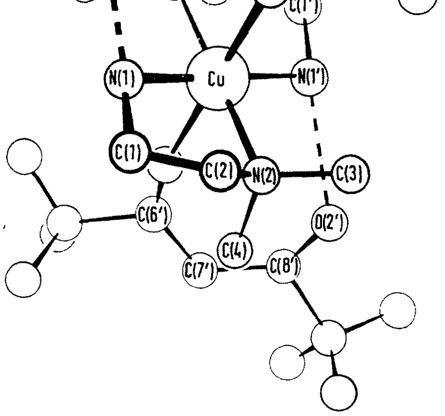

FIGURE. *One molecule of the complex* $(CF_3{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}CF_3)_2(Me_2NCH_2{\cdot}CH_2{\cdot}NH_2)_2Cu$ *showing the designations of the atoms involved in the interatomic distances given in the Table*; C(3) *and* C(4) *represent methyl groups. The broken line represents an* N–H ··· O *hydrogen bond,* 2·92 ± 0·04 Å. *Primed atoms are centrosymmetrically related to the unprimed ones.*

Intensities were measured with a Picker four-circle diffractometer up to $2\theta = 50°$. The structure was solved by Fourier methods and refined by full-matrix least-squares to an R value of 0·15 on 2360 reflections. The stereochemistry of the complex is established as that shown in the Figure. Important interatomic distances and their standard deviations are given in the Table. The copper atom occupies a centre of symmetry and is chelated by the asym-DMED, with the Cu–N(Me_2) significantly longer than Cu–N(H_2), while the fifth and sixth positions of an octahedron are occupied by one oxygen from each β-diketone, with a long Cu–O distance. The unco-ordinated oxygen forms a hydrogen bond with the NH_2 group, the N–H $\cdots$ O distance is 2·92 Å. In the β-diketonate the bond lengths are consistent with delocalisation, rather than a formulation as $CF_3C(=O)CH=C(O^-)CF_3$, and explain the single C $\cdots$ O stretching frequency in the i.r. spectrum. Further discussion is deferred until more observations are available.

TABLE

Bond lengths and, in parentheses, estimated standard deviations, Å

Cu–N(1)	2·01(2)	Cu–O(1)	2·76(1)
Cu–N(2)	2·11(2)	O(1)–C(6)	1·23(2)
N(1)–C(1)	1·51(3)	C(6)–C(7)	1·40(2)
C(1)–C(2)	1·53(2)	C(7)–C(8)	1·41(2)
C(2)–N(2)	1·49(2)	C(8)–O(2)	1·23(2)
N(2)–C(3)	1·48(2)		
N(2)–C(4)	1·49(2)		

This compound is one of a series[1] with stoicheiometry Cu(hfac)$_2$L$_2$ having similar physical properties including the i.r. spectra; L is a chelating diamine which contains at least one N–H group.

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