The EPR Spectrum and Structure of the Mixed Alkali Metal Trimer Cluster Na_2Li Prepared using a Rotating Cryostat

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The EPR spectrum of the mixed alkali metal cluster Na_2Li in an adamantane matrix has the isotropic parameters $g = 2.001$, $a(2\ ^{23}Na) = 12.66$ mT and $a(^7Li) = 0.35$ mT indicating a static obtuse-angled structure with an apical lithium atom in C_{2v} symmetry with a $^2B_2$ ground state.

We have recently reported[1] the first observation of a mixed septameric cluster Na_2K_5 which is a pentagonal bipyramidal molecule and has a $^2A_2$ ground state in D_{5h} symmetry with 41% of the unpaired electron density in the 3s orbitals of the two apical sodium atoms. Here we report the first EPR spectrum of a mixed trimeric alkali metal cluster, Na_2Li, prepared in an adamantane matrix using a rotating cryostat.[2] The homonuclear trimeric alkali metal clusters Li_3, Na_3 and K_3 have been studied extensively by EPR[3,4] and provide interesting examples of both static and fluxional Jahn–Teller molecules. In an argon matrix, Na_3 and K_3 have been observed as rigid obtuse triangular structures, and as pseudo-rotating Jahn–Teller molecules.[3] In an adamantane matrix only a fluxional Na_3 cluster was observed.[4] Li_3 exists only as a fluxional molecule even at 4 K in both matrices.[3,4] [A laser Raman spectroscopic study by Moskovits and Mejean[5] in xenon indicated the presence of an acute-angled Li_3 cluster. This is static on the much shorter timescale of vibrational spectroscopy (10^{-12} s).] The obtuse structures have SOMOs with *ca.* 0.9 s-orbital character on the two terminal nuclei, while the fluxional forms have three magnetically equivalent nuclei with, again, a total s-spin density of *ca.* 0.9 for Na_3 and K_3 and 0.69 for Li_3. It is of interest to prepare and observe the mixed cluster Na_2Li in order to determine whether this molecule is fluxional or static and has either the lower total s-spin density as in Li_3 (0.69) or the much higher value of 0.9 as in Na_3 and K_3.

Mixtures of sodium and lithium (1 : 4 to 1 : 6; only at these ratios was the yield of mixed cluster significant) were alloyed and vaporised from a resistively heated Knudsen cell (890–930 K) to produce monatomic mixed vapours of both metals. These vapours were condensed rapidly on to the cold surface of an adamantane matrix deposited on the surface of the rotating drum from a previous jet. After 20 min the deposit, several millimetres deep and containing 0.01–0.1% alkali metal, interleaved into an adamantane spiral, was transferred from the surface of the drum into an EPR tube still at 77 K and $< 10^{-6}$ Torr. No mixed clusters were generated when sodium and lithium were deposited separately on to the matrix in close sequence (approx. 10^{-3} s) from individual adjacent Knudsen cells.

Fig. 1 shows the composite EPR spectrum at 77 K of a deposit prepared from a sodium–lithium alloy. Although complex, the complete spectrum can be analysed by comparing it with spectra obtained from depositing sodium and lithium alone. The prominent central feature is the conduction EPR (CEPR) band from very large clusters and colloidal particles.[6] The transitions *a* and *b* arise from sodium and lithium atoms trapped in a range of matrix sites, while lines *c* and *d* are those from the fluxional homonuclear Na_3 and Li_3 clusters.[4] This leaves transitions *x* whose prominent features are most clearly observed away from the congested centre of the spectrum. These lines were observed *only* when both sodium and lithium were co-vaporised, showing that they arise from a mixed sodium–lithium cluster. (Transitions *y* also arise from a mixed Na–Li cluster or clusters, but have not yet been fully assigned.) Unfortunately, annealing of the sample did not reduce the congestion in the central region of the spectrum since the mixed cluster was no less labile than the homonuclear trimers Li_3 and Na_3 and the trapped sodium and lithium atoms. Nevertheless, annealing did result in a markedly enhanced resolution of the outer, unoverlapped mixed cluster transitions, particularly the outer pair ($M_I = \pm3$). The clear quartet of lithium hyperfine lines at 170 K is shown in the inset of Fig. 1.

The isotropic spectrum of the mixed cluster arises from a doublet moiety, tumbling rapidly in the adamantane matrix, which shows an equal, large hyperfine interaction (hfi) with two equivalent ^{23}Na nuclei ($I = 3/2$) and a much smaller interaction with a single ^7Li nucleus ($I = 3/2$). The hfi with the two sodium nuclei is so large that second order effects are significant and result in a complete separation of the $(2I + 1)^2$ lines, so that sixteen rather than the seven lines expected from the high field approximation result. An exact solution of the spin hamiltonian gives the following EPR parameters: $g_{iso} = 2.001$ and $a(2\ ^{23}Na) = 12.66$ mT. The predicted line positions[†] based on these parameters are shown in the stick diagram below the experimental spectrum in Fig. 1. All molecular orbital calculations show that this distribution of spin density can result only from an obtuse angled molecule with a $^2B_2$ ground state in C_{2v} symmetry with the two sodium nuclei in terminal positions.[3] There is little indication of lithium hfi in the 77 K spectrum, but at 170 K a fully resolved quartet with a spacing of 0.35 mT is clearly evident (Fig. 1). This indicates that the carrier has one lithium atom, *i.e.* the cluster being observed is NaLiNa with an

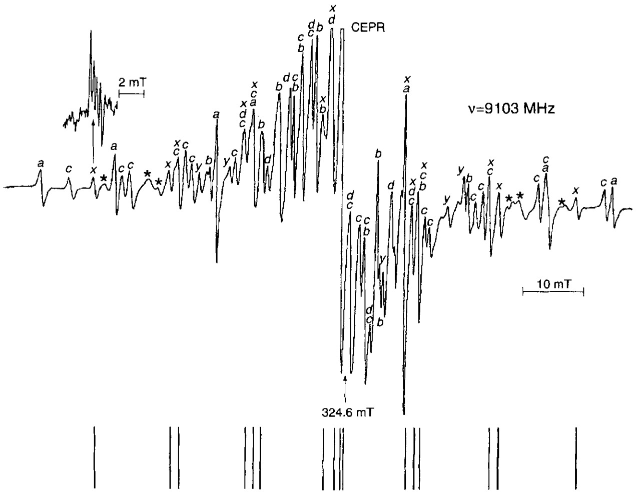

Fig. 1 EPR spectrum of the sample produced from the vaporisation of a Na–Li alloy into an adamantane matrix at 77 K. The transitions are assigned as follows: (*a*) Na atoms; (*b*) Li atoms; (*c*) fluxional Na_3; (*d*) fluxional Li_3; (*x*) Na_2Li; (*y*) unassigned Na/Li cluster; (*) unassigned transitions arising from a sodium species. Transitions *x* and *y* are not observed when sodium and lithium are deposited alone at similar concentrations. The stick diagram indicates the predicted line positions based upon the EPR parameters given in the text. The inset shows the $M_I = +3$ transition of the Na_2Li cluster in expanded scale after annealing to 170 K.

obtuse structure having the lithium atom at the central position.

Dividing the observed hfi by the one electron parameters for unit spin density in sodium 3s and lithium 2s orbitals gives spin densities of 0.40 for each sodium nucleus and 0.02 at the lithium nucleus. Assuming the spin density on the lithium is negative, since it probably arises by spin polarisation, gives a total s-spin population of 0.78. This lies between the values of 0.90 and 0.69 for Na_3 and Li_3, respectively. The departure from unity of the total s-spin population indicates a substantial p contribution to the SOMO which is also consistent with a small negative shift in the g value ($\Delta g = -0.0013$).

Unlike all the other alkali metal trimers in adamantane, the mixed trimer Na_2Li has a static obtuse-angled geometry, similar to that of the homonuclear trimer clusters of the coinage metals Ag_3,[7] Cu_3[8] and Au_3.[9] The three identical wells along the rim of the 'Mexican Hat' potential surface for the homonuclear trimers is replaced by a contour with two isometric shallow wells with one sodium at the apical position and one much deeper well with lithium at this unique position. This accords with the theoretical Diatomics in Molecules (DIM) calculations of Dixon and coworkers[10] which predict the most stable Na_2Li structure to have a lithium-centred obtuse structure with a bond angle of 100°. This NaLiNa configuration is calculated to have the highest binding energy with respect to dissociation into three atoms of 120 kJ mol^{-1}, compared to 112 kJ mol^{-1} for LiNaNa. Interestingly, the most stable trimer is predicted to be LiNaLi (binding energy 137 kJ mol^{-1}) and it is possible that this trimer is the carrier of the, as yet, unassigned transitions y, indicated in Fig. 1, which are presently being analysed. Theoretical calculations of the spin density distributions in these mixed trimeric clusters are clearly needed and are being undertaken in our laboratories.

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