Chromium(II) Molybdenum(II) Tetra-acetate, [CrMo(OAc)$_4$]; A Metal(II) Carboxylate with a Heteronuclear Metal–Metal Bond

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Summary [CrMo(OAc)$_4$] has been prepared and characterised by elemental analyses, i.r. and Raman spectroscopy, and mass spectrometry; it probably contains a reasonably strong direct Cr^{II}–Mo^{II} interaction.

DIMERIC metal(II) carboxylates of general formula [M$_2$(O$_2$CR)$_4$] (M = Cr,[1] Mo,[2] Rh,[3], or Cu[4]) are well characterised. However, no compounds of this type containing two different metal atoms have been reported previously. In view of the strength of the Mo–Mo bond in such compounds[3] and the reasonable stability of the isoelectronic chromium derivatives, it seemed probable that [CrMo(OAc)$_4$] and related complexes should be isolable.

[CrMo(OAc)$_4$] has been obtained by the gradual addition of an excess of Mo(CO)$_6$ in AcOH–CH$_2$Cl$_2$ (5:1) to a refluxing solution of [Cr$_2$(OAc)$_4$(H$_2$O)$_2$] in AcOH–Ac$_2$O (10:1). The subsequent removal of solvent *in vacuo* afforded a pale yellow solid which was purified by sublimation (170 °C; 10^{-2} mmHg) to yield a pale yellow crystalline solid, which gave satisfactory analytical data. Its mass spectrum supports its formulation as [CrMo(OAc)$_4$] and contains a set of parent ion peaks centred at *m/e* 384 (^{96}Mo) together with sets of peaks corresponding to fragmentation of this ion. Using a 70 eV electron beam a weaker mass spectrum characteristic of [Mo$_2$(OAc)$_4$] was also obtained. The intensity of this latter spectrum may be reduced by using a 10 eV electron beam and the dimolybdenum species probably result from decomposition and recombination reactions at the source and/or on ionisation in the mass spectrometer. [CrMo(OAc)$_4$] exhibits a reasonably strong Raman effect at 394 cm^{-1} which may be assigned to the vibrational mode which involves Cr–Mo stretching; a band at the same frequency is also observed in the i.r. spectrum. However the presence of ν(Cr–O) stretching frequencies in the same region of the spectra suggest that this assignment may not be completely unequivocal. Assuming that the frequencies 406[5] and 394 cm^{-1} represent the stretching of the metal–metal bonds alone in [Mo$_2$(OAc)$_4$] and [CrMo(OAc)$_4$] respectively, the simple harmonic motion approximation suggests that the Cr–Mo force constant is 0·66 times that of the Mo–Mo one.

Consistent with this latter conclusion, preliminary studies of the reactions of [CrMo(OAc)$_4$] suggest that this metal–metal bond is more readily cleaved and less thermodynamically stable than corresponding Mo–Mo ones. Thus the title compound reacts with CF_3CO_2–$(CF_3CO)_2O$ at *ca.* 25 °C to afford a mixture which contains both [CrMo(O_2CCF_3)$_4$] and [$Mo_2(O_2CCF_3)_4$] and reaction with aqueous HCl (12M) at 0 °C produces $[Mo_2Cl_8]^{4-}$ as the only isolable product.

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