N.M.R. Spectrum of Na^- in Sodium–Hexamethylphosphoric Triamide Solutions

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Summary The ^{23}Na n.m.r. spectrum of the sodium anion in solutions of sodium in hexamethylphosphoric triamide is reported, and gives the first direct indication of a genuine sodium anion formed in a metal solution without added cation-complexing agents.

THE existence of alkali-metal anions in the gas-phase has been recognised for over 30 years.[1,2] In 1953 Bingel[3] gave a guarded prediction that the species Na^- was possibly a major component in sodium–ammonia solutions. On the basis of the metal-, solvent-, and temperature-dependence of visible absorption spectra, the existence of alkali-metal anions in metal–amine solutions has also been proposed.[4] There is currently no conclusive experimental evidence for genuine metal anion species in metal–ammonia solutions (see, for example, refs. 5 and 7). In contrast Dye and his collaborators[5] isolated a crystalline salt of Na^- from solutions of sodium in ethylamine containing the added cation-complexing agent 2,2,2-cryptand. Ceraso and Dye[6] have also reported the characteristic n.m.r. spectra of the sodium anion in metal–solvent–cryptand systems. However, the presence of these (added) cation-complexing agents may alter the basic integrity of electronic states, both paramagnetic and diamagnetic, in metal solutions. In our view the solvent hexamethylphosphoric triamide (HMPA) by itself appeared to fulfil many of the requirements generally sought[7] from macrocyclic complexing agents: high metal solubility *via* cation complexation, stability to electron reduction, weak anion-solvation, *etc.* We report preliminary studies to determine whether genuine metal anions do indeed exist in simple two-component metal solutions.

Sodium–HMPA solutions were prepared under stringent high vacuum conditions ($< 10^{-5}$ Torr); experimental procedures will be published later. ^{23}Na ($I = 3/2$, abundance 100%) n.m.r. spectra were recorded on a Jeol FX-90Q pulsed Fourier transform spectrometer operating at 23·6 MHz. Resonance shifts (uncorrected for bulk susceptibilities) were measured relative to a solution of NaCl in

TABLE. ^{23}Na Chemical shifts and line widths.

Ion	Temp./K	Solvent	δ/p.p.m.	$\Delta\nu_{\frac{1}{2}}$/Hz	Ref.
Na^+(NaCl)	298	D_2O	reference	32	a
Na^+(NaCl)	274	HMPA	+3·9	30	a
	298		+3·8	30	
Na^-	—	Gas	−63·8 (calc.)	—	Cited in ref. 8
Na^- (Na^+C, Na^-)[b]	258	$MeNH_2$	−62·6	11	6, 8
Na^- (Na^+C,Na^-)	256—274	$EtNH_2$	−62·8	6 to 11	6, 8
Na^-	274	HMPA	−61·7	10	a
	263		−62	13	

[a] This work. [b] C ≡ 2,2,2-cryptand.

D_2O, negative shifts corresponding to an increase in nuclear shielding. We adopt this convention to minimise possible confusion with the magnetic properties of species which may properly be termed paramagnetic or diamagnetic (*i.e.* $e^-_{solv.}$ *etc.*).

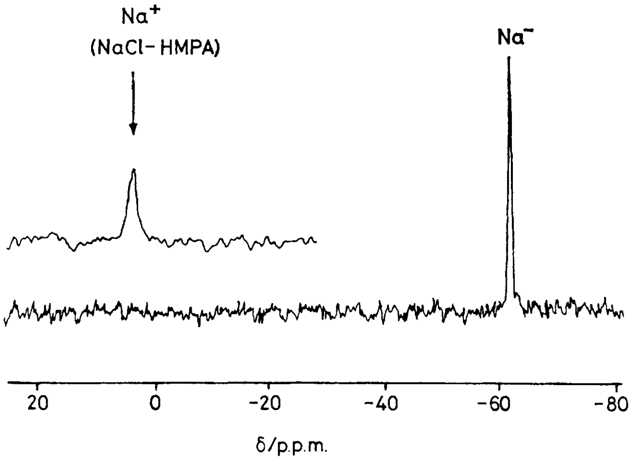

FIGURE. ^{23}Na N.m.r. spectrum of a solution of Na in anhydrous HMPA at 274 K. Chemical shifts are referenced to a solution of NaCl in D_2O.

The Figure shows a representative spectrum from an Na–HMPA solution at 274 K together with the signal from a solution of NaCl in HMPA. Our experimental resonance shifts (δ) and peak-widths at half height ($\Delta\nu_{\frac{1}{2}}$) are compared in the Table with the earlier results[8] for solutions of sodium in anhydrous methylamine and ethylamine in the presence of 2,2,2-cryptand.

The signal from Na^+ in the NaCl–HMPA solution is rather broad ($\Delta\nu_{\frac{1}{2}} = 30$ Hz), and suggests that the symmetry of the array of solvent molecules around the cation is lower than tetrahedral. This is reasonable in view of the bulk of the HMPA molecule. The observed shift of +3·8 p.p.m. (deshielded) for Na^+ in the NaCl–HMPA solution is in agreement with earlier studies[9] and is consistent with the very high electron lone-pair donating ability[10] of HMPA. In contrast no resonance was observed from Na^+ in Na–HMPA possibly owing to its extreme width in the paramagnetic solution.[7]

A signal shifted some 62 p.p.m. to low frequency of the external reference in Na–HMPA has a width of only 10 Hz. Both features are symptomatic of a genuine sodium anion in the Na–HMPA system. Most noteworthy, the virtual absence of a solvent-induced decrease in the nuclear shielding for Na^- (Table) indicates[6,7] that the metal anion is truly 'gas-like' in that the sodium 2p-electrons are effectively shielded from solvent interactions by the presence of two spin-paired electrons in an almost unperturbed 3s-orbital on the metal. The relative widths of the n.m.r. signal from Na^+ in NaCl–HMPA and Na^- in Na–HMPA then suggest that exchange processes of the type (1) are more rapid than

$$^*Na_se_s^- + Na_s^+ \rightleftharpoons {}^*Na_s^+ + Na_s^+e_s^- \qquad (1)$$

those of the type (2). This is indeed consistent with the

$$^*Na_s^+e_s^- + Na^- \rightleftharpoons {}^*Na^- + Na_s^+e_s^- \qquad (2)$$

observed n.m.r. spectrum, and also with our recent generalised treatment[11] of ion-pairing and e.s.r. of metal solutions which yields an average lifetime for the Na_s^+–e_s^- encounter process of *ca.* 10^{-11} s at 298 K. However, a more detailed concentration study is required to probe the overall exchange processes in these systems.

We note that the currently accepted chemical definition of a metal[12] is now in doubt, even for the 'prototype' group 1 alkali metals, and the controversial question as to what is a metal remains unanswered.[13]

We thank the S.R.C. for financial support and J. V. Acrivos for advice.

(*Received, 7th August* 1981; *Com.* 957.)

[1] V. M. Dukel'skii, E. Ya. Zandberg, and N. I. Ionov, *Dokl. Akad. Nauk. SSSR*, 1948, **62**, 232.
[2] T. A. Patterson, H. Totop, A. Kasdan, D. W. Norcross, and W. C. Lineberger, *Phys. Rev. Lett.*, 1974, **32**, 189.
[3] W. Bingel, *Ann. Physik.*, 1953, **12**, 57.
[4] S. Matalon, S. Golden, and M. Ottolenghi, *J. Phys. Chem.*, 1969, **73**, 3098.
[5] F. J. Tehan, B. L. Barnett, and J. L. Dye, *J. Am. Chem. Soc.*, 1974, **96**, 7203.
[6] J. M. Ceraso and J. L. Dye, *J. Chem. Phys.*, 1974, **61**, 1585.
[7] J. L. Dye, C. W. Andrews, and S. E. Mathews, *J. Phys. Chem.*, 1975, **79**, 3065; J. L. Dye in 'Progress in Macrocyclic Chemistry,' Vol. 1, Eds. R. M. Izatt and J. J. Christensen, Wiley–Interscience, New York, 1979, p. 63.
[8] J. L. Dye, C. W. Andrews, and J. M. Ceraso, *J. Phys. Chem.*, 1975, **79**, 3076.
[9] M. Herlem and A. I. Popov, *J. Am. Chem. Soc.*, 1972, **94**, 1431.
[10] V. Gutmann, 'Co-ordination Chemistry in Non-Aqueous Solvents,' Springer–Verlag, New York, 1968.
[11] R. Catterall, P. P. Edwards, J. Slater, and M. C. R. Symons, *Chem. Phys. Lett.*, 1979, **64**, 275.
[12] R. V. Parish, 'The Metallic Elements,' Longman, London, 1977.
[13] H. Davy, *Philos. Trans. R. Soc., London*, 1808, **98**, 1; N. F. Mott, *Nuovo Cimento* (*Suppl.*), 1958, **7**, 312; P. P. Edwards and M. J. Sienko, *J. Am. Chem. Soc.*, in the press.