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Copper(II) Complexes of α-Oximinoketones

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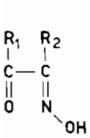
Three compounds of the unusual formula type (LCuOH), where L is the anion of $R_1C{:}NOHCR_2{:}O$ have been characterized. Two had been previously prepared, one is a new compound of a new ligand. In each case, the subnormal magnetic moment of the copper ion suggests a dimeric structure. The copper promoted conversion of a *syn*-oximinoketone to its *anti*-isomer is noted.

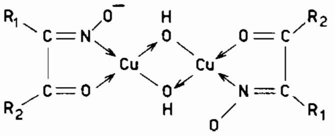
While complexes of α-oximinoketones acting as mono-anionic bidentate chelating ligands (L) with nickel(II) and cobalt(III), conform to the accepted ideas of coordination number (*i.e.* forming NiL_2 and CoL_3), cases were known[1,2] where the copper complex had the apparently unusual stoichiometry (LCuOH). Ia and Ib are two of these.



I

(Ia) R_1 = Ph, R_2 = CH_4
(Ib) R_1 = Ph, R_2 = Ph
(Ic) R_1 = 3,4-difluorophenyl, R_2 = CH_3

In connection with our studies on the copper complexes of ephedrine analogues,[3] we recently prepared the copper complex of the α-oximinoketone Ic and find that it also has this stoichiometry. All three complexes [LCu(OH)] have magnetic moments (per copper ion) at room temperature of *ca.* 0.8 B.M. (Ia, 0.80, Ib, 0.86, and Ic, 0.76 B.M.), and we attribute this to a magnetic interaction between neighbouring copper ions, suggesting a dimeric structure such as II in which the coordination number of copper is four. This interaction is confirmed by the observed decrease of the magnetic moment with temperature. These variable temperature measurements indicate a selective interaction of the solid complexes with molecular nitrogen, which will be described later.



Unfortunately, all the solids are exceedingly insoluble in common solvents. However, the present results do establish that the coordination number of the copper ion is greater than three, but cannot rule out the other possible geometrical isomer of (II) or indeed oligomers or polymers higher than the dimer. The infrared spectra of the complexes show a strong broad band at *ca.* 3,300 cm^{-1}. This suggests that the bridging hydroxy groups are not strongly hydrogen bonded, and certainly very much less so than in bis-1,2-dioximato complexes.[6] The diffuse reflectance spectra of the complexes all show a band maximum at *ca.* 610 nm and although this is at a slightly lower wavelength than might have been predicted, it is consistent with the proposed structures.

Following the studies of Taylor and Roberts[4] on *syn* and *anti* Ia, we find that the *anti*-form of the α-oximinoketone Ic (m.p. 117–118 °C) forms a copper complex much more readily than the *syn* form (m.p. 103–104 °C)[5], although over a period of a few days the *syn*-form will give the complex derived from the *anti*-form.

N,N,N'-triethylethylenediamine and N,N,N',N'-tetramethylethylenediamine form bridged diol complexes and not *bis*-complexes with copper(II) due[7] to steric interaction between the N-alkyl groups. A similar argument would seem to be precluded for α-oximinoketones since both the nickel and cobalt complexes are of the normal type.[1,2] The isolation of the dimeric compounds in these particular cases may be a reflection of their extreme insolubility. Copper(II) compounds are labile, and dimeric structures are often found in aqueous solutions of copper salts.[8,9] The dimerisation constant for the formation of hydroxy bridged dimeric species (3*M* $NaClO_4$; 25 °C) is approximately 10^5.

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Experimental

Preparation of complexes

The complexes were prepared under dust free conditions by adding an aqueous methanol (1:1) solution of cupric acetate (0.1 mol) to an equimolar methanol solution of the α-oximinoketone. The resulting suspension was allowed to stand for one hour and then filtered. The products were washed with water followed by methanol and then ether, and dried at 60 °C under high vacuum for 8–12 hours. Ia, Found: C, 44.9; H, 3.9; N, 5.5; Cu, 25.0%. Calc. for $C_9H_9NO_3Cu$: C, 44.5; H, 3.7; N, 5.8; Cu, 26.2%. Ib, Found: C, 55.2; H, 4.0; N, 4.5; Cu, 20.5%. Calc. for $C_{14}H_{11}NO_3Cu$: C, 55.2; H, 3.6; N, 4.6; Cu, 20.5%. Ic, Found: C, 39.1; H, 3.0; N, 4.6; Cu, 21.9%. $C_9H_7F_2NO_3Cu$ requires C, 38.8; H, 2.5; N, 5.0; Cu, 22.8%.

Decomposition of the copper complex of Ic

The copper(II) complex (1.24 g) was shaken with ether (100 ml) and 5*M* hydrochloric acid (100 ml) until all the solid dissolved. The two layers were separated and the aqueous phase extracted again with ether. The organic phases were combined, washed with water, dried over anhydrous sodium sulphate and evaporated to dryness. The residue was a white crystalline solid (830 mg), m.p. 117–118°C. The material was shown to be unchanged 3′,4′-difluoro-2-oximinopropiophenone by mixed m.p. and thin layer chromatography and represents a 93.5% recovery.

Copper analysis was performed by precipitating the aqueous layer with a solution of salicylaldoxime, and weighing the product.

Magnetic susceptibility measurements were made on a Gouy balance at room temperature using tris-ethylenediaminenickel(II) thiosulphate as calibrant. Infra-red spectra were measured for Nujol mulls on a Perkin Elmer 337 grating spectrophotometer. Diffuse reflectance spectra were obtained using the S.P. 890 accessory of a Unicam S.P. 850 spectrophotometer.

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