^{7}Li$^+$ N.M.R. Studies of an Li$^+$ – Ethyl Acetoacetate Enolate Triple Ion–Li$^+$ Cryptate Complex

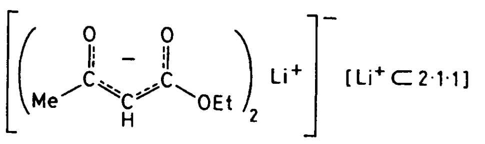
By Christian Cambillau* and Michèle Ourevitch
(*Centre National de la Recherche Scientifique, GR 12, BP 28, 94320 Thiais, France*)

Summary Two ^{7}Li n.m.r. signals are observed in the spectra of the title compound, the chemical shift of Li$^+$ in the triple ion being strongly solvent dependent.

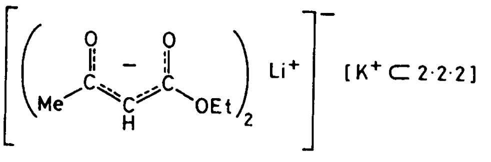
IN the course of our general study of the structure and reactivity of ethyl acetoacetate alkali enolates (E^-M^+),[1] 'trapped' triple-ion cryptates[2] $[E\text{–}Li\text{–}E]^-$ $[M^+ \subset$ cryptand] have been isolated.[3] Since lithium salts frequently lead to (Li^+, Li^+ triple-ion) couples[4] it seems useful to have a simple probe for their detection in solution. We propose ^{7}Li n.m.r. spectroscopy as a fast and efficient technique for this.† Of special interest is the fact that $[Li^+ \subset 2.1.1]$ cryptate does not exchange at room temperature and has a ^{7}Li chemical shift independent of solvent.[5]

We recorded the ^{7}Li n.m.r. spectra‡ of complexes (**1**) and (**2**) at room temperature in CH_2Cl_2 and Me_2SO, solvents in which their structure is maintained.[3] The spectra are shown in the Figure.

Complex (**1**) exhibits *two sharp* $^7Li^+$ *n.m.r. signals*, while (**2**) shows only one absorption, corresponding to $E^-\text{–}Li^+\text{–}E^-$, with the same shift as the lower-field signal of (**1**). Therefore, the signal at higher field belongs to the Li^+ cryptate. The value of the high-field chemical shift (δ + 0·4 p.p.m.), which is independent of solvent, and the lack of exchange of Li^+ are in agreement with the results of Popov and his co-workers[5] and confirm our assignments. In spite of the great stability of the triple ion, it must be pointed out that the chemical shift of the $[E\text{–}Li\text{–}E]^-$ signal *is* strongly affected by the solvent. It seems that the solvent molecules fit into (or are close to) the first sphere of solvation of Li^+. This is not very surprising since they can even penetrate the sphere of a non-specific cryptate such as $[Li^+ \subset 2.2.1]$.[5] We assume that the tetrahedral structure of $[E\text{–}Li\text{–}E]^{-3}$ can be slightly distorted, thus allowing solvation by a basic solvent. We are currently investigating whether such species as $[E\text{–}Li\text{–}E]^-$ $[Li^+\text{–}(S)_n]$ can be formed from E^-Li^+ solutions.[6]



(**1**)



(**2**)

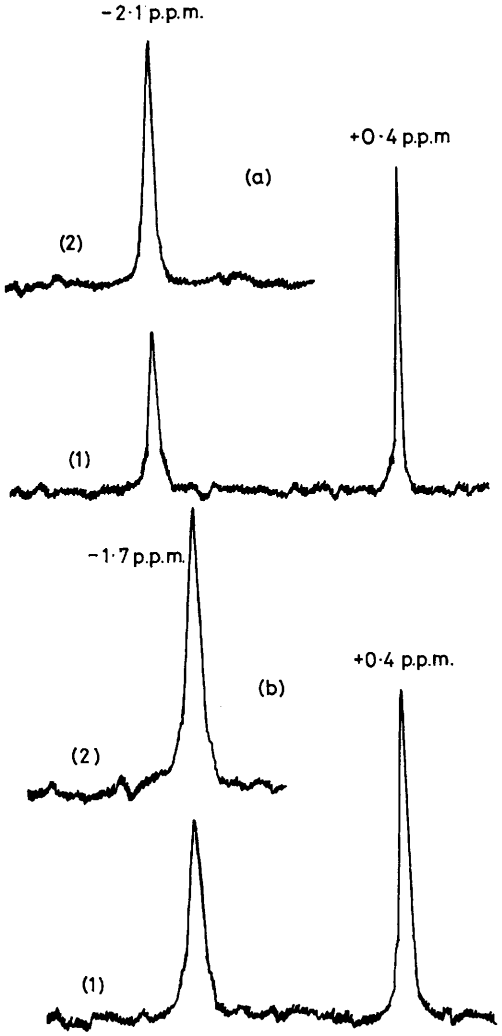


FIGURE. ^{7}Li N.m.r. spectra of complexes (**1**) and (**2**) [0·1 M solutions in (a) CH_2Cl_2 and (b) Me_2SO]. $LiClO_4$ at infinite dilution in water was used as external reference.

(*Received*, 19*th June* 1981; *Com.* 716.)

---

† The natural abundance of ^{7}Li is 92·58% and its relative n.m.r. sensitivity *vs.* ^{1}H is 0·293.

‡ Spectra were recorded at 34·976 MHz on a Brücker WH 90 spectrometer.

[1] C. Cambillau, G. Bram, J. Corset, C. Riche, and C. Pascard-Billy, *Tetrahedron*, 1978, **34**, 2675.

[2] J. M. Lehn, *Pure Appl. Chem.*, 1980, **52**, 2303.

[3] C. Cambillau, G. Bram, J. Corset, and C. Riche, *Nouv. J. Chim.*, 1979, **3**, 9.

[4] A. Regis and J. Corset, *Chem. Phys. Lett.*, 1975, **32**, 462; M. Raban and D. Haritos, *J. Am. Chem. Soc.*, 1979, **101**, 5178, and references therein.

[5] Y. M. Cahen, J. L. Dye, and A. I. Popov, *J. Phys. Chem.*, 1975, **79**, 1289, 1292, and references therein.

[6] Recently, G. Fraenkel *et al.* have detected triple ions of peralkylcyclohexadienyl-lithium compounds at −40 °C by ^{7}Li n.m.r. spectroscopy (personal communication; to be published).