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Chemical Effects of Osmium Neutron Capture Recoils. III. Cation Effect in Crystalline Mixtures of $K_4Os(CN)_6$-$K_4Fe(CN)_6$-$Cs_4Fe(CN)_6$

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Changes in retention between crystals with different cations and the same Szilard-Chalmers component have been attributed to a cation effect. The effect is closely associated in many cases with that of changing crystal structure and thermal effects. The latter refers to the thermal response of the lattice and its effect on product distribution and is thought to differ for each crystalline modification. Studies of the effects of changing crystalline environment or cations have made us to realize the importance of certain factors involved.[1–5]

Observations with a wide variety of crystalline compounds[1] have shown that compounds with a similar crystal structure but different cations or Szilard-Chalmers elements show large variations in initial parent retention, so that cation effects may be more important than crystal structure effects. The role played by the cation in the retention reaction is not completely understood. Although the effect has been interpreted in certain cases as one of electron affinity of the cation,[5] and in others as being attributable to the state of hydration of the crystal,[2] the results do not agree. Explanations were given based on the differences due to radiation dose effects and to radiation chemical processes resulting from cation activation,[6] or to cage effects arising from differences in the masses of surrounding atoms or ions.[4]

We have studied osmium recoil effects in crystalline mixtures of the type $K_4Os(CN)_6$–$K_4Fe(CN)_6$–$Cs_4Fe(CN)_6$ in order to investigate the role of the cation in diluted systems. Crystals of the pure components were either available commercially or prepared as previously described.[7] Crystalline mixtures of $K_4Os(CN)_6$–$K_4Fe(CN)_6$–$Cs_4Fe(CN)_6$ containing a fixed Os– to Fe– mole ratio (1: 1) and cesium to potassium mole ratios ranging from 0: 1 to 1 : 1 were precipitated from a hot saturated solution of pure components by adding absolute alcohol. Each mixture was then filtered, washed several times with alcohol, and vacuum dried at about 100 °C. Chemical analysis of each mixture agrees well with the composition of the solution of pure components. X-Ray powder diffraction spectroscopy of the pure components and their mixtures show that the X-ray pattern for $Cs_4Fe(CN)_6$ differs from that for $K_4Fe(CN)_6$ and $K_4Os(CN)_6$; the mixture gives diffraction lines which is not properly related to the pure components.[8] This indicates that the cesium and potassium salts are not isomorphous and hence their crystalline mixtures are not true mixed crystals.

Neutron irradiations were carried out at a thermal neutron flux of 1.8×10^{12} n/cm^2/s, fast neutron flux of 1.8×10^{12} n/cm^2/s and gamma ray dose rate of about 1.4×10^7 rad/hr. The potassium-cesium salt mixtures were each irradiated for 6.0 hr and then analyzed by paper electrophoresis.[7] The duration of the electrophoretic separation was three hours and the counting of paper strips started several hours after the completion of irradiation in order to minimize the effect of any radiocesium contamination. The osmium activity appeared mainly in two peaks,[7,8] one due to OsO_2 remaining at the starting point and the other due to the parent peak migrating towards the anode. Since only the parent species should be stable in aqueous solution, it is believed that all partially reconstituted species hydrolyze or react immediately in solution to give OsO_2 and that most of the activity found in the parent peak actually comes from a cyanoosmate precursor present as such in the irradiated crystal.[7,8]

The results of cyanoosmate(II) parent retention determined as a function of $Cs_4Fe(CN)_6$ mole fraction in the cesium–potassium crystalline mixtures are given in Table 1. We see that replacement of cesium for potassium causes a large decrease in parent retention.

TABLE 1. CYANOOSMATE(II) RETENTIONS IN $K_4Os(CN)_6$–$K_4Fe(CN)_6$–$Cs_4Fe(CN)_6$ CRYSTALLINE MIXTURES WITH A FIXED 1:1 Os– to Fe– mol RATIO

$Cs_4Fe(CN)_6$ mole fraction	Cesium-to-potassium mole ratio	Percent retention
0.0	0.0	51±3
0.166	0.20	25±3
0.286	0.40	32±3
0.375	0.60	25±4
0.445	0.80	20±3
0.500	1.00	20±4

The observed decrease in cyanoosmate(II) retention due to the replacement of potassium by cesium cannot be explained on the basis of cage effects, as this would predict an increase in retention because of better caging around the recoil atom being provided by the massive Cs^+ ions. Potassium cation has a higher affinity for

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[1] G. Harbottle and N. Sutin, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 1, ed. by H. J. Emeleus and A. G. Sharp, Academic Press, New York (1959), p. 267.

[2] G. Harbottle, *J. Chem. Phys.*, **22**, 1083 (1954).

[3] T. Anderson and A. G. Maddock, *Radiochim. Acta*, **2**, 93 (1963).

[4] T. Anderson and A. G. Maddock, *ibid.*, **1**, 220 (1963).

[5] N. Saito, F. Ambe, and H. Sano, *ibid.*, **7**, 131 (1967).

[6] C. H. Collins, K. E. Collins, and C. M. Hyche, R53, 152nd, ACS Meeting, N.Y., Sept. 1966.

[7] E. M. Diefallah and J. G. Kay, *Radiochim. Acta* (in press).

[8] E. M. Diefallah, Ph. D. Thesis, Univ. of Illinois (Feb. 1968). Available from University Microfilms, Ann Arbor, Michigan, U.S.A.

electrons than cesium, and this could provide an explanation.[5] However, the increase in absorbed radiation dose and neutron activation with increasing cesium mole fraction in the crystalline mixtures causes excessive damage which may also account for the lowering in parent retention.

In general, the probability of parent reformation is not only determined by the density of lattice defects and radiation damage in the crystal, but also by the energy of activation for release from traps. It is believed that an increase in parent retention would correspond to an increased probability for an electron capture reaction by the parent precursor fragment taking place in the solid.[7] Changes in initial parent retention could be discussed on the basis of an electron acceptor-donor mechanism involving electron-hole traps and electron recombination centers. The energy of activation for defect release depends on the details of electronic structure of the solid which is determined by the crystal structure and types of cations, anions and ligands or the nature of the chemical bonds.[9] Thus it is expected that the more ionic cesium salt with a larger band gap would increase the trap depth and activation energy for reactions giving rise to initial retention. This interpretation is more reasonable than that based only on differences in density of lattice defects.

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[9] F. A. Kröger, "The Chemistry of Imperfect Crystals," North-Holland Publishing Co., Amsterdam, and Wiley, New York (1963).