Crystal and Molecular Structure of a Heterobinuclear Copper(II)–Magnesium Complex: Bis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)magnesium–*NN*′-ethylenebis(salicylideneaminato)copper(II)

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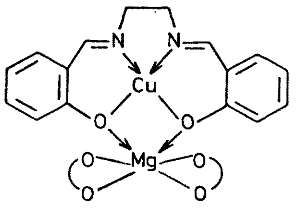
Summary The crystal and molecular structure of a heterobinuclear copper(II)–magnesium complex derived from *NN*′-ethylenebis(salicylideneaminato)copper(II), (Cusalen), and bis(aqua)bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)magnesium, $Mg(hfac)_2.2H_2O$, is reported together with other bimetallic complexes derived from metal β-diketonates.

Co-ordinative saturation of divalent metal β-diketonates by the addition of bidentate ligands is well established,[1,2] as is the use of metal salicylideneamines as donor ligands in the synthesis of bi- and tri-nuclear centres.[3,4] There is, however, a paucity of information concerning binuclear centres involving alkaline earth metals.



(1)

O⌒O = $CF_3C(:O)\bar{C}HC(:O)CF_3$

We report here the crystal and molecular structure of the heterobinuclear complex bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)magnesium–*N,N*′-ethylenebis(salicylideneaminato)copper(II), $[(hfac)_2Mg\{Cu(salen)\}]$ (**1**), readily prepared by reaction of its components in dichloromethane.

The molecular structure of (**1**) has been solved by *X*-ray diffraction data analysis. The crystals are triclinic with cell parameters $a = 9{\cdot}501(7)$, $b = 15{\cdot}43(1)$, $c = 12{\cdot}042(8)$ Å, $\alpha = 83{\cdot}7(1)$, $\beta = 112{\cdot}8(1)$, $\gamma = 107{\cdot}8(1)^\circ$; $U = 1550{\cdot}2$ Å^3, $D_c = 1{\cdot}64$ g cm^{-3}, $D_m = 1{\cdot}64$ g cm^{-3}, $Z = 2$, $M = 768{\cdot}3$ for $CuMgN_2O_6F_{12}C_{26}H_{16}$; space group $P\bar{1}$ (from structure refinement). The structure was solved by conventional Patterson and Fourier methods and refined by least-squares methods to $R = 4{\cdot}6\%$, using 2540 independent reflections with $I > 3\sigma(I)$ and collected on an automated SIEMENS diffractometer up to $\theta_{\max}$ 26° using Mo-K_α radiation. The crystals consist of neutral [(hfac)$_2$Mg{Cu(salen)}] units held together by Van der Waals forces (Figure).†

The magnesium is octahedrally surrounded by oxygen donors, having achieved co-ordinative saturation through *cis*-addition of the donor metal complex. The co-ordination polyhedron of the magnesium ion may be described as a distorted octahedron with nearly equal Mg–O distances [2·053—2·109(5) Å] in fair agreement with the sum of ionic radii of 2·05 Å.

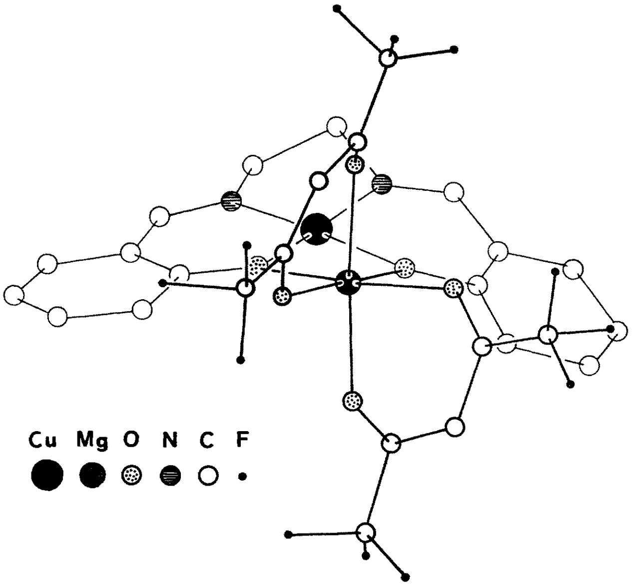


FIGURE. Molecular structure of [(hfac)$_2$Mg{Cu(salen)}] (**1**).

The O–Mg–O angles defining the opposite vertices of the octahedron are in the range 164·2—174·5(2)°, whereas the others are in the range 76·2—97·6(2)°. The sum of the angles around copper is 360°, showing an essentially square planar stereochemistry. The Cu–O bond lengths of 1·913 and 1·921(5) Å are not far from the values found for {[Cu(salen)]$_2$NaClO$_4$}[5] [1·90(1) Å] and for other Cu(salen) complexes, where oxygen atoms are not further co-ordinated[6] [1·886—1·920(9) Å]. This result confirms the previous observation[7] that where Schiff base metal oxygen atoms of Schiff base metal complexes undergo further co-ordination by d° metals no significant variation in the metal–oxygen bond lengths may be detected. The Cu · · · Mg distance is 3·031(5) Å.

A 1 : 1 complex is also formed from the reaction of Cu(salen) and bis(1,1,1-trifluoropentane-2,4-dionato)magnesium but not with bis(pentane-2,4-dionato)magnesium, in keeping with the observed series of Lewis acid strengths for magnesium β-diketones.[2]

A series of complexes Cu(salen).M(hfac)$_2$ has been prepared with first row transition metals (M = Mn, Fe, Co, Ni, Cu, and Zn). The Cu–Co complex has been previously reported.[8] These complexes provide an opportunity to investigate the influence of metals on each other when juxtaposed in unusual environments, *e.g.* square planar and octahedral copper in the homobinuclear copper complex. We have found that the Cu–Mn complex is isomorphous with the Cu–Mg complex. Manganese has been postulated and used as a structural probe for magnesium in biological systems;[9] the structural similarity noted here lends support to this approach.

Analogously the Cu–Zn derivative appears to be isomorphous with the Cu–Mg complex. In contrast *X*-ray powder spectra do not show the Fe, Ni, and Cu analogues to be isomorphous with (**1**).

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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