

The Garnet-Like Cyanide Framework of Ammonium Ferrocyanide Hydrate† with a Channel System for Ionic Conductivity‡

BY ERWIN HELLNER AND ELKE KOCH

Institut für Mineralogie, Universität, 3550 Marburg, Federal Republic of Germany

(Received 6 May 1981; accepted 14 July 1981)

Dedicated to Professor Heinz Jagodzinski on the occasion of his 65th birthday

Abstract

The CN dumb-bells in the cyanide framework of ammonium ferrocyanide hydrate occupy almost exactly the O positions in the garnet structure. In contrast to other crystal structures with a garnet-like framework all large voids are filled up. Two interpenetrating systems of channels are formed by the voids with centers at 16(b) $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$, i.e. a Y^{**} configuration, and at 24(c) $0, \frac{1}{4}, \frac{1}{8}$, i.e. a V^* configuration. These voids are occupied by one quarter of the NH_4^+ ions and by the H_2O molecules, respectively.

Introduction

According to an NMR study of Whittingham, Connell & Huggins (1972) crystals of ammonium ferrocyanide hydrate show ionic conductivity. The authors could not distinguish, however, between NH_4^+ and H^+ motions.

In order to obtain more information on the transport mechanism, Morosin (1978*b*) solved the crystal structure (Table 1). He found space group $Ia3d$ with lattice constant $a = 18.261 \text{ \AA}$. The coordinates of N and C reported by Morosin have been transformed by $-x, \frac{1}{2} - y, z$.

For the point position of $NH_4(2)$ the information 48(g) $\frac{1}{8}, 0.2074$, given by Morosin, is not sufficient. Apparently, it must be interpreted not as $\frac{1}{8}, x, \frac{1}{4} - x$, but as $\frac{1}{8}, x, \frac{3}{4} - x$ or $\frac{1}{8}, \frac{1}{2} - x, \frac{3}{4} - x$. For the distribution of H_2O and NH_4^+ on the positions 16(b), 24(c), and 48(g), Morosin does not exclude the possibility of some disordering. He describes the crystal structure as consisting of $Fe(CN)_6^{4-}$ ions loosely packed with NH_4^+ and H_2O groups. With the aid of distance calculations he shows the unlikelyhood of an H^+ ion transport mechanism [as found in $HUO_2PO_4 \cdot 4H_2O$ (Morosin, 1978*a*)] that is based on a network of hydrogen

Table 1. Positional parameters for $(NH_4)_4[Fe(CN)_6] \cdot 1.5H_2O$ according to Morosin (1978*b*)

	Position	x	y	z
N	96(h)	-0.0395	0.0557	0.1525
C	96(h)	0.0255	0.0354	0.0946
Fe	16(a)	0	0	0
H_2O	24(c)	0	$\frac{1}{4}$	$\frac{1}{8}$
$NH_4(1)$	16(b)	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$
$NH_4(2)$	48(g)	$\frac{1}{8}$	0.2926	-0.0426

bondings. He proposes spiral paths connecting the H_2O positions and the $NH_4(1)$ positions. The description of these paths, however, is not very clear.

Morosin also extends the NMR measurements of Whittingham *et al.* to lower temperature. He confirms the former results but he is not able to distinguish between the motion of NH_4^+ and H_3O^+ ions.

In the following the crystal structure will be described in more detail, and its analogy to the garnet framework will be shown. Two interpenetrating systems of channels which contain the positions of H_2O and $NH_4(1)$ will be discussed with respect to ionic conductivity.

Description of the cyanide framework

The coordinates of the N atoms of the cyanide groups in $(NH_4)_4[Fe(CN)_6] \cdot 1.5H_2O$ are similar to those of the O atoms in grossularite (Abrahams & Geller, 1958):

$(NH_4)_4[Fe(CN)_6] \cdot 1.5H_2O$	N	-0.0395	0.0557	0.1525
$Ca_3Al_2Si_3O_{12}$	O	-0.0389	0.0456	0.1524

The F^- ions in cryolithionite, $Na_3Al_2Li_3F_{12}$, (Geller, 1971) build up a framework analogous to the O framework in garnet. The F coordinates and the coordinates of the centers of the CN dumb-bells of $(NH_4)_4[Fe(CN)_6] \cdot 1.5H_2O$ are closely related:

$(NH_4)_4[Fe(CN)_6] \cdot 1.5H_2O$	CN	-0.0325	0.0456	0.1236
$Na_3Al_2Li_3F_{12}$	F	-0.0289	0.0427	0.1399

† Ammonium hexacyanoferrate(II) 1.5 hydrate.

‡ Part XII of the series 'Verwandschaftskriterien von Kristallstrukturtypen' [Part XI: Hellner, Koch & Reinhardt (1981)].

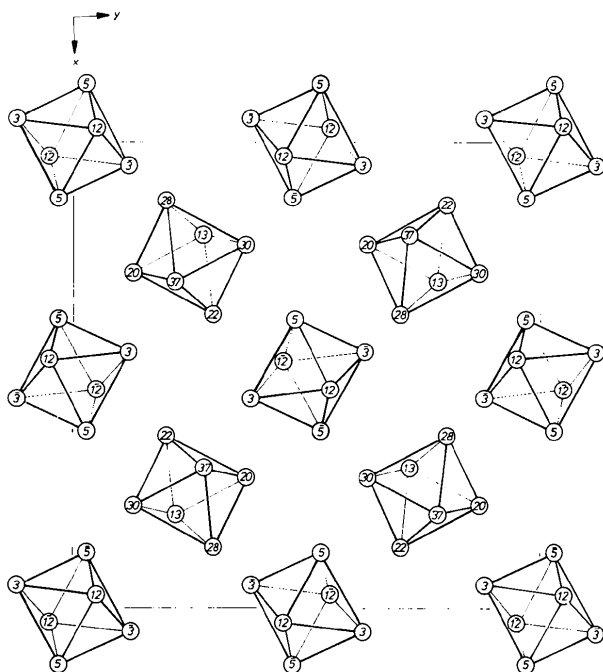


Fig. 1. The $I_2[6o]$ framework of ammonium ferrocyanide hydrate. The small circles indicate the centers of the CN dumb-bells; z coordinates are given in hundredths of a ($a/100$). The octahedra around I_2 are drawn for the lower half of the unit cell.

For this reason, the crystal structure of ammonium ferrocyanide hydrate may be described as a garnet-like framework of CN dumb-bells (Fig. 1) with the remaining atoms filling up the voids within this framework.

The O framework of garnet is formed by octahedra, the centers of which are placed at the points of a body-centered cubic lattice I_2 . The translations of this lattice are halved with respect to the translations of $Ia3d$. The octahedra are not in parallel orientations. As a consequence, all octahedra are connected by additional short O—O distances. Such a framework has been symbolized $I_2[6o]$. Its correlation to sphere packings, the voids in the framework, and the connections of these voids by common corners, edges and faces are discussed in detail by Hellner, Gerlich, Koch & Fischer (1979).

Six kinds of voids exist in an $I_2[6o]$ framework. The corresponding coordination polyhedra and the positions of their centers* are described in Table 2. The crystal structures of grossularite, hydrogarnet (Bartl, 1969), α -RhBi₄ (Glagoleva & Zdanov, 1956), mercury tellurate (Falqui, 1963), and ammonium ferrocyanide hydrate contain $I_2[6o]$ frameworks. They are compared (Table 3) with respect to the occupancies of their voids.

* For the description of point configurations with the aid of symbols of invariant lattice complexes and coordination polyhedra see Hellner (1979) and Hellner, Koch & Reinhardt (1981).

Table 2. Description of the voids in an $I_2[6o]$ framework

Position of the center		Coordination polyhedron
I_2	16(a) 0,0,0	(6o) octahedron
Y^{**}	16(b) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	(6r) trigonal prism
V^*	24(c) $0, \frac{1}{4}, \frac{1}{4}$	(8a) tetragonal antiprism
S^*	24(d) $0, \frac{1}{4}, \frac{1}{4}$	(4t) tetrahedron
$W'_2x\bar{x}$	48(g) $\frac{1}{2}, x, \frac{1}{4} - x$	(6o) (distorted) octahedron
$ P'_4 - Y^{**} (2r)$	96(h) x, y, z	(4t) (distorted) tetrahedron
		$x \sim 0.30$
		$x \sim 0.14$
		$y \sim 0.04$
		$z \sim 0.08$

Table 3. Occupancies of voids in crystal structures of different types with $I_2[6o]$ framework

Compound	I_2	Y^{**}	V^*	S^*	$W'_2x\bar{x}$	$ P'_4 - Y^{**} (2r)$
Ca ₃ Al ₂ Si ₃ O ₁₂	Al	—	Ca	Si	—	—
Ca ₃ Al ₂ (OH) ₁₂	Al	—	Ca	—	—	—
α -RhBi ₄	—	—	Rh	—	—	—
Hg ₃ TeO ₆	Te	—	—	—	Hg	—
(NH ₄) ₄ [Fe(CN) ₆].1.5H ₂ O	Fe	NH ₄	H ₂ O	—	NH ₄	—

Except in ammonium ferrocyanide hydrate, occupied voids do not share faces. They are corner-connected or at most edge-connected. In (NH₄)₄[Fe(CN)₆].1.5H₂O, however, the trigonal prisms around Y^{**} have their large quadrangular faces in common with the tetragonal antiprisms around V^* . In addition each antiprism shares small triangular faces with four distorted octahedra around $W'_2x\bar{x}$. The face-sharing prisms and antiprisms build up two three-dimensional systems of channels. These channel systems interpenetrate each other in the same manner as the interpenetrating sphere packings which correspond to the Y^{**} and to the V^* configuration (Fischer & Koch, 1976). One channel system consists of polyhedra with centers in $+Y^*$ and $+V$, the other of polyhedra with centers in $-Y^*$ and $-V$ (Fig. 2).

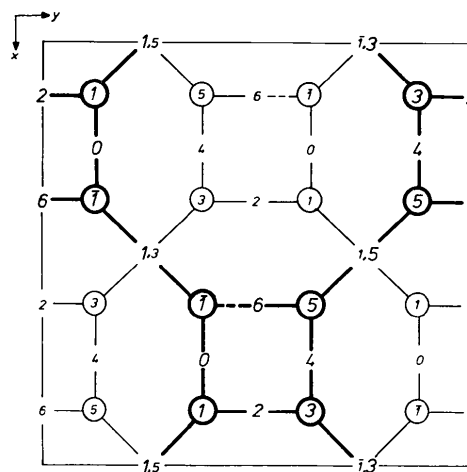


Fig. 2. The two interpenetrating systems of channels within the CN framework. The centers of the voids around Y^{**} (circles) and around V^* are indicated by their z coordinates (in units of $a/100$).

The zeolite analcite $\text{Na}[\text{AlSi}_2\text{O}_6] \cdot \text{H}_2\text{O}$ (Ferraris, Jones & Yerkess, 1972) contains analogous systems of channels formed by the O framework $[P'_4-Y^{**}][4t_c]$. Again the channels are formed by voids with centers in Y^{**} and in V^* . In this case, however, the voids around Y^{**} are large icosahedra which overlap in very flat tetrahedra around V^* (Hellner & Koch, 1979).

The influence of the CN dumb-bells on the coordination polyhedra

The replacement of the framework atoms in $I_2[6o]$ by dumb-bells leaves the voids within the framework essentially unchanged. Some very flat tetrahedra occur in addition, and the coordination number increases in some cases. For the occupied voids the coordination polyhedra formed by the centers of the dumb-bells will be compared with the coordination polyhedra formed by the dumb-bells themselves:

The shape of the octahedral voids around I_2 remains unchanged because the CN dumb-bells point to the centers of these octahedra (Fig. 3); only the size is influenced. Each Fe^{2+} ion is octahedrally surrounded by six C atoms.

A similar situation occurs for the tetragonal antiprisms around V^* . Each water molecule is coordinated by eight N atoms, again forming a tetragonal antiprism (Fig. 4).

In contrast to these simple polyhedra around I_2 and V^* , the dumb-bells at the vertices of the trigonal prisms around Y^{**} (in the garnet framework) are arranged in

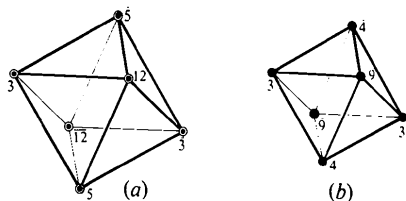


Fig. 3. The I_2 coordination polyhedron around 0,0,0. (a) Centers of the CN dumb-bells. (b) Positions of the C atoms. The z coordinates are given in units of $a/100$.

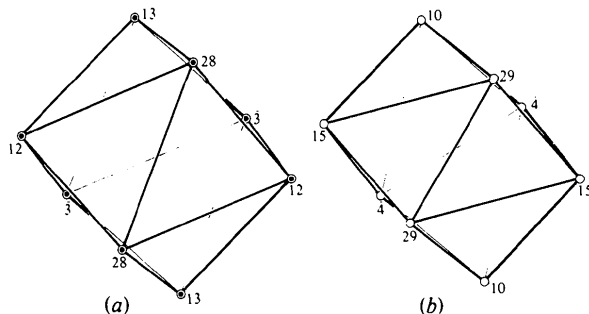


Fig. 4. The V^* coordination polyhedron around $0, \frac{1}{4}, \frac{1}{8}$. (a) Centers of the CN dumb-bells. (b) Positions of the C atoms. The z coordinates are given in units of $a/100$.

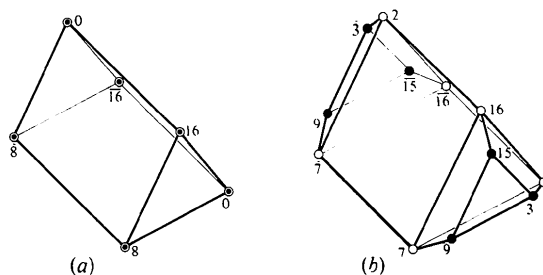


Fig. 5. The Y^{**} coordination polyhedron around $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$. (a) Centers of the CN dumb-bells. (b) Positions of the C atoms (filled circles) and of the N atoms (open circles). The z coordinates are given in units of $a/100$.

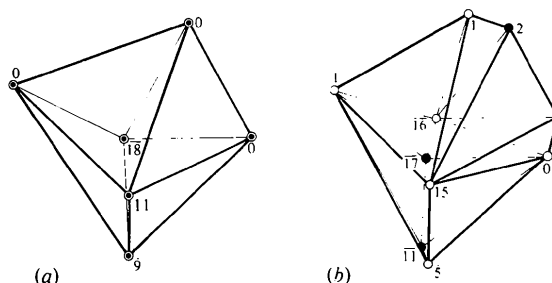


Fig. 6. The W'_{2xx} coordination polyhedron around $\frac{1}{2}, 0.30, -0.05$. (a) Centers of the CN dumb-bells. (b) Positions of the C atoms (full circles) and of the N atoms (open circles). The z coordinates are given in units of $a/100$.

such a way that the coordination polyhedron of $\text{NH}_4(1)$ shows 12 vertices almost equally distant from the center (Fig. 5).

The dumb-bells that replace the vertices of the octahedra with centers on the twofold axes in W'_{2xx} are oriented in such a way that each $\text{NH}_4(2)$ group has six N and four C atoms as neighbors (Fig. 6).

Distance calculations for the channel systems

The proposed channel system (Fig. 2) is formed by voids around V^* in the shape of tetragonal antiprisms and around Y^{**} as 12-coordinated polyhedra. The radii of these voids (shortest distances from the center to the corners) are 3.64 and 3.25 Å, respectively. The polyhedra are connected by almost flat quadrangular faces which are nearly squares. The corners of the squares are occupied by N atoms. These squares are the most narrow locations within the $Y^{**}-V^*$ channels. The corresponding smallest radius is 3.05 Å. This value may be compared with the radius of 2.98 Å for the voids around W'_{2xx} , which are filled with $\text{NH}_4(2)$. It follows that NH_4^+ or H_3O^+ ions can move in the $Y^{**}-V^*$ channel system without difficulty.

On the other hand, the polyhedra around W'_{2xx} and around V^* have triangular faces in common. The

corresponding smallest radius for such a triangle is only 2.72 Å. The $W'_2x\bar{x}$ polyhedra share additional triangular faces with empty tetrahedra in the general position. The radius of these tetrahedra is 2.78 Å, and the radius corresponding to the common triangles is 2.71 Å. It is unlikely, therefore, that the $\text{NH}_4(2)$ group could move within the CN framework.

Summing up, it may be said that the CN framework of $(\text{NH}_4)_4[\text{Fe}(\text{CN})_6] \cdot 1.5\text{H}_2\text{O}$ may be derived from the O framework in garnet. The $Y^{**}-V^*$ channel system in this framework is wide enough to allow a motion of NH_4^+ or H_3O^+ ions.

We thank the Fachinformationszentrum Energie, Physik, Mathematik GmbH, Karlsruhe, for financial support.

References

ABRAHAMS, S. C. & GELLER, S. (1958). *Acta Cryst.* **11**, 437–441.

- BARTL, H. (1969). *Neues Jahrb. Mineral. Monatsh.* pp. 404–413.
 FALQUI, M. T. (1963). *Ric. Sci. Parte 2: Sez. A*, **3**, 627–634.
 FERRARIS, G., JONES, D. W. & YERKES, J. (1972). *Z. Kristallogr.* **135**, 240–252.
 FISCHER, W. & KOCH, E. (1976). *Acta Cryst.* **A32**, 225–232.
 GELLER, S. (1971). *Am. Mineral.* **56**, 18–22.
 GLAGOLEVA, V. P. & ZDANOV, G. N. (1956). *Sov. Phys. JETP*, **3**, 155–158.
 HELLNER, E. (1979). *Struct. Bonding (Berlin)*, **37**, 61–140.
 HELLNER, E., GERLICH, R., KOCH, E. & FISCHER, W. (1979). *Phys. Daten – Phys. Data*, **16**–1, 1–31.
 HELLNER, E. & KOCH, E. (1979). *Mineral. Petrogr. Acta*, **23**, 303–311.
 HELLNER, E., KOCH, E. & REINHARDT, A. (1981). *Phys. Daten – Phys. Data*, **16**–2. In the press.
 MOROSIN, B. (1978a). *Phys. Lett. A*, **65**, 53–54.
 MOROSIN, B. (1978b). *Acta Cryst.* **B34**, 3730–3731.
 WHITTINGHAM, M. S., CONNELL, P. S. & HUGGINS, R. A. (1972). *J. Solid State Chem.* **5**, 321–327.

Acta Cryst. (1982). **B38**, 379–382

Structure Cristalline d'un Oxysulfure Isotype de la Mélilite, $\text{La}_{3,33}\text{Ga}_6\text{O}_2\text{S}_{12}$

PAR A. MAZURIER, M. GUITTARD ET S. JAULMES

Laboratoire de Chimie Minérale Structurale (Laboratoire associé au CNRS n° 200), Faculté des Sciences Pharmaceutiques et Biologiques de l'Université René Descartes, 4 avenue de l'Observatoire, 75270 Paris CEDEX 06, France

(Reçu le 26 janvier 1981, accepté le 28 juillet 1981)

Abstract

The structure of $\text{La}_{3,33}\text{Ga}_6\text{O}_2\text{S}_{12}$ has been determined from single-crystal X-ray data. The cell is tetragonal, with $a = 9.351(4)$, $c = 6.049(3)$ Å, $Z = 1$, space group $P4_21m$, $V = 529$ Å³, $D_x(293\text{ K}) = 4.12$, $D_c = 4.06$ Mg m⁻³. The structure was refined to a final R of 0.053 for 619 reflexions. The Ga, S and O atoms are in fourfold, and the La atoms in eightfold coordination. This structure is essentially built up from sheets of (GaS_4) and (GaOS_3) tetrahedra, parallel to the plane (010). The La atoms ensure the cohesion between two $(\text{Ga}_3\text{S}_6\text{O})_n^{5n-}$ sheets.

Introduction

Au cours de l'étude du système $\text{La}_2\text{S}_3\text{-Ga}_2\text{S}_3$, une phase de composition $\text{La}_{10,3}\text{Ga}_6\text{S}_{14}$ a été isolée; son réseau quadratique fut trouvé semblable à celui de la mélilite (Loireau-Lozac'h, Guittard & Flahaut, 1972, 1973). Plus récemment, dans l'étude du système

$\text{La}_2\text{O}_2\text{S-Ga}_2\text{S}_3$ apparaissait une phase de composition non définie, proche de $3\text{La}_2\text{O}_2\text{S-7Ga}_2\text{S}_3$ (Guittard, Pardo & Loireau-Lozac'h, 1977), dont le diagramme de rayons X possède d'étroites analogies avec celui de $\text{La}_{10,3}\text{Ga}_6\text{S}_{14}$. L'étude de la structure devait permettre d'établir la composition exacte de ces phases et d'examiner la possibilité de substitution partielle de l'oxygène au soufre.

Les cristaux étudiés ici ont été réalisés par fusion et refroidissement lent d'un mélange $3\text{La}_2\text{O}_2\text{S-7Ga}_2\text{S}_3$ introduit dans un creuset de graphite lui-même à l'intérieur d'une ampoule de silice, scellée sous vide.

Le chauffage est réalisé dans un four programmé; la température de 1473 K est atteinte en 24 h, puis le refroidissement entre 1473 K et la température ambiante est effectué en 6 jours.

Techniques expérimentales

Les cristaux ont un aspect brillant, de couleur jaune clair. Nous avons choisi un cristal de forme sensible-