sharing a tetrahedron. The tetrahedral sites are occupied by Ga, while the octahedral sites are statistically occupied by V and Ga atoms. The two types of chains are alternating, bound by corner-shared octahedra and tetrahedra. In Figs. 3, 4 and 5, this structure type is compared to those of rutile, β-Ga_2O_3 and $Ti_{21}Ga_4O_{48}$ (Lloyd, Grey & Bursill, 1976). The octahedral sites of the cations are very distorted with the exception of those in particular positions at the corners of the cell. However, these structure distortions are of the same order of magnitude as those observed for V_nO_{2n-1}, β-Ga_2O_3 or the mixed oxide $Ti_{21}Ga_4O_{48}$. The O—O distances lie between 2·52 and 2·99 Å. The metal–oxygen bonds and the oxygen–metal–oxygen angles show these deformations. However, some of the cations in the edge-sharing octahedra are particularly out of the centre and this displacement results in unusually short (1·793 Å) and long (2·160 Å) M—O bond lengths.

Characteristic bond lengths and angles are listed in Table 2.

Discussion

The structure of β-Ga_2O_3 is such that half of the Ga atoms occupy tetrahedral sites. V atoms are usually octahedrally coordinated in the oxides; pentahedral environments (square-based pyramid) are very seldom found (Cros, Tourné & Philippot, 1975). In V_2GaO_5, two of the nine cationic sites are tetrahedral, containing $\frac{4}{5}$ of the Ga atoms. One Ga atom out of five statistically occupies an octahedral site with a V atom. It has been shown that this distribution involves only the octahedra belonging to the β-Ga_2O_3-like blocks. Such a random distribution of Ga and Ti atoms over a small number of octahedral sites has also been found in $Ti_{21}Ga_4O_{48}$.

Like $Ti_{21}Ga_4O_{48}$, the compound $V^{III}V^{IV}GaO_5$ exhibits close analogies with β-Ga_2O_3: monoclinic symmetry, space group $C2/m$; the structure is generated from exactly superposed layers perpendicular to the b axis ($\simeq$ 3 Å). The β-Ga_2O_3 elements, linked by corner-shared polyhedra in the pure oxide, are separated by large tunnels within rutile-type blocks in $Ti_{21}Ga_4O_{48}$. In V_2GaO_5, two adjacent β-Ga_2O_3-like blocks share a tetrahedron in order to give chains parallel to the columns of VO_6 octahedra.

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The Structure of Sodium Pentacyanosulphitoferrate(II) $10\frac{1}{2}$-Water

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Abstract

$Na_5[Fe(CN)_5(SO_3)].10\frac{1}{2}H_2O$ is monoclinic, space group $P2_1/n$, with $a = 8{\cdot}756$ (1), $b = 31{\cdot}866$ (6), $c = 15{\cdot}390$ (3) Å, $\beta = 90{\cdot}67$ (1)°, $Z = 8$. Final $R = 0{\cdot}036$ for 550 parameters and 7142 reflections. The two complex ions in the asymmetric unit are essentially similar and have distorted octahedral configurations. The sulphite ions are coordinated to Fe through S with Fe—S = 2·255 (1) and 2·277 (1) Å. The mean Fe—C and C—N = 1·911 (1) and 1·163 (2) Å for ion (1) and 1·908 (1) and 1·160 (2) Å for ion (2). There is no evidence for a sulphite *trans* effect.

Introduction

In connection with structural studies of hexa- and pentacyano complexes of transition metals the mode of coordination of sulphite in the presence of cyanide and

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the effect of this ligand on the metal → π^*(CN) transfer is of interest. Recent structural studies on simple sulphites of Fe^{II} demonstrated O coordination of sulphite to Fe in all cases (Johansson & Lindqvist, 1979; Johansson & Ljungström, 1979,1980). From the infrared spectrum of sodium pentacyanosulphitoferrate(II) it was suggested (Baran & Müller, 1969) that sulphite is coordinated to Fe through S, but this had not been confirmed by a crystal structure investigation. A comparison of the frequencies of the Fe^{II}—C and C—N bands in the infrared spectra of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5SO_3]^{5-}$ (Tosi & Danon, 1964) suggested comparable Fe^{II}—C π bonding in the two complex ions. This is also borne out by the Fe—C lengths determined in the present investigation.

Crystal data

$Na_5[Fe(CN)_5SO_3].10\frac{1}{2}H_2O$, $M_r = 570{\cdot}2$, monoclinic, $a = 8{\cdot}756$ (1), $b = 31{\cdot}866$ (6), $c = 15{\cdot}390$ (3) Å, $\beta = 90{\cdot}67$ (1)°, $Z = 8$, $D_c = 1{\cdot}76$, $D_m = 1{\cdot}74$ Mg m^{-3}, space group $P2_1/n$, μ(Mo $K\alpha$) = 0·99 mm^{-1}. The compound crystallizes as pale-yellow needles.

Experimental

The compound was prepared from sodium nitroprusside (Hofmann, 1896) and separated as an orange-red oil by the addition of ethanol. Repeated dissolution in water and precipitation with ethanol yielded a yellow powder which was dissolved in water and allowed to crystallize over ethanol in a desiccator. Pale-yellow needles of $Na_5[Fe(CN)_5SO_3].10\frac{1}{2}H_2O$ were deposited within 24 h. Crystals of $Na_5[Fe(CN)_5SO_3]$ have been reported to contain various amounts of water, *i.e.* 2, 4 or 9 H_2O per formula unit. According to the structural analysis, crystals deposited from aqueous solution should, however, be formulated as $Na_5[Fe(CN)_5SO_3].10\frac{1}{2}H_2O$.

Diffracted intensities from a crystal, 0·35 × 0·35 × 0·25 mm, were measured at 168 K on a Syntex $P2_1$ diffractometer with graphite-monochromatized Mo $K\alpha$ radiation and the ω-scan technique. Data were collected for $\sin\theta/\lambda \leq 0{\cdot}62$ Å^{-1} with $h \geq 0$ and $k \geq 0$. That the crystal was not subject to decay was verified by periodical measurement of the intensities of two reflections. Correction was made for Lorentz and polarization effects but not for absorption or extinction. Symmetry-related reflections were averaged giving 8595 unique reflections. Of these, the 7142 reflections for which $F_o^2 \geq 3\sigma(F_o^2)$ were used in the subsequent calculations. A few reflections with low k index which were partially screened by the beam-stop have been classed as unobserved. The cell parameters and their e.s.d.'s at 168 K were determined by least squares from

Table 1. *Fractional coordinates*

E.s.d.'s are given in parentheses. Aq denotes the O atom of a water molecule.

	x	*y*	*z*
Fe(1)	0·51556 (4)	0·26427 (1)	0·47203 (3)
S(1)	0·62093 (8)	0·21644 (2)	0·56258 (5)
O(11)	0·6451 (3)	0·1745 (1)	0·5196 (2)
O(12)	0·7749 (3)	0·2295 (1)	0·5975 (2)
O(13)	0·5219 (3)	0·2074 (1)	0·6390 (2)
C(11)	0·6475 (3)	0·3083 (1)	0·5097 (2)
N(11)	0·7240 (3)	0·3372 (1)	0·5268 (2)
C(12)	0·6614 (3)	0·2501 (1)	0·3836 (2)
N(12)	0·7487 (3)	0·2459 (1)	0·3285 (2)
C(13)	0·3676 (3)	0·2226 (1)	0·4395 (2)
N(13)	0·2702 (3)	0·1986 (1)	0·4257 (2)
C(14)	0·3688 (3)	0·2797 (1)	0·5572 (2)
N(14)	0·2755 (3)	0·2867 (1)	0·6081 (2)
C(15)	0·4365 (3)	0·3035 (1)	0·3908 (2)
N(15)	0·4008 (3)	0·3282 (1)	0·3383 (2)
Fe(2)	0·25893 (4)	0·47023 (1)	0·75181 (3)
S(2)	0·18917 (8)	0·53905 (2)	0·74889 (5)
O(21)	0·1170 (3)	0·5504 (1)	0·6625 (1)
O(22)	0·0744 (3)	0·5512 (1)	0·8159 (2)
O(23)	0·3219 (3)	0·5691 (1)	0·7612 (2)
C(21)	0·1095 (3)	0·4561 (1)	0·8365 (2)
N(21)	0·0151 (3)	0·4453 (1)	0·8837 (2)
C(22)	0·4183 (3)	0·4787 (1)	0·8367 (2)
N(22)	0·5199 (3)	0·4815 (1)	0·8855 (2)
C(23)	0·4006 (3)	0·4817 (1)	0·6611 (2)
N(23)	0·4853 (3)	0·4872 (1)	0·6052 (2)
C(24)	0·1103 (3)	0·4572 (1)	0·6653 (2)
N(24)	0·0230 (3)	0·4463 (1)	0·6126 (2)
C(25)	0·3161 (3)	0·4128 (1)	0·7479 (2)
N(25)	0·3487 (3)	0·3776 (1)	0·7431 (2)
Na(1)	0·2499 (2)	0·03857 (4)	0·1073 (1)
Na(2)	0·0772 (2)	−0·05227 (4)	0·0374 (1)
Na(3)	0·2976 (2)	0·15519 (5)	0·2804 (1)
Na(4)	0·4932 (2)	−0·04846 (6)	0·4564 (1)
Na(5)	0·1360 (2)	0·13887 (4)	0·5040 (1)
Na(6)	0·7301 (2)	−0·21168 (5)	0·3179 (1)
Na(7)	0·5898 (2)	−0·17895 (4)	0·1041 (1)
Na(8)	0·6465 (1)	0·18317 (4)	0·2304 (1)
Na(9)	0·3435 (2)	−0·07160 (5)	0·2463 (1)
Na(10)	0·0220 (2)	0·22450 (4)	0·3721 (1)
Aq(1)	0·8128 (3)	−0·0736 (1)	0·0280 (2)
Aq(2)	0·2791 (3)	0·0024 (1)	0·2533 (2)
Aq(3)	0·3504 (3)	−0·0272 (1)	0·0531 (2)
Aq(4)	0·0650 (3)	0·1914 (1)	0·2368 (2)
Aq(5)	0·2162 (3)	0·0979 (1)	0·3803 (2)
Aq(6)	0·9737 (3)	−0·0784 (1)	0·4226 (2)
Aq(7)	0·9120 (3)	0·1590 (1)	0·4257 (2)
Aq(8)	0·6385 (3)	−0·1257 (1)	0·4166 (2)
Aq(9)	0·5052 (3)	−0·2309 (1)	0·0044 (2)
Aq(10)	0·4051 (3)	−0·2106 (1)	0·1929 (2)
Aq(11)	0·4782 (3)	0·1426 (1)	0·1476 (2)
Aq(12)	0·1682 (3)	0·1034 (1)	0·1713 (2)
Aq(13)	0·1029 (3)	−0·0828 (1)	0·1827 (2)
Aq(14)	0·4115 (3)	0·2249 (1)	0·2310 (2)
Aq(15)	0·5455 (3)	0·1474 (1)	0·3514 (2)
Aq(16)	0·8133 (4)	0·1146 (1)	0·0231 (2)
Aq(17)	0·9692 (3)	−0·1808 (1)	0·3707 (2)
Aq(18)	0·7687 (3)	−0·1531 (1)	0·2100 (2)
Aq(19)	0·2878 (3)	−0·0976 (1)	0·3927 (2)
Aq(20)	0·2905 (3)	0·0013 (1)	0·4930 (2)
Aq(21)	0·4435 (4)	−0·1180 (1)	0·1108 (3)

diffractometer setting angles determined for 15 reflections.

The main features of the structure were determined with *MULTAN* (Main, Woolfson, Germain & Declercq, 1977). Subsequent Fourier syntheses revealed the positions of the O atoms of all the water molecules. No attempt was made to locate the H atoms. Block-diagonal least-squares refinement of atomic coordinates, anisotropic thermal parameters and a scale factor gave a final R of 0·036 for 550 parameters; when the 1453 unobserved reflections were included $R = 0{\cdot}053$. The F_o values were weighted according to $w = (a + F_o + cF_o^2 + dF_o^3)^{-1}$ (Cruickshank, 1970) with $a = 80{\cdot}0$, $c = 0{\cdot}008$ and $d = 0{\cdot}0$. Scattering factors were those of the neutral atoms (Doyle & Turner, 1968). A final difference map showed a maximum electron density of 0·6 e Å^{-3}. Atomic coordinates are listed in Table 1.*

Calculations were carried out on an IBM 360/65-370/145 computer system with local versions of the following programs: data reduction, *SYN* (O. Lindqvist & E. Ljungström); direct methods, *MULTAN* 77 (Main, Woolfson, Germain & Declercq, 1977); Fourier syntheses, *DRF* (A. Zalkin); block-diagonal least-squares refinement, *BLOCK* (O. Lindgren); distances and angles, *DISTAN* (A. Zalkin); least-squares planes, *PLANEFIT* (F. Wengelin); stereoscopic drawings, *ORTEP* (Johnson, 1965).

Discussion

Stereoscopic projections of the two complex ions in the asymmetric unit are shown in Figs. 1 and 2. Bond distances and angles within these ions are given in Table 2. O···O and O···N contacts <3 Å are listed in Table 3.

Although the two crystallographically independent complex ions are essentially similar, some bond lengths and angles differ significantly between the two ions (Table 2). The sulphite ligands are coordinated to Fe through S in both cases, but the Fe–S distances differ [Fe(1)–S(1) 2·255 (1), Fe(2)–S(2) 2·277 (1) Å]. Similar variations have been found in the Co–S distance in S-bonded sulphite complexes of Co^{III}

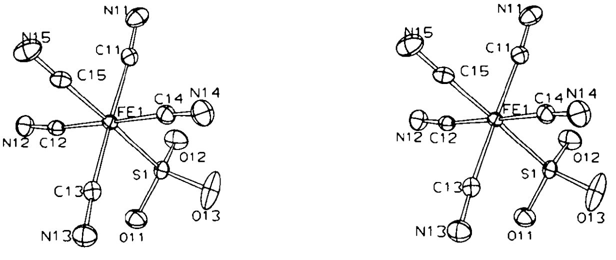

Fig. 1. Stereoscopic projection of ion (1). The thermal ellipsoids enclose 50% probability.

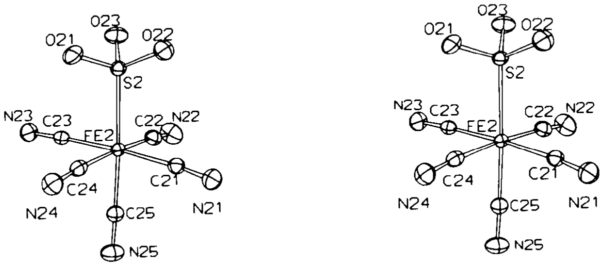

Fig. 2. Stereoscopic projection of ion (2). The thermal ellipsoids enclose 50% probability.

Table 2. *Bond lengths* (Å) *and angles* (°) *within the* $[Fe(CN)_5(SO_3)]^{2-}$ *ion*

Fe(1)–S(1)	2·255 (1)	Fe(2)–S(2)	2·277 (1)
Fe(1)–C(11)	1·903 (3)	Fe(2)–C(21)	1·911 (3)
Fe(1)–C(12)	1·931 (3)	Fe(2)–C(22)	1·920 (3)
Fe(1)–C(13)	1·917 (3)	Fe(2)–C(23)	1·913 (3)
Fe(1)–C(14)	1·910 (3)	Fe(2)–C(24)	1·897 (3)
Fe(1)–C(15)	1·894 (3)	Fe(2)–C(25)	1·900 (3)
S(1)–O(11)	1·506 (2)	S(2)–O(21)	1·509 (2)
S(1)–O(12)	1·505 (2)	S(2)–O(22)	1·499 (2)
S(1)–O(13)	1·497 (3)	S(2)–O(23)	1·516 (2)
C(11)–N(11)	1·167 (4)	C(21)–N(21)	1·160 (4)
C(12)–N(12)	1·156 (4)	C(22)–N(22)	1·161 (4)
C(13)–N(13)	1·164 (4)	C(23)–N(23)	1·156 (4)
C(14)–N(14)	1·160 (4)	C(24)–N(24)	1·161 (4)
C(15)–N(15)	1·167 (4)	C(25)–N(25)	1·160 (4)
S(1)–Fe(1)–C(11)	93·9 (1)	S(2)–Fe(2)–C(21)	93·1 (1)
S(1)–Fe(1)–C(12)	90·5 (1)	S(2)–Fe(2)–C(22)	94·0 (1)
S(1)–Fe(1)–C(13)	87·9 (1)	S(2)–Fe(2)–C(23)	88·7 (1)
S(1)–Fe(1)–C(14)	91·3 (1)	S(2)–Fe(2)–C(24)	90·9 (1)
S(1)–Fe(1)–C(15)	176·4 (1)	S(2)–Fe(2)–C(25)	177·0 (1)
C(11)–Fe(1)–C(12)	89·0 (1)	C(21)–Fe(2)–C(22)	93·9 (1)
C(11)–Fe(1)–C(13)	174·7 (1)	C(21)–Fe(2)–C(23)	175·8 (1)
C(11)–Fe(1)–C(14)	90·7 (1)	C(21)–Fe(2)–C(24)	87·6 (1)
C(11)–Fe(1)–C(15)	86·0 (1)	C(21)–Fe(2)–C(25)	88·7 (1)
C(12)–Fe(1)–C(13)	96·0 (1)	C(22)–Fe(2)–C(23)	89·8 (1)
C(12)–Fe(1)–C(14)	178·2 (1)	C(22)–Fe(2)–C(24)	174·8 (1)
C(12)–Fe(1)–C(15)	85·9 (1)	C(22)–Fe(2)–C(25)	88·2 (1)
C(13)–Fe(1)–C(14)	84·2 (1)	C(23)–Fe(2)–C(24)	88·6 (1)
C(13)–Fe(1)–C(15)	92·5 (1)	C(23)–Fe(2)–C(25)	89·3 (1)
C(14)–Fe(1)–C(15)	92·3 (1)	C(24)–Fe(2)–C(25)	86·8 (1)
Fe(1)–C(11)–N(11)	174·3 (3)	Fe(2)–C(21)–N(21)	174·9 (3)
Fe(1)–C(12)–N(12)	173·1 (3)	Fe(2)–C(22)–N(22)	175·2 (3)
Fe(1)–C(13)–N(13)	174·0 (3)	Fe(2)–C(23)–N(23)	177·6 (3)
Fe(1)–C(14)–N(14)	176·0 (3)	Fe(2)–C(24)–N(24)	175·2 (3)
Fe(1)–C(15)–N(15)	174·1 (3)	Fe(2)–C(25)–N(25)	177·9 (3)
Fe(1)–S(1)–O(11)	112·8 (1)	Fe(2)–S(2)–O(21)	110·9 (1)
Fe(1)–S(1)–O(12)	113·1 (1)	Fe(2)–S(2)–O(22)	114·7 (1)
Fe(1)–S(1)–O(13)	112·3 (1)	Fe(2)–S(2)–O(23)	113·6 (1)
O(11)–S(1)–O(12)	105·8 (1)	O(21)–S(2)–O(22)	105·5 (1)
O(11)–S(1)–O(13)	105·0 (2)	O(21)–S(2)–O(23)	105·8 (1)
O(12)–S(1)–O(13)	107·3 (2)	O(22)–S(2)–O(23)	105·7 (1)

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* Lists of structure factors and anisotropic thermal parameters and a stereoview of the unit cell have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35343 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. O···O *and* O···N *contacts* <3 Å *with e.s.d.'s*

Symmetry code

(i)	$1+x, y, z$	(v)	$2-x, -y, 1-z$
(ii)	$\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$	(vi)	$\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$
(iii)	$x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$	(vii)	$1\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$
(iv)	$1-x, -y, 1-z$		

Within the sulphite ligands

O(11)···O(12)	2·401 (3)	O(21)···O(22)	2·395 (3)
O(11)···O(13)	2·383 (4)	O(21)···O(23)	2·413 (3)
O(12)···O(13)	2·418 (4)	O(22)···O(23)	2·403 (3)

Intermolecular

Aq(1)···O(21^{ii})	2·802 (3)	Aq(11)···N(24^{iii})	2·912 (4)
Aq(1)···N(11^{vii})	2·982 (4)	Aq(11)···N(11^{iii})	2·954 (4)
Aq(3)···N(24^{vi})	2·918 (4)	Aq(11)···Aq(14)	2·980 (4)
Aq(3)···O(21^{ii})	2·956 (4)	Aq(12)···N(11^{iii})	2·967 (4)
Aq(4)···N(25^{iii})	2·904 (4)	Aq(13)···O(23^{iii})	2·788 (3)
Aq(5)···N(21^{ii})	2·957 (4)	Aq(13)···N(15^{vi})	2·856 (4)
Aq(6)···O(23^{ii})	2·819 (4)	Aq(14)···O(12^{iii})	2·775 (4)
Aq(6)···Aq(19^{i})	2·861 (4)	Aq(15)···O(11)	2·857 (3)
Aq(7)···O(11)	2·807 (3)	Aq(17)···O(12^{v})	2·765 (4)
Aq(8)···O(22^{ii})	2·886 (4)	Aq(18)···O(23^{ii})	2·829 (3)
Aq(9)···O(12^{vii})	2·797 (4)	Aq(19)···O(11^{iv})	2·857 (4)
Aq(10)···O(13^{iv})	2·661 (4)	Aq(20)···N(22^{iii})	2·925 (4)
Aq(10)···N(15^{vi})	2·984 (4)	Aq(21)···O(21^{iii})	2·748 (4)

(Raston, White & Yandell, 1979, and references therein). In disodium *cis*-bis(ethylenediamine)disulphitocobaltate(III) perchlorate trihydrate (Raston, White & Yandell, 1979) the two sulphite ligands are bonded to Co with Co—S = 2·206 (1) and 2·233 (1) Å. Both the Fe—S distances in $Na_5[Fe(CN)_5SO_3].10\frac{1}{2}H_2O$ lie within the range of values reported for Fe^{II}—S.

The Fe atom lies in the best plane through the equatorial C atoms, the distances from this plane of all five atoms being 0·01–0·02 Å for ion (1) and 0·01–0·05 Å for ion (2). The Fe—C distances are in the range 1·894 (3)–1·931 (3), mean 1·911 (1) Å, in ion (1) and 1·897 (3)–1·920 (3), mean 1·908 (1) Å, in ion (2). In both ions the longest Fe—C bond is *cis* to the sulphite ligand. There is thus no evidence for a sulphite *trans* effect as found in some Co^{III} sulphite complexes (*e.g.* Raston, White & Yandell, 1978*a*,*b*, 1979; Elder & Trkula, 1974). The mean C—N distances are 1·163 (2) Å for ion (1) and 1·160 (2) Å for ion (2). There would seem to be little or no tendency towards a short C—N bond accompanying the apparently longer *cis*-Fe—CN. All Fe—C—N linkages deviate somewhat from 180°, presumably for steric reasons.

The mean Fe—C and C—N distances, 1·910 (1) and 1·161 (1) Å respectively, based on the ten experimental values for each bond, suggest an Fe → π*(CN) transfer comparable to that in $[Fe(CN)_6]^{4-}$, *e.g.* $Na_4[Fe(CN)_6].10H_2O$ (Tullberg & Vannerberg, 1974) in which the mean Fe—C and C—N = 1·904 (4) and 1·173 (6) Å, respectively. In $[Fe(CN)_5(NO)]^{2-}$ (Bottomley & White, 1979) in which the Fe → π* (ligand) transfer is generally assumed to be predominantly to the nitrosyl group, the mean Fe—C and C—N = 1·930 (2) and 1·152 (3) Å, respectively.

Coordination of the sulphite group through S contrasts sharply with coordination through O observed in the simple sulphites of Fe^{II}, α-$FeSO_3.3H_2O$ (Johansson & Lindqvist, 1979), β-$FeSO_3.3H_2O$ (Johansson & Ljungström, 1979) and $FeSO_3.2\frac{1}{2}H_2O$ (Johansson & Ljungström, 1980). The sulphite ligands are polydentate in the simple sulphites, forming bridges between Fe^{II}, whereas unidentate coordination of a sulphite group to a transition metal is often through S (Baggio & Baggio, 1976). On the other hand, unidentate O—Fe coordination is present in $(NH_4)_9[Fe(SO_3)_6]$ (Larsson & Niinistö, 1973). It is perhaps somewhat surprising that the Fe → π*(CN) transfer in $[Fe(CN)_5(SO_3)]^{5-}$, which could be expected to result in an effectively higher oxidation state of Fe with respect to coordination by sulphite, does not lead to bonding through O, particularly since the simple Fe^{II} state appears to show a preference for O coordination. Apparently, the Fe → π*(CN) transfer in $[Fe(CN)_5(SO_3)]^{5-}$ is more than compensated for by cyanide σ donation, resulting in a low effective charge on the metal atom.

As can be seen from Table 2, the S—O distances and O—S—O angles are fairly constant, ion (1) showing a slightly greater disparity between angles than ion (2), and ion (2) showing a slightly greater disparity between distances. The mean S—O length is 1·503 (1) Å for ion (1) and 1·508 (1)Å for ion (2). The mean non-bonded O···O contacts are 2·401 (2) and 2·404 (2) Å for ions (1) and (2), respectively.

The mean S—O distance, based on the six observed values, 1·505 (1) Å, appears to be somewhat longer than that usually found in unidentate S-bonded sulphite complexes, 1·457–1·490 Å (Baggio & Baggio, 1976), and more closely resembles that quoted for a sulphite ion in a compound of ionic character, 1·504 (3) Å (Kierkegaard, Larsson & Nyberg, 1972). It is conceivable that the slightly elongated S—O distance indicates Fe—S d_π–d_π bonding. More structural information on analogous complexes would, however, be required before any firm conclusions could be reached on this point.

The shortest S—O bonds are those involving O atoms with short contacts to Na^+ ions, *i.e.* O(22) and O(13) for which O(22)···Na(4) 2·286 (3), O(22)···Na(9) 2·368 (3) and O(13)···Na(6) 2·316 (3) Å. All the O atoms are at distances from water molecules compatible with hydrogen bonding (Table 3). A similar situation, *i.e.* fairly constant S—O lengths despite differences in the environment of the O atoms, occurs in disodium *cis*-bis(ethylenediamine)disulphitocobaltate(III) perchlorate trihydrate (Raston, White & Yandell, 1979). Here the disparity in Co—S distances [2·206 (1), 2·233 (1) Å] was attributed to the dissimilar environment of the O atoms of the sulphite groups. It is conceivable that the disparity between Fe—S distances in $Na_5[Fe(CN)_5(SO_3)] . 10\frac{1}{2}H_2O$ can be explained in a similar way.

Both the difference in Fe—S lengths between the two ions and the tendency towards long Fe(1)—C(12) and Fe(2)—C(22) bonds *cis* to sulphite were evident from a refinement based on data from a crystal of quality inferior ($R = 0{\cdot}059$, 4060 reflections) to that finally used. This suggests that these trends are likely to be real effects.

The majority of the Na^+ ions have irregular environments of nearest neighbours comprising 5–7 N or O atoms at distances of 2·286 (3)–2·709 (4) Å. The shortest distance between two Na^+ ions is Na(7)···Na(10) 3·251 (2) Å. As is apparent from Table 3, there are several O···O or O···N contacts of an order compatible with hydrogen bonding. Since the H atoms have not been located it is not, however, possible to describe the hydrogen-bonding network.

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The Structure of Tantalum Disulfide Thiophosphate $Ta[PS_4|S_2]$

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Abstract

Crystals of $Ta[PS_4|S_2]$ have been grown by vapor transport. They are tetragonal, space group $I4_1/acd$; $a = 15{\cdot}849$ (3), $c = 13{\cdot}143$ (4) Å; $Z = 16$. Final $R = 0{\cdot}030$. Each Ta atom has eight nearest S neighbors, arranged in the form of a bicapped triangular prism. Two such prisms, sharing a common face, form $[Ta_2S_{12}]$ units. These units, linked by $[PS_4]$ tetrahedra, form endless chains, spiralling around the 4_1 and 4_3 axes. Rather large channels extend along these screw axes. One third of the S atoms are present as $[S{-}S]^{2-}$ pairs, two thirds as S^{2-} ions.

Introduction

In the course of an investigation of the system Ta—P—S, the formation of a new compound of overall

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