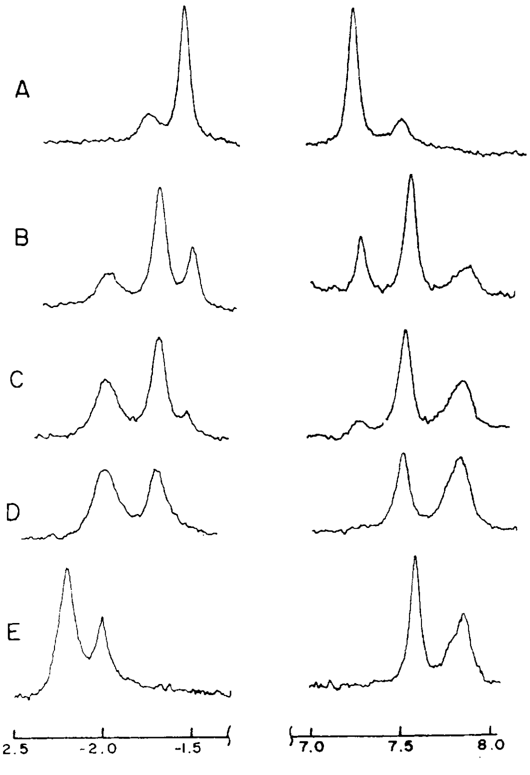
Nuclear Magnetic Resonance Spectra and Modes of Co-ordination in Aluminium–Hypophosphite Complexes

By H. D. Gillman and T. E. Haas*
(*Department of Chemistry, Tufts University, Medford, Massachusetts* 02155)

The ^1H n.m.r. spectrum of an aqueous solution of sodium hypophosphite is a doublet with a P–H coupling constant of 518 c./sec. and chemical shift τ 2·98. When the anion is protonated or complexed an increase in J_{PH} is observed accompanied by a slight decrease in chemical shift.[1,2] With aluminium, it is possible to observe more than one mode of co-ordination of hypophosphite with the metal.

When aluminium perchlorate is added to a solution of sodium hypophosphite, the expected increase in coupling constant is observed. Upon cooling, the single resonance peak is resolved into two or three components, depending on aluminium and hypophosphite concentrations.

The Figure shows the ^1H n.m.r. spectra of solutions containing aluminium and hypophosphite at −10°. When the aluminium to hypophosphite concentration ratio is small, two doublets are observed (Figure A). As the $Al^{2+}:H_2PO_2^-$ ratio is increased a third doublet appears and grows at the expense of the other two (Figure B, C, D). The doublet of lowest J_{PH} has a coupling constant characteristic of slightly protonated hypophosphite anion,[2] which together with its disappearance upon increasing aluminium concentration, leads us to assign this peak to unco-ordinated $H_2PO_2^-$. The other two doublets must then be assigned to co-ordinated hypophosphite. The doublet of intermediate J_{PH} (552 c./sec.) is assigned to $Al(H_2PO_2)_n$ complexes, J_{PH} being apparently, within the instrumental resolution, the same for all values of n. The doublet of largest J_{PH} (591 c./sec.) is assigned to dinuclear co-ordinated (bridging) hypophosphite $Al_2(H_2PO_2)$. Additional evidence for this assignment comes from the observation that on addition of excess acid, J_{PH} of the doublet assigned to $Al(H_2PO_2)_n$ increases, whereas that assigned to the dinuclear complex is



^1H *n.m.r. spectra of solutions containing* Al^{3+} *and* $H_2PO_2^-$. *All solutions contain* 0·8 M *sodium hypophosphite. Aluminium concentrations (as perchlorate) are*: A, 0·1 M; B, 0·3 M; C, 0·4 M; D, 0·5 M; E, 0·5 M + 1·5 M $HClO_4$.

not significantly changed. Hypophosphite co-ordinated to one metal atom has one oxygen atom still available for protonation, but in bridging $H_2PO_2^-$ both oxygen atoms are already involved in bonds to aluminium, and further protonation would be expected to be much less favourable if it were to occur at all. There is also a significant chemical-shift change when the co-ordinated hypophosphite is protonated (Figure E).

These results show a variety of modes of co-ordination of hypophosphite in a single system, as a monodentate anion $H_2PO_2^-$, as the acid $H_2P(O)(OH)$, and as a bidentate bridging group.

(*Received, May 6th,* 1968; *Com.* 559.)

---

[1] K. Moedritzer, *Inorg. Chem.*, 1967, **6**, 939.

[2] T. E. Haas and H. D. Gillman, to be published.