⁶³Cu- and ⁶⁵Cu-³¹P Spin-Spin Coupling in Copper(1) Trialkyl Phosphite Complexes

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OWING to rapid relaxation of nuclear spin, coupling to a nucleus having an electrical quadrupole moment is not normally observed unless the electrical environment of the quadrupolar nucleus has a high degree of symmetry. We report the observation of copper-phosphorus coupling in the ³¹P n.m.r. spectra of Cu[P(OR)₃]₄ClO₄ (I, R=Me₃; II, R=Et) wherein the symmetry of the complex cation is tetrahedral. Spectra were obtained at 24·3 Mc./sec. on saturated methylene chloride copper nucleus or the presence of traces of copper(II) and have a width at half height of 150 c./sec. The outermost peaks are slightly lower in intensity than the inner two and have minor peaks on their outer sides attributed to a superimposed four-line pattern arising from coupling to the less abundant 65 Cu isotope (63 Cu, 69% natural abundance, spin 3/2; 65 Cu, 31% natural abundance, spin 3/2). The observed ratio of 65 Cu- and 62 Cu- 31 P couplings is 1.07, in agreement



³¹P n.m.r. spectrum of Cu[P(OCH₃)₃]₄ClO₄

solutions with 85% aqueous phosphoric acid as external reference. These complexes are part of a series whose preparations will be reported later.

The ³¹P spectrum of (I) is made up of four peaks of approximately equal intensity centred at -125 p.p.m. with a coupling constant J (⁶³Cu-³¹P) of 1190 ± 30 c./sec. The peaks are considerably broadened by proton-phosphorus coupling and possibly by residual quadrupole relaxation of the with the value of 1.071 calculated from magnetogyric ratios.

The spectrum of (II) shows a similar 63 Cu splitting pattern ($\delta = -122$ p.p.m.; $J = 1210 \pm 30$ c./sec.) but the peak width of 200 c./sec. is greater than for (I) and the 65 Cu satellites are not observed. Spectra of other similar metal complexes are being investigated.

(Received, September 6th, 1965; Com. 560.)