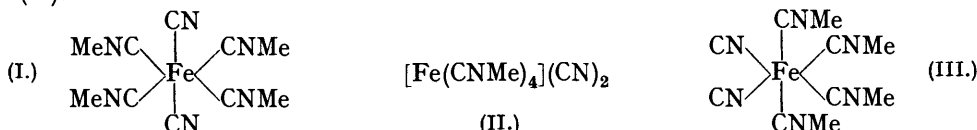


240. Co-ordination by Methyl isoNitrile : Structure of β -Tetramethyl Ferrocyanide.

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Hartley's β -form of tetramethyl ferrocyanide is shown by X-ray examination to be the *trans* six-co-ordinated compound with four methyl *isonitrile* molecules attached to iron by links similar to that found in the monometallic carbonyls.

Two isomers of composition $\text{Fe}(\text{CH}_3\cdot\text{NC})_4(\text{NC})_2$ were shown to exist by Hartley (J., 1913, 103, 1196) and were called the α - and the β -form. Hölzl, Hauser, and Eckmann (*Monatsh.*, 1927, 48, 71) also prepared similar compounds, but although they agreed with Hartley as to the properties of the α -isomer, the compound they described as the β -form was different from his. They attributed the isomerism to a change of co-ordination number, the α -form being regarded as the *trans* six-co-ordinated compound (I), and the β -form as a salt (II).



It was later shown by Hartley (J., 1933, 101) that his original α - and β -forms both gave hexa-alkylated compounds $[\text{Fe}(\text{CH}_3\cdot\text{NC})_4(\text{RNC})_2]\text{I}_2\cdot 2\text{HgI}_2$ (IV) on treatment with methyl or ethyl iodide and mercuric iodide. Crystallographic examination showed that the two hexamethyl compounds (IV; R = Me) were identical, but the tetramethyldiethyl compounds (IV; R = Et) from the two isomers were different. These facts, together with the known molecular weights in solution, agree with the suggestion that the α - and the β -form of tetramethyl ferrocyanide are *cis*- and *trans*-isomers, (I) and (III). In connexion with other work on these compounds it was necessary to know their configuration, and this has been determined by an X-ray examination.

Both isomers, the α especially, tend to take up solvent of crystallisation, but it was found possible to obtain crystals of the β -form free from solvent by use of *n*-propyl alcohol or *hot* methyl alcohol for recrystallisation. The material used was part of Hartley's original preparation (*loc. cit.*).

The crystals belong to the orthorhombic system. The unit cell dimensions, determined from oscillation photographs (copper radiation) are $a = 8.46$, $b = 13.24$, $c = 11.64$ Å., and, with the density (by flotation) 1.372 g./c.c., this gives four molecules per unit cell. No pyroelectric effect is detectable by the liquid-air method. Absent spectra are $hk0$ when h is odd, $h0l$ when l is odd, and $0kl$ when k is odd, and the space group is therefore *Pbca*. Only four-fold positions are available for the iron atoms, and since these lie in symmetry centres it follows that the molecule has the *trans*-form. In spite of solvent in the α -form, it has

been possible to show that it has the *cis*-configuration, but details are withheld pending completion of other work on the properties of this form.

The detailed Fourier analysis of the β -crystal structure, to be published elsewhere, shows that the $\text{CH}_3\cdot\text{NC}$ groups are linear and the compound therefore has four co-ordinated methyl isonitrile molecules attached to iron, the link being similar to that found in the metallic carbonyls: $\text{CH}_3\text{N}\equiv\text{C}\rightarrow\text{Fe}$ and $\text{O}\equiv\text{C}\rightarrow\text{Fe}$. The compound obeys the rule given by Sidgwick and Bailey (*Proc. Roy. Soc.*, 1934, A, 144, 521) applicable to the monometallic carbonyls and similar substances containing CN, CO, and NO groups, *i.e.*, that the effective atomic number (E.A.N.) of the metal shall be that of the next higher inert gas. In this case, covalent links with two CN groups, each contributing one electron, and four co-ordinate links from CH_3NC groups each contributing two electrons make up an E.A.N. of 36, thus conforming to the rule, and at the same time the compound achieves the co-ordination number six, which is impossible for the monometallic iron carbonyl. Cobalt, with one more electron than iron, co-ordinates only three $\text{CH}_3\cdot\text{NC}$ groups to form $\text{Co}(\text{CH}_3\cdot\text{NC})_3(\text{CN})_3$, also obeying the rule. This suggests the possibility of the existence of similar manganese and chromium compounds, $\text{Mn}(\text{CH}_3\cdot\text{NC})_5(\text{CN})$ and $\text{Cr}(\text{CH}_3\cdot\text{NC})_6$, the latter analogous to chromium hexacarbonyl. This chromium compound would be of interest if an accurate determination of the chromium-carbon distance could be made. In order to account for the abnormal metal-carbon distance in the monometallic carbonyls (Brockway, Ewens, and Lister, *Trans. Faraday Soc.*, 1938, 34, 1350), it has been necessary to postulate some double-bond character in the link with resonance between the structures $(\text{OC})_5\text{Cr}:\text{C}::\text{O}:$ and $(\text{OC})_5\text{Cr}::\text{C}::\ddot{\text{O}}:$, but it is unlikely that a similar resonance could occur if CH_3NC groups replace CO, since in the double-bonded form the atoms would not occupy similar linear positions to those in the triple-bond form, because there must be bending at the nitrogen atom with only three bonds $\text{Cr}=\text{C}=\ddot{\text{N}}\backslash\text{CH}_3$. A greater chromium-carbon distance than that found in chromium hexacarbonyl would therefore be evidence for the reality of the double-bond effect.

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