

Synthesis and Crystal Structure of the Tris(hexafluoroacetylacetonato)copper(II) Salt of Monoprotonated 1,8-bis(dimethylamino)naphthalene and of the Isomorphous Magnesium Derivative

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Summary The compound $[\text{C}_{14}\text{H}_{19}\text{N}_2]^+[(\text{CF}_3\text{CO-CH-CO-CF}_3)_3\text{Cu}]^-$ has been synthesised and its constitution established by X-ray crystal structure analysis; the Cu-O bonds, four short and two long, contrast with six equal Mg-O lengths in the isomorphous magnesium derivative.

A STOICHEIOMETRIC mixture (1:1:1) in benzene of 1,8-bis(dimethylamino)naphthalene¹ (I), 1,1,1,5,5,5-hexafluoropentane-2,4-dione (hfacH), and bis-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)quo copper, $[\text{Cu}(\text{hfac})_2\text{H}_2\text{O}]$, reacts to give yellow-green acicular crystals of the same composition. These can be recrystallised from benzene [*M*(osmometry) 962]. In nitromethane the conductivity is $46.9 \text{ cm}^{-2} \text{ ohm}^{-1} \text{ mole}^{-1}$ intermediate between that for a non-electrolyte and a (1:1) electrolyte. The i.r. spectrum of the solid shows a single sharp carbonyl frequency at 1650 cm^{-1} , indicative of *O*-chelating hfac.²

The compound may also be prepared, in considerably reduced yield, by reaction of (I) and $\text{Cu}(\text{hfac})_2\text{H}_2\text{O}$ in benzene or ethanol. From ethanol the main product is the dimer $[\text{Cu}(\text{hfac})(\text{OEt})]_2$. This reaction is analogous to that³ of bis(pentane-2,4-dionato)copper(II) with methanol in the presence of a strong base which deprotonates the alcohol; it provides further evidence for the remarkable basicity¹ of (I). From $\text{Mg}(\text{hfac})_2$ a colourless compound, isomorphous with the copper one, is obtained. Crystal structure analysis has shown that the solids contain (I)H⁺ cations and $\text{Cu}(\text{hfac})_3^-$ or $\text{Mg}(\text{hfac})_3^-$ anions with the metal surrounded by 6 oxygen atoms from three chelate rings.

Crystal data: $[\text{C}_{14}\text{H}_{19}\text{N}_2]^+[\text{C}_{15}\text{H}_3\text{F}_{18}\text{O}_6\text{Cu}]^-$. *M* = 904. m.p. 110–112°. Monoclinic, *a* = 12.878, *b* = 20.998,

c = 13.620 Å, β = 98° 44', *U* = 3640 Å³, *D_m* (floatation) = 1.66, *Z* = 4, *D_c* = 1.64 g/cm³. Space group $P2_1/n$ (C_{2h}^5). No molecular symmetry required. 2558 observations were made with Mo-*K α* (λ = 0.7107 Å, 1 Å = 10⁻¹⁰m) on an automatic diffractometer.

Crystal data: $\text{C}_{29}\text{H}_{22}\text{F}_{18}\text{N}_2\text{O}_6\text{Mg}$. *M* = 865, m.p. 117–118°, *a* = 12.774, *b* = 21.268, *c* = 13.594 Å, β = 99° 10', *U* = 3645.5 Å³, *D_m* = 1.60, *D_c* = 1.57. 1998 observations. Other conditions as for the copper compound.

The structures were solved by direct methods and refined by full-matrix least-squares to the present *R* values of 0.11 (Cu) and 0.10 (Mg). Both compounds give the same dimensions for the cation (I)H⁺ as shown in the Figure.

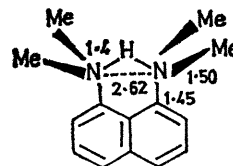


FIGURE. The cation (I)H⁺ showing the average interatomic distances round the nitrogen atoms. The cationic hydrogen atom is in the plane of the naphthalene ring, and the methyl groups lie above and below this plane.

All hydrogen atoms have been located, the proton in the cation completes a tetrahedron about each of the two nitrogen atoms.

No crystallographic symmetry is imposed on the anions, the Mg-O distances are equal, 2.062(5) Å but the copper compound shows Jahn-Teller distortion, the four Cu-O bonds in a plane average 2.015(5) Å and the two axial ones

2.176(7) Å. Both compounds give the same dimensions within the chelate rings, C...O 1.26(1) Å and C...C 1.38(2) Å; the six independent values are equal in the copper compound and there is no evidence for the alternation found in bis(hexafluoroacetylacetonato)bipyridylcopper(II).⁴

Tris(chelate) complexes of magnesium and copper are isomorphous for another ligand, octamethylphosphoramide.⁵ The crystallographic symmetry results in equal metal-oxygen bond lengths of 2.065(2) Å for Cu-O, and 2.061(2) Å for Mg-O. The copper complex may involve a dynamic

Jahn-Teller distortion as has been suggested for other copper complexes with three equivalent ligands.^{6,7} In $[(I)H^+][Cu(hfac)_3^-]$ a static distortion is established; the chelating ligands may impose a restriction on the tetragonal extent of this distortion.

We have synthesised other derivatives of the anions $Cu(hfac)_3^-$ and $Mg(hfac)_3^-$ with potassium, triethylammonium, and 1,4-diazobicyclo[2,2,2]octonium as counter ions.⁸

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