Letters

Apparent short potassium–hydrogen distances in potassium fluoride–malonic acid

In their paper on $KF-CH_2(CO_2H)_2$ Emsley *et al.*[1] infer, from the positions assigned to some of the hydrogen atoms, that the crystal structure contains some very short H–F–H bonds, which they seek to explain by postulating the transfer of hydrogen atoms from the malonic acid molecules to give H–F distances as short as 0.70 Å. This conclusion should be received with caution because the final R value of the analysis (0.116) does, as the authors say, indicate ' uncertainty regarding the locations of the protons of the hydrogen bonds,' and the more so since they could not locate the C–H protons, which are usually more readily defined (by X-ray diffraction at room temperature) than are those in hydrogen bonds. However, a stronger reason for caution, not noted by Emsley *et al.*, is displayed in the Table, which shows (*a*) strands of hydrogen bonding as in ref. 1, p. 1181, and (*b*) potassium–hydrogen distances less than 3.2 Å. Such distances are very short for ions of like charge and certainly have not hitherto been found in the neighbourhood of potassium ions. Until this remarkable result can be explained it would seem premature to draw any conclusions about the nature of the hydrogen bonding in potassium fluoride–malonic acid.

Table. Strand distances (Å) with H···K distances <3.2 Å in square brackets

(*a*)	O(14) 0.95 H(014) 1.53 F(1) 0.92 H(011) 1.89 O(11)
(*b*)	[H(011) 2.56 K(3^{I}), H(011) 2.81 K(5^{I})]
(*a*)	O(24) 1.89 H(024) 0.70 F(2) 1.94 H(021) 0.66 O(21)
(*b*)	[H(024) 3.11 K(3^{II})]
(*a*)	O(34) 0.92 H(034) 1.54 F(3) 1.59 H(031) 0.89 O(31)
(*b*)	[H(024) 3.17 K(4^{II})]
(*a*)	O(44) 0.55 H(044) 2.47 F(4) 1.25 H(041) 1.65 O(41)
(*b*)	[H(041) 2.68 K(2^{III})]
(*a*)	O(54) 1.51 H(054) 1.13 F(5) 1.72 H(051) 0.84 O(51)
(*b*)	[H(054) 2.53 K(4^{II})]

Roman numeral superscripts define the relations: I x, $1-y$, $-\frac{1}{2}+z$; II x, y, $-z$; III x, $1-y$, $\frac{1}{2}+z$.

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1 J. Emsley, D. J. Jones, and R. Kuroda, *J. Chem. Soc., Dalton Trans.*, 1982, 1179.

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Emsley, Jones, and Kuroda reply. We are of course aware of the inaccuracies in the positions of the hydrogen atoms as described in our work on potassium fluoride–malonic acid. The reader can see this in Table 2 of our paper,[1] where the standard deviations of bond lengths involving hydrogens are an order of magnitude greater than those for bond lengths between the heavier atoms in the structure. That potassium–hydrogen interatomic distances are also in the former category comes as no surprise.

Whatever the uncertainty surrounding the location of the protons, the basic premise, that we have here a system with very short hydrogen bonds between oxygen and fluorine, remains unchallenged: $R(O\cdots F) = 2.41$—2.49 Å. We were perhaps rather rash in seeing in the hydrogen-atom locations evidence for proton transfer from the malonic acid to the fluoride ions. It seems likely that the compound contains strands of $\cdots HO_2C-CH_2-CO_2^- \cdots H-F \cdots$ rather than $\cdots HO_2C-CH_2-CO_2H \cdots F^- \cdots$ because this would fit with the observed loss of HF from the crystals as they decompose. Moreover, it is also in accord with the relative acidities of malonic and hydrofluoric acids. In the similar system potassium fluoride–succinic acid (H form,[2a] D form [2b]), proton transfer would not be expected and the hydrogen-atom locations, although again uncertain, indicate that this is so.

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1 J. Emsley, D. J. Jones, and R. Kuroda, *J. Chem. Soc., Dalton Trans.*, 1982, 1179.
2 (*a*) J. Emsley, D. J. Jones, R. S. Osborn, and R. E. Overill, *J. Chem. Soc., Dalton Trans.*, 1982, 809; (*b*) J. Emsley, D. J. Jones, and R. Kuroda, *ibid.*, 1981, 2141.