



the thiocyanate bridge is formed through both the sulphur and nitrogen atoms. We have therefore examined its infra-red spectrum and find that the SCN stretching vibration frequency ($2,149 \text{ cm.}^{-1}$) is closely similar to those observed in our isomers (α , $2,162 \text{ cm.}^{-1}$; β , $2,169 \text{ cm.}^{-1}$). This supports the possibility of bridging by $\text{Pt}-\text{S}-\text{C}\equiv\text{N}\rightarrow\text{Pt}$ in our isomers, and if they have structures (II) and (III) we might expect (III) to be the unstable α -isomer.

We have now examined the structure of the α -isomer by X-rays and do indeed find that it has structure (III). Until we know the structure of the β -isomer, which is now under investigation, the exact nature of the isomerism is uncertain, but it is not a geometrical isomerism of the type previously proposed².

We have sought this type of isomerism in other similar complexes and find that the tetrathiocyanate (I; $A=B=C=D=\text{SCN}$) also exists in two isomeric forms. In this case the unstable form is too labile to be isolated in a pure condition.

Full details will be published elsewhere.

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¹ Chatt, J., and Hart, F. A., *Nature*, **169**, 673 (1952).

² Chatt, J., and Duncanson, L. A., *Nature*, **173**, 997 (1956).

³ Lindqvist, I., *Acta Cryst.*, **10**, 29 (1957).

A New Superstructure in Gamma-Ferric Oxide

SINCE 1935 it has been generally accepted that gamma-ferric oxide has the structure of magnetite (spinel structure) with cation vacancies¹. The vacancies were assumed to be randomly distributed on all octahedral iron sites of magnetite. Magnetite contains 8 molecules of Fe_2O_3 in the face-centred cubic unit cell and has the space group $Fd\bar{3}m$. Gamma-ferric oxide contains $10\frac{2}{3}$ molecules of Fe_2O_3 in the unit cell. Due to the occurrence of a number of extra reflexions in the X-ray diagram of gamma-ferric oxide also occurring in the diagram of ordered lithium ferrite $\text{Fe}_8[\text{Li}_4\text{Fe}_{12}]\text{O}_{32}$, and to the fact that the material he used contained some water, P. B. Braun² of this Laboratory suggested that in these gamma-ferric oxide specimens the same super-

structure occurs as in ordered lithium ferrite. The ideal composition for ordering would be $\text{Fe}_8[\text{H}_4\text{Fe}_{12}]\text{O}_{32}$. For compositions between $\text{Fe}_8[\text{H}_4\text{Fe}_{12}]\text{O}_{32}$ and $\text{Fe}_8[(\text{Fe}_{14}\square_{2\frac{2}{3}})\text{Fe}_{12}]\text{O}_{32}$ the same superstructure reflexions were observed. (The square brackets [] denote the cations on octahedral sites, the ordinary brackets () those on the Li-sites in ordered LiFe_8O_8 .)

If the $1\frac{1}{3}$ Fe-atoms and the $2\frac{2}{3}$ vacancies are randomly distributed on the positions of the four lithium atoms in ordered lithium ferrite the space group of gamma-ferric oxide would be the same as that of ordered lithium ferrite, namely, $P4_13$ (or $P4_33$). This is a sub-group of $Fd\bar{3}m$. The extra reflexions found by Braun are compatible with a primitive cubic unit cell, but not with the face-centred cubic cell of spinel.

In the X-ray diagrams of a number of commercial samples of gamma-ferric oxide of different origin and in the diagrams of a number of our own preparations we have found a faint reflexion between $\Sigma h^2 = 6$ and $\Sigma h^2 = 8$. In order to be certain that this reflexion is not caused by an impurity we prepared³ gamma-ferric oxide by decomposing very pure ferrous oxalate dihydrate in an atmosphere of steam and nitrogen followed by oxidation with a mixture of nitrogen and air at 250°C . The water content is less than one-half weight per cent.

In the X-ray diagram made of this material on a 'Norelco' diffractometer with cobalt K_α radiation, even the strongest reflexion of alpha-iron oxide could not be detected. Beside the superstructure reflexions found by Braun, the reflexion between $\Sigma h^2 = 6$ and $\Sigma h^2 = 8$ mentioned above and fourteen others between 12° and 46° (2θ) have been found.

It has been possible to assign indices to all the reflexions using a tetragonal unit cell having $c/a = 3$ and $a_0 = 8.33 \text{ \AA}$. Absence of the reflexions $00l$ with $l \neq 4n$ points to a fourfold screw axis with a translation of $\frac{1}{4}c$. There are no indications of a non-primitive unit cell.

On the assumption that the structure is still practically that of spinel, the new unit cell must contain 32 molecules of Fe_2O_3 , and the space group is $P4_1$ (or $P4_3$). This is a subgroup of $P4_13$.

The position of the $3 \times 1\frac{1}{3} = 4$ iron atoms and the $3 \times 2\frac{2}{3} = 8$ vacancies distributed on the $3 \times 4 = 12$ lithium sites is determined by the fourfold screw axis. (Iron at $4a$: x, y, z ; $\bar{x}, \bar{y}, \frac{1}{2} + z$; $\bar{y}, x, \frac{1}{2} + z$; $y, \bar{x}, \frac{1}{2} + z$.) A verification of the proposed structure by calculation of the intensities is in progress and will be published in detail.

In the course of the present work a paper by R. Collongues came to our attention⁴. He found a number of superstructure lines compatible with a tetragonal unit cell with $c/a = 2$. The discrepancy between his and our results is due to the fact that he has observed a smaller number of extra reflexions and because his samples contain alpha-ferric oxide.

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² Braun, P. B., *Nature*, **170**, 1123 (1952).

³ British Patent 688903.

⁴ Collongues, R., thesis (Paris, 1957).