A New Potassium Cluster in Zeolites X and A

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The reaction of potassium vapour with zeolites K-X and K-A gives rise to a new ionic cluster, K_3^{2+}.

Although the ability of zeolites to stabilize charged clusters such as Na_4^{3+},[1] and Ag_6^{n+},[2] is well established, the extension of this work to prepare clusters of metals other than silver and sodium has been limited.[3,4] Here we report the observation of a new potassium cluster whose ESR spectrum is consistent with the formulation K_3^{2+}.

The reaction of potassium vapour with zeolites K-X and K-A was carried out in sealed, evacuated quartz reaction tubes, as described earlier by Harrison *et al.*[4] First and second derivative ESR spectra were recorded on a Varian E-109 spectrometer operating at X-band frequencies with 100 kHz field modulation. Exposure of the dehydrated zeolites to potassium vapour at temperatures between 200 and 250 °C caused the white solids to assume an intense blue colour. The ESR spectra of these compounds at room temperature (298 K) and 77 K are shown in Figs. 1 and 2. In both cases at room temperature the spectrum consisted of a strong resonance at $g = 1.9992 \pm 0.0001$ with a peak-to-peak linewidth of *ca.* 5 G, which could not be saturated with the microwave power available. These lines are similar to those previously ascribed to small metallic clusters of potassium in zeolite Y.[3-5] In the case of K-X the line was symmetric, but in K-A its shape was complex, probably as a result of the presence of an additional, narrower resonance. In both cases when the samples were cooled to 77 K these signals were joined by a pattern of ten lines with hyperfine splitting $a = 12.8 \pm 0.2$ G.

A pattern of ten lines is expected for an unpaired electron interacting with three equivalent potassium ions, and indeed the spectra in Fig. 3, simulated on this basis, are good reproductions of those observed from K/K-X (Fig. 1). There are two possible candidates for the origin of this ESR spectrum: a K_3 molecule like that observed in frozen argon matrices,[6] or an ionic cluster K_3^{2+} similar to the K_4^{3+} that occurs in K/K-Y.[3,4] Possessing only one valence electron, K_4^{3+} may also be regarded as a single electron trap, whose formation may be written as shown in eqn. (1), where M = Na, K or Rb.[3] That the spectrum of ten lines in K-X and K-A was observed only in samples containing modest amounts of additional potassium, and therefore many more potassium cations than potassium atoms, suggests that K_3^{2+} is the more likely source. Support for this view comes from the observa-

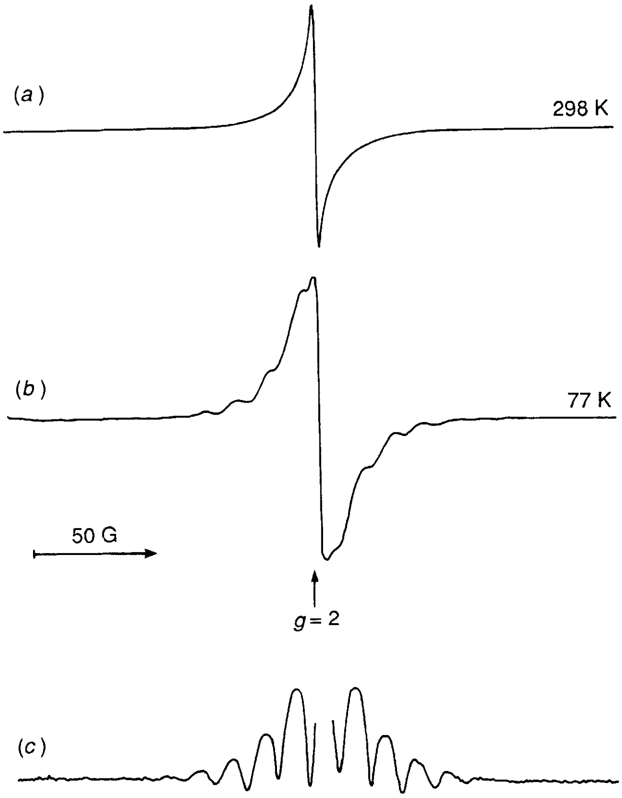

Fig. 1 The first derivative ESR spectrum of K/K-X at (*a*) 298 K, and (*b*) 77 K. Also shown (*c*) is the second derivative spectrum at 77 K.

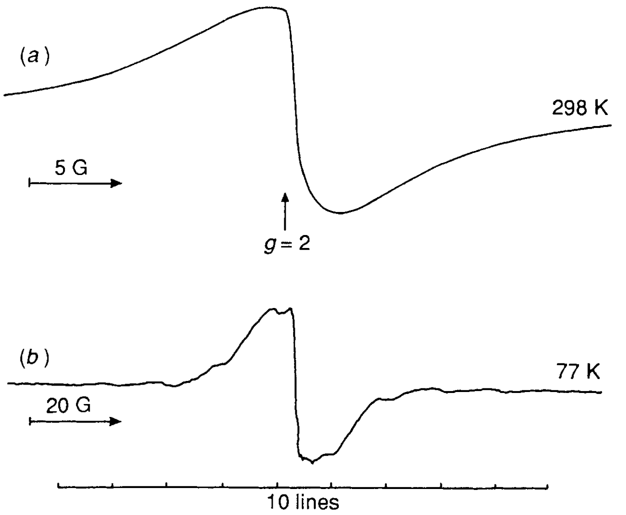

Fig. 2 The first derivative ESR spectrum of K/K-A at (*a*) 298 K, and (*b*) 77 K

tion that the hyperfine splitting of the spectrum in zeolites was just over half that of K_3 trapped in frozen argon.[6] The presence of the identical hyperfine pattern in both zeolites X and A is strong evidence that the cluster, like Na_4^{3+} and K_4^{3+},[4] is located in the sodalite cage structural unit, which is common to both.

$$M^0\,(\text{vapour}) + 4K^+\,(\text{zeolite}) \rightarrow M^+\,(\text{zeolite}) + K_4^{3+}\,(\text{zeolite}) \qquad (1)$$

The 'percentage atomic character' of the cluster may be obtained through the comparison of its hyperfine splitting with that of a potassium atom. The hyperfine splitting of the cluster is just less than 16% of that of the free atom, but allowing for the fact that the unpaired electron interacts with three potassium ions, the value obtained is 47% (compared with 90% for K_3 in argon), similar to those of F-centres in potassium halides.[7] This low value in the new K_3^{2+} cluster may be taken as a measure of the tendency for the electron to occupy the space between the ions, and so the cluster may be pictured as an excess electron trapped, but substantially delocalized, within a sodalite cage containing three potassium ions. It is important to note that, in both K/K-X and K/K-A, the ESR spectrum of the new ionic cluster K_3^{2+} can be observed only at low temperatures. It is not yet clear whether the loss of the hyperfine pattern at temperatures above 77 K arises from a more extensive delocalization of the electron spins into other parts of the zeolite structures, or whether it is a product of thermally induced line broadening as a result of enhanced electron spin relaxation.

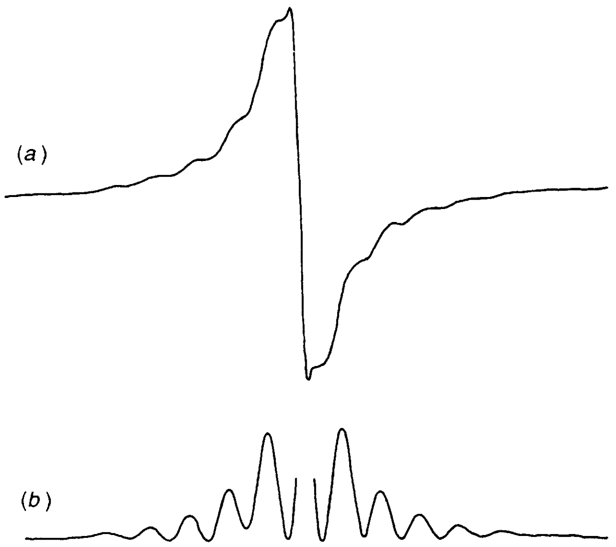

Fig. 3 The simulated ESR spectrum of K/K-X at 77 K: (*a*) first, and (*b*) second derivative. The spectrum comprises both a contribution from an electron interacting with three equivalent potassium ^{39}K ions (93% abundant) and a symmetric singlet signal.

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