# ${ }^{63} \mathbf{C u}$ - and ${ }^{65} \mathbf{C u}-{ }^{31} \mathbf{P}$ Spin-Spin Coupling in Copper(I) Trialkyl Phosphite Complexes 

By Roy W. King, T. J. Huttemann, and J. G. Verkade
(Department of Chemistry, Iowa State University, Ames, Iowa)

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 ${ }^{31} \mathrm{P}$ n.m.r. spectra of $\mathrm{Cu}\left[\mathrm{P}(\mathrm{OR})_{3}\right]_{4} \mathrm{ClO}_{4}$ ( $\mathrm{I}, \mathrm{R}=\mathrm{Me}_{3}$; II, $R=E t$ ) wherein the symmetry of the complex cation is tetrahedral. Spectra were obtained at $24 \cdot 3 \mathrm{Mc} . / \mathrm{sec}$. on saturated methylene chloride
copper nucleus or the presence of traces of copper(II) and have a width at half height of $150 \mathrm{c} . / \mathrm{sec}$. 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 ${ }^{65} \mathrm{Cu}$ isotope $\left({ }^{63} \mathrm{Cu}, 69 \%\right.$ natural abundance, spin $3 / 2$; ${ }^{65} \mathrm{Cu}, 31 \%$ natural abundance, spin $3 / 2$ ). The observed ratio of ${ }^{65} \mathrm{Cu}$ - and ${ }^{62} \mathrm{Cu}-{ }^{31} \mathrm{P}$ couplings is $1 \cdot 07$, in agreement

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

The ${ }^{31} \mathrm{P}$ spectrum of ( I ) is made up of four peaks of approximately equal intensity centred at -125 p.p.m. with a coupling constant $J\left({ }^{63} \mathrm{Cu}-{ }^{31} \mathrm{P}\right)$ of $1190 \pm 30 \mathrm{c} . / \mathrm{sec}$. 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 ${ }^{63} \mathrm{Cu}$ splitting pattern ( $\delta=-122$ p.p.m. $; ~ J=1210 \pm 30$ c. $/ \mathrm{sec}$.) but the peak width of $200 \mathrm{c} . / \mathrm{sec}$. is greater than for (I) and the ${ }^{65} \mathrm{Cu}$ satellites are not observed. Spectra of other similar metal complexes are being investigated.
(Received, September 6th, 1965; Com. 560.)

