Evidence for Near-neighbour Interactions in Some Carboxymethyl Transition-metal Complexes

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THE chemistry of some simple organic groups which are σ-bonded to transition metals is frequently different from that of common organic analogues. For example, transition-metal alkyl derivatives readily loose a hydride ion when treated with triphenylmethyl salts. It has been suggested that the reactions are facilitated by a direct interaction between the metal atom and the carbon atom in the β-position,[1] *viz*:

We have prepared and studied acids of the type $M–CH_2·CO_2H$ in an attempt to find evidence for metal–β-carbon interactions. The acids, $M–CH_2·CO_2H$, where $M = \pi\text{-}C_5H_5(Mo \text{ or } W)(CO)_3$, $(Mn \text{ or } Re)(CO)_5$, or $\pi\text{-}C_5H_5Fe(CO)_2$ were prepared by hydrolysis of the corresponding amides and they all react with diazomethane giving methyl esters, *e.g.*,

$$M^- + ClCH_2·CONH_2 \longrightarrow M–CH_2·CONH_2 \xrightarrow{HClaq}$$

$$M–CH_2·CO_2H \xrightarrow{CH_2N_2} M–CH_2·CO_2Me$$

All the amides, acids, and methyl esters have been fully characterised. Determination of pK_a in water showed the iron acid ($pK_a = 6·7$) and manganese acid ($pK_a = 6·1$) to be unusually weak. Low solubility prohibited the determination of the pK_a's of the other acids in water, however determination in aqueous ethanol or aqueous tetrahydrofuran mixtures showed that rhenium acid is also a very weak acid whilst the molybdenum and tungsten acids are much stronger being about as acidic as benzoic acid. We have determined the crystal structure of the acids $\pi\text{-}C_5H_5Fe(CO)_2·CH_2·CO_2H$ and $\pi\text{-}C_5H_5Mo(CO)_3·CH_2·CO_2H$.

$\pi\text{-}C_5H_5Fe(CO)_2·CH_2·CO_2H$: triclinic, $a = 7·89 \pm 0·02$, $b = 7·89 \pm 0·02$, $c = 7·96 \pm 0·02$ Å, $\alpha = 101·7 \pm 0·02$, $\beta = 102·9 \pm 0·2$, $\gamma = 91·1 \pm 0·2°$, $D_m = 1·666$, Z = 2; space group $P\bar{1}$ (C_i^1 No. 2) Cu-K_α radiation, $\mu = 123$ cm.$^{-1}$, 1348 independent reflections estimated visually from Weissenberg film.

$\pi\text{-}C_5H_5Mo(CO)_3·CH_2·CO_2H$: monoclinic, $a = 6·82 \pm 0·02$, $b = 13·17 \pm 0·03$, $c = 12·27 \pm 0·03$ Å, $\beta = 92·7 \pm 0·2°$, $D_m = 1·853$, $Z = 4$; space group $P2_1/_n(C_{2n}{}^5$ No.14) Cu-K_α raidation, $\mu = 103·7$ cm.$^{-1}$, 1115 independent reflections estimated visually from Weissenberg film and corrected for absorption.

In both analyses the trial structure was derived from the sharpened Patterson function and refined by full matrix least-squares. The final residuals were 0·132 for the iron acid and 0·098 for the molybdenum acid. For heavy to light atom contacts the estimated standard distances in bond

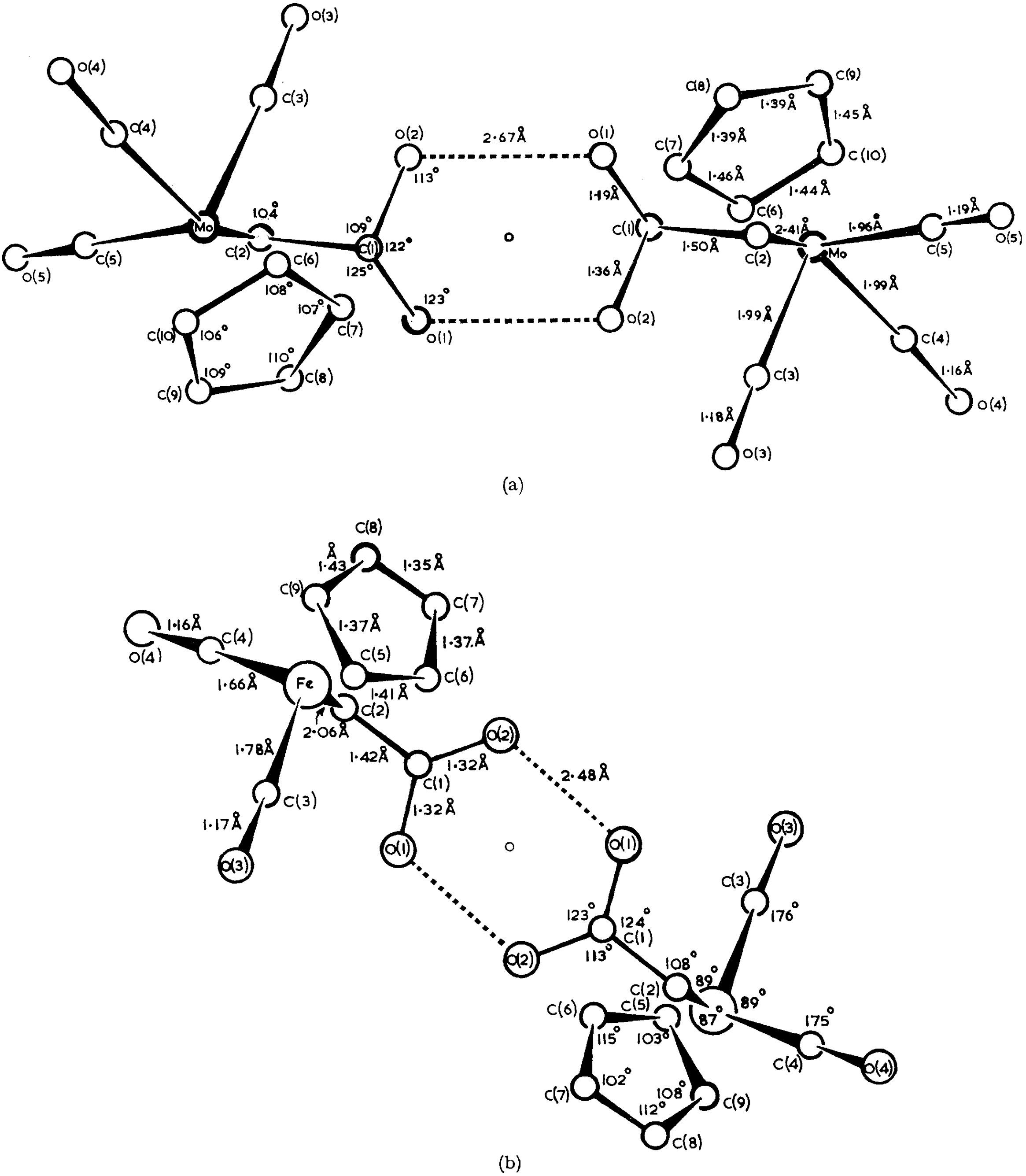
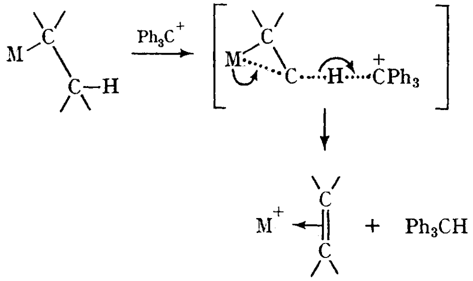


FIGURE. *The dimeric carboxymethyl derivatives of* (a) *molybdenum and* (b) *iron, each projected on to the least-squares best plane of the carboxylic acid groups. In both crystals the dimeric molecules lie at centres of symmetry.*

length are less than 0·02 Å and other contacts less than 0·035 Å. Both crystals are made up from hydrogen-bonded dimers, shown in Figures 1a and 1b, sited about the centres of symmetry. There are two points of particular interest in the molecular structure of the iron acid. The C–O distances of the CO_2H group are the same (1·32 Å) within the experimental error. Usually a difference of about 0·15 Å is found.[2] Also, the O · · · H · · · O distance (2·48 Å) is noticably shorter than is found in the majority of carboxylic acids. In contrast the C–O distances of the CO_2H group of the molybdenum acid are unequal (1·36 and 1·19 Å) as is normally the case and the O · · · H · · · O bond length (2·67 Å) is typical of that found in the large majority of carboxylic acid dimers.[2] It is reasonable to assume that the unusual structure found for the iron acid may be associated with the unusually low pK_a value of this acid especially, since the molybdenum acid, which in many respects is very similar to the iron analogue, has both a typical pK_a for a carboxylic acid and a normal structure. The anomalies found with the iron acid provide evidence for a direct interaction between the iron atom and the carbon atom of the carboxyl group. The interaction would result in the donation of electrons from the electron-rich low-oxidation state iron atom to the unsaturated CO_2H system. The CO_2H system would therefore become less unsaturated and it would be expected that the C–O bonds would take on a greater single bond character and would lengthen. In support of this postulate, it is found that the average of the two C–O distances for a wide range of carboxylic acids lies between 1·25—1·28 Å whereas a value of 1·32 Å is found for the iron acid. Also it has been found that 'unusually' short O · · · H · · · O distances are found in the compounds $M^+HX_2^-$, where M = Na or K and X^- is a carboxylate anion.[3] The weighted mean value of the O · · · H · · · O distance for this group of compounds is 2·446 Å. These short distances arise when a CO_2^- system is hydrogen bonded to a CO_2H group and perhaps an unusually high electron density on the carboxyl systems in the iron acids may give rise to short O · · · H · · · O distances similarly.

The normal pK_a and structure of the molybdenum acid show that no strong Mo–β-carbon interaction is present although, after the greater covalent radius of molybdenum is taken into account, the Fe–β-carbon distance (2·85 Å) is found not to be significantly shorter than the Mo–β-carbon distance (3·13 Å). The difference between the molybdenum and iron acids may be due to several factors. The molybdenum (and tungsten) acid is formally seven co-ordinate whilst the Re, Mn, and Fe acids are formally six co-ordinate. Therefore the molybdenum orbitals are more involved in direct bond formation than the metal orbitals of the weak acids. Differences in the energies of the metal orbitals may also be important.



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