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## The Nature of the S—S Bonds in Different Compounds. V. The Crystal Structure of ZnS<sub>2</sub>O<sub>4</sub>·Pyridine

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X-ray diffraction data, collected with a CAD-4 diffractometer, were used to determine the structure of the zinc dithionite–pyridine complex. Crystals of the compound are orthorhombic, space group *Pnma*,  $Z = 4$ , with  $a = 8.493$  (2),  $b = 11.095$  (3) and  $c = 9.161$  (2) Å. The structure was found from a Patterson map. Least-squares refinement with 998 independent observed reflexions led to an  $R_w$  of 0.030. The conformation of the dithionite ion in ZnS<sub>2</sub>O<sub>4</sub>·pyridine is very similar to that observed in Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, i.e. eclipsed with a very long S—S bond (2.386 Å). However, slight differences in the valence angles can be explained qualitatively from packing differences in the two compounds. A qualitative explanation of the dithionite conformation has been obtained by comparison of the S<sub>2</sub>O<sub>4</sub><sup>2-</sup> ion with the isoelectronic species P<sub>2</sub>F<sub>4</sub> and Cl<sub>2</sub>O<sub>4</sub> (hypothetical molecule) and with N<sub>2</sub>O<sub>4</sub>.

### Introduction

The present paper is part of a series in which the variations in bond lengths and valence angles in groups or ions of the type  $-(SO_x)-(SO_y)-$  with  $x, y = 1-3$  are studied (part IV: Kiers, Piepenbroek & Vos, 1978). The

structure of the dithionite ion  $^-O_2S-SO_2^-$  especially attracted our attention. Dunitz (1956) had found an eclipsed conformation and a very long S—S bond of 2.39 Å for this ion in Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> from two-dimensional X-ray data. In solutions of dithionites SO<sub>2</sub><sup>-</sup> radical ions are present, as has been shown by Raman (Simon &

Küchler, 1949) and EPR (Rinker, Gordon, Mason & Corcoran, 1959) experiments. Lynn, Rinker & Corcoran (1964) have ascribed the strongly reducing power of dithionites in solution to the presence of these radical ions. Solid  $\text{Na}_2\text{S}_2\text{O}_4$  has been reported by Klemm (1937) to be diamagnetic, however. This was confirmed in our laboratory by magnetic-susceptibility measurements up to  $60^\circ\text{C}$  on crystals of  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$ . On the other hand, from EPR measurements Hodgson, Neaves & Parker (1956) have found evidence for the presence of  $\text{SO}_2^-$  radicals in solid  $\text{Na}_2\text{S}_2\text{O}_4$  purified by vacuum techniques, but they do not exclude radicals being present on the surface of the crystals only. According to Clark, Horsfield & Symons (1961) the paramagnetic behavior of solid  $\text{Na}_2\text{S}_2\text{O}_4$  becomes stronger by moistening the crystals or by exposing them to X-rays.

To gain a better insight into the properties and structure of the dithionite ions we wanted to investigate whether the unexpected eclipsed conformation and the long S—S bond found for  $\text{S}_2\text{O}_4^{2-}$  in  $\text{Na}_2\text{S}_2\text{O}_4$  also occurred in other crystalline dithionites. Attempts were therefore made to grow crystals of the pyridine complexes of  $\text{ZnS}_2\text{O}_4$  and  $\text{CdS}_2\text{O}_4$ , which compounds had been reported to be stable by Scholder & Denk (1935). Crystals were only obtained for the former compound, however. For the Cd salt the crystallization procedure described in the next section, as well as slightly modified procedures, yielded crystals with composition  $\text{CdSO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  in all cases. The crystal structure of this compound will be reported elsewhere.

### Experimental

Crystals of  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$  were grown by diffusion. To this end a flask containing an aqueous solution of Zn acetate and  $\text{Na}_2\text{S}_2\text{O}_4$  was connected to a flask containing pyridine. After a few days white crystals had been formed in the aqueous solution.

Weissenberg photographs showed the space group to be either  $Pn2_1a$  or  $Pnma$ . The latter was adopted and proved to be correct during the structure refinement. Crystallographic data are given in Table 1. The determination of accurate cell dimensions and intensity measurements were carried out on a CAD-4 diffractometer by the use of  $\text{Cr}$ -filtered Mo radiation and the  $\theta/2\theta$  scan with a crystal having approximate dimensions  $0.4 \times 0.2 \times 0.2$  mm. 3712 independent reflexions with  $\theta \leq 45^\circ$  were scanned first with the fastest motor speed; for 999 reflexions whose intensities exceeded a

Table 1. *Crystal data of  $\text{ZnS}_2\text{O}_4 \cdot \text{C}_5\text{H}_5\text{N}$  not given elsewhere*

FW 272.6,  $D_o = 2.1$ ,  $D_c = 2.10$  g cm $^{-3}$   
 $\lambda(\text{Mo } K\alpha_1) = 0.70926$ ,  $\lambda(\text{Mo } K\alpha_2) = 0.71354$  Å  
 $\mu(\text{Mo } K\alpha) = 33.7$  cm $^{-1}$

preset value the scan was repeated at the optimum speed. These 999 reflexions were used for the structure determination. Corrections for Lorentz and polarization effects, for changes in the primary beam (maximal  $\pm 1.5\%$ ) and for absorption, by the method of Busing & Levy (1957), were applied.

Since  $Z = 4$  and the general position in  $Pnma$  is eightfold, the Zn and dithionite ions and the pyridine molecule have to lie at special positions with multiplicity 4. The positions of the Zn and S atoms were deduced from a Patterson map. Zn lies on the mirror plane ( $x, \frac{1}{4}, z$ ) and S at a general position. Thereafter, a difference Fourier map showed the positions of the O, N and C atoms.

The structure was refined by full-matrix least-squares calculations, with anisotropic S, O, N and C atoms and scattering factors reported by Cromer & Mann (1968). H atoms were refined isotropically with the scattering factor reported by Stewart, Davidson & Simpson (1965). During the final cycles the C—H directions were kept fixed and C—H was constrained at approximately 1.08 Å. The very strong reflexion 020 for which  $|F_o|$  was considerably lower than  $|F_c|$  (because of extinction, Zachariasen, 1968) was given zero weight. For the remaining 998 reflexions  $w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$ ,  $\sigma(F_o)$  being based on counting statistics. The values of the final residuals  $R_w = [\sum w(F_o - k^{-1}F_c)^2 / \sum wF_o^2]^{1/2}$  and  $R = \sum |F_o - k^{-1}F_c| / \sum |F_o|$  are 0.030 and 0.061 respectively. The goodness of fit  $G = [\sum w(F_o - k^{-1}F_c)^2 (N_o - N_v)]^{1/2}$  is 2.43.

The results of the final least-squares cycles are given in Table 2.\* The final difference map showed maxima near the centres of the S—S and S—O bonds, varying in height between 1.5 and  $2.5\sigma$  ( $\sigma = 0.20$  e Å $^{-3}$ ).

Calculations were performed with the set of programs of the XRAY system (1973).

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33277 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final fractional atomic coordinates ( $\times 10^4$ , for H  $\times 10^3$ )*

Standard deviations as calculated by the least-squares program are given in parentheses in units of the last digit.

	x	y	z
Zn	6714.8 (8)	2500	3199.4 (8)
S	3524.0 (12)	1424.8 (11)	4539.9 (11)
O(1)	5201 (3)	1268 (3)	4021 (3)
O(2)	2385 (3)	1261 (3)	3281 (3)
N	8375 (5)	2500	4825 (5)
C(1)	8872 (5)	1466 (4)	5419 (5)
C(2)	9855 (5)	1421 (5)	6633 (5)
C(3)	10356 (8)	2500	7215 (7)
H(1)	830	64	504
H(2)	1009	56	713
H(3)	1082	250	830

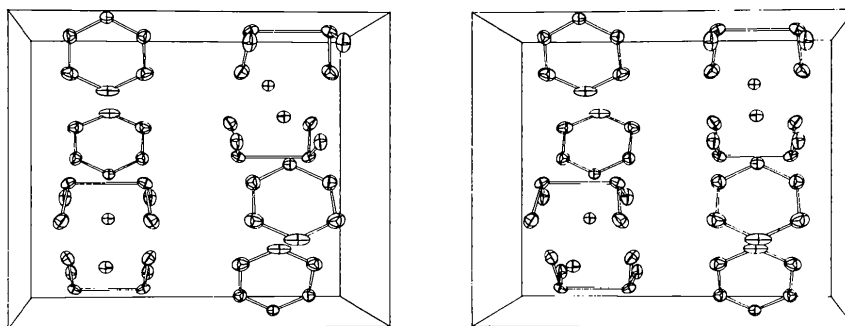


Fig. 1. Stereoscopic view of the structure of  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$  along the  $x$  axis, which is pointing upwards.

### Description of the structure

#### Crystal packing

Fig. 1 shows a stereoscopic picture of the crystal structure of  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$  and in Fig. 2 the numbering scheme is given. Bond lengths and short non-bonded distances are listed in Table 3. From the figures and Table 3 we see that the  $\text{Zn}^{2+}$  ion is surrounded at short

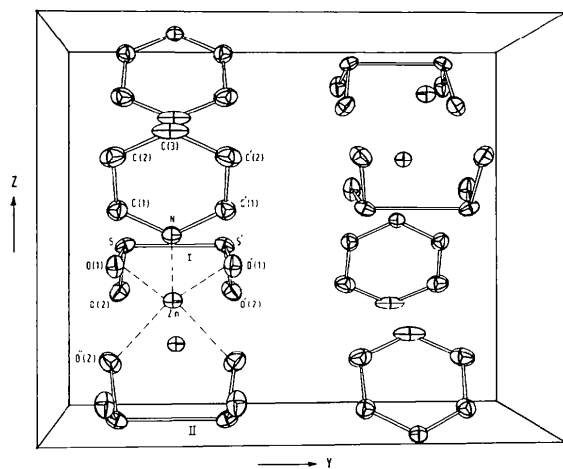


Fig. 2. Numbering and short distances in  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$ .

distances by one N and four O atoms, which form a slightly deformed tetragonal pyramid with the N as apex. The  $\text{Zn}^{2+}$  ion lies slightly (0.47 Å) above the approximately square base, formed by two O atoms of type O(1) of  $\text{S}_2\text{O}_4^{2-}$  (I) and two O atoms of type O''(2) of  $\text{S}_2\text{O}_4^{2-}$  (II). Thus one  $\text{S}_2\text{O}_4^{2-}$  unit is coordinated to two successive  $\text{Zn}^{2+}$  ions related by the  $a$  glide plane perpendicular to  $z$ . In this way a zigzag chain structure along  $x$  is formed. Apart from the  $\text{Zn} \cdots \text{O}$  and  $\text{Zn} \cdots \text{N}$  distances mentioned above there are no distances shorter than the sum of the relevant van der Waals radii.

#### The pyridine ring

The pyridine ring is planar. Atomic distances to the best plane are given in Table 4. Bond lengths and angles are in reasonable agreement with the values found in pyridine itself (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958). Only the CNC angle tends to be larger than in pyridine ( $116.8^\circ$ ). This is most likely caused by the coordination to the  $\text{Zn}^{2+}$  ion, which can be considered as an electron-withdrawing substituent. The angle  $\text{Zn} \cdots \text{N} \cdots \text{C}(3)$  is  $174^\circ$ .

From Figs. 1 and 2 it can be seen that the atoms of the pyridine ring, as well as the O atoms of the  $\text{S}_2\text{O}_4^{2-}$  ions, have rather large thermal parameters. For C(3) especially the thermal motion is considerable. This is

Table 3. Bond lengths (Å), short non-bonded distances (Å) and angles ( $^\circ$ )

Standard deviations calculated from the standard deviations in Table 2 are given in parentheses in units of the last digit. Corresponding values for  $\text{Na}_2\text{S}_2\text{O}_4$  (Dunitz, 1956) are given in square brackets, with  $\sigma(\text{S}-\text{S}) = 0.016$ ,  $\sigma(\text{S}-\text{O}) = 0.018$  Å.

S-S'	2.386 (2) [2.389]	O(1)SS'O'(2)	111.5 [110.0]	C'(1)NC(1)	118.0 (4)
S-O(1)	1.511 (3) [1.496]	S'S^O(1)SO(2)	101.8 [105.3]	NC(1)C(2)	123.1 (4)
S-O(2)	1.517 (3) [1.515]	Zn...O(1)	2.022 (3)	C(1)C(2)C(3)	117.6 (5)
S'SO(1)	96.61 (12) [98.0]	Zn...O''(2)	2.013 (3)	C(2)C(3)C'(2)	120.6 (5)
S'SO(2)	96.89 (12) [99.4]	Zn...N	2.051 (5)	NC(1)H(1)	116.6 (25)
O(1)SO(2)	110.37 (17) [108.3]	ZnNC(1)	120.8 (3)	C(2)C(1)H(1)	119.4 (25)
O(1)...O(2)	2.486 (4) [2.439]	N-C(1)	1.338 (5)	C(1)C(2)H(2)	118.8 (26)
O(1)...O'(1)	2.734 (4) [2.868]	C(1)-C(2)	1.390 (6)	C(3)C(2)H(2)	123.3 (26)
O(2)...O'(2)	2.750 (4) [2.868]	C(2)-C(3)	1.378 (7)	C(2)C(3)H(3)	118.3 (7)
O(1)...O''(2)	2.808 (4)				

Table 4. *The pyridine ring in ZnS<sub>2</sub>O<sub>4</sub>·pyr*

Atoms included: N, C(1), C(2), C(3), C'(2), C'(1)				
Equation of least squares plane				
$0.794X - 0.607Z = 1.753$				
Distances of atoms to this plane ( $\text{\AA} \times 10^3$ )				
N	-3	C(1) and C'(1)	6	Zn 207
C(3)	3	C(2) and C'(2)	-6	
Angle between the plane and Zn...N: 174.1 (3)°				

due to a large extent to a strong libration of the pyridine ring around an axis perpendicular to its plane and going through the N atom in good approximation.

#### The dithionite ion

Because of its special location about the mirror plane at  $y = \frac{1}{4}$ , the  $\text{S}_2\text{O}_4^{2-}$  ion possesses  $C_s (m)$  symmetry, which means that the ion has the eclipsed conformation. In good approximation the ion also has a twofold (non-crystallographic) axis, so that it has approximate  $C_{2v} (mm2)$  symmetry. In this respect the conformation of the  $\text{S}_2\text{O}_4^{2-}$  ion in  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$  agrees with that observed in  $\text{Na}_2\text{S}_2\text{O}_4$  (Dunitz, 1956). In the latter case there is strict twofold symmetry, however, whereas the mirror planes are of non-crystallographic nature. From Table 3 it can be seen that corresponding S—S and S—O bond lengths in the  $\text{S}_2\text{O}_4^{2-}$  ions in the two compounds do not show significant differences. Small differences are observed, however, between short intramolecular non-bonded distances and angles. These differences have tentatively been ascribed to the differences in packing between  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$  described below.

#### Comparison of the packing in $\text{Na}_2\text{S}_2\text{O}_4$ and $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$

In the crystal structure of  $\text{Na}_2\text{S}_2\text{O}_4$ , the  $\text{Na}^+$  ion has short distances to six O atoms (Dunitz, 1956). Four of the coordinating atoms (at 2.33–2.38  $\text{\AA}$  from  $\text{Na}^+$ ) form a deformed square and  $\text{Na}^+$  lies at a short distance (0.44  $\text{\AA}$ ) from this square. In this respect  $\text{Na}_2\text{S}_2\text{O}_4$  resembles  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$ . As is shown in Fig. 3 there are also differences in the packing of the two structures. In

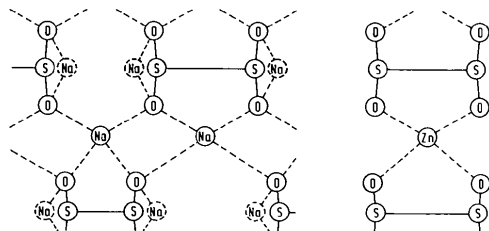


Fig. 3. The interactions between O and positive ions in  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$ .

$\text{Na}_2\text{S}_2\text{O}_4$  the four O atoms forming the square around the  $\text{Na}^+$  ion belong to three  $\text{S}_2\text{O}_4^{2-}$  units instead of two, as is the case in  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$ . In this way the packing for  $\text{Na}_2\text{S}_2\text{O}_4$  is such that (double) layers perpendicular to the  $y$  axis are formed (see also Fig. 3 of Dunitz, 1956). Because each O atom is coordinated to three  $\text{Na}^+$  ions, the forces exerted on the (charged) O atoms by the  $\text{Na}^+$  ions cancel in good approximation. In contrast to this, Fig. 3 shows that for  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$  a rather large resulting force on the O atoms is present, which makes  $\text{O}(1) \cdots \text{O}'(1)$  and  $\text{O}(2) \cdots \text{O}'(2)$  short and  $\text{O}(1) \cdots \text{O}(2)$  large. This means that the angles  $\text{SSO}$  and  $\text{SS} \wedge \text{OSO}$  are smaller in  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$  than those in  $\text{Na}_2\text{S}_2\text{O}_4$ , whereas the angles  $\text{OSO}$  and  $\text{OSSO} \wedge \text{OSSO}$  are larger, in agreement with experiment (Table 3).

#### Discussion of the dithionite ion

The S—O and S—S bonds in  $\text{S}_2\text{O}_4^{2-}$  have been compared with corresponding bonds in a large number of compounds by Kiers (1976); some examples are given here.

The S—O bonds of 1.514 (3)  $\text{\AA}$  in the  $-\text{O}_2\text{S}-\text{SO}_2^-$  ion in  $\text{ZnS}_2\text{O}_4 \cdot \text{pyr}$  and of 1.506 (10)  $\text{\AA}$  in  $\text{Na}_2\text{S}_2\text{O}_4$  may be compared with the S—O bonds in sulfites, for instance in  $\text{Na}_2\text{SO}_3$  [1.504 (3)  $\text{\AA}$ ; Larsson & Kierkegaard, 1969]. In neutral species with three-coordinated sulfur the S—O bond lengths are considerably shorter, for instance 1.476 (4)  $\text{\AA}$  in the sulfoxide  $\text{PhS}(\text{SO})\text{SPh}$  (Kiers & Vos, 1978). If only S 3s and 3p orbitals are assumed to be used for the bonding the three-coordinated S atoms in the above compounds have one lone-pair of electrons. A decrease in S—O bond lengths is found if this lone pair is involved in the bonding to an O atom. The S—O bond length is 1.452 (1)  $\text{\AA}$  for the dithionate ion in  $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  (Kiers, Piepenbroek & Vos, 1978), 1.484 (1)  $\text{\AA}$  for the  $\text{SO}_4^{2-}$  ion in  $\text{Na}_2\text{SO}_4$  (Nord, 1973) and 1.428 (1)  $\text{\AA}$  in diphenyl disulfone (Kiers & Vos, 1972).

The valence angles in the  $\text{S}_2\text{O}_4^{2-}$  ion are smaller than the tetrahedral value on average (Table 3) due to the presence of the lone pair, with relatively strong s

Table 5. *Comparison of Q—S bond lengths ( $\text{\AA}$ ) between sulfates ( $\text{QSO}_2^-$ ) and sulfonates ( $\text{QSO}_3^-$ )*

$\text{Q}-\text{SO}_2^-$	$\text{Q}-\text{S}$	$\text{Q}-\text{SO}_3^-$	$\text{Q}-\text{S}$
$(\text{CH}_2\text{OH})-\text{SO}_2^-$	1.83 (a)	$-\text{O}_3\text{S}(\text{CH}_2)-\text{SO}_3^-$	1.77 (e)
$(\text{NH}_3)_2\text{C}^+-\text{SO}_2^-$	1.85 (b)		
$-\text{O}_3\text{S}-\text{SO}_2^-$	2.17 (c)	$-\text{O}_3\text{S}-\text{SO}_3^-$	2.14 (f)
$-\text{O}_2\text{S}-\text{SO}_2^-$	2.39 (d)	$-\text{O}_2\text{S}-\text{SO}_3^-$	2.17 (c)

References: (a) Truter (1962a), (b) Sullivan & Hargreaves (1962), (c) Baggio (1971), (d) present work, (e) Truter (1962b), (f) Kiers, Piepenbroek & Vos (1978).

character, at the S atoms. The partial double-bond character of the S—O bonds causes the angle OSO ( $110.4^\circ$ ) to be larger than the angles SSO ( $96.8^\circ$ ).

The S—S bond in  $S_2O_4^{2-}$  (2.39 Å) is considerably longer than the S—S bonds in PhSSPh [2.03 (1) Å; Lee & Bryant, 1969],  $Ph(SO_2)(SO_2)Ph$  [2.193 (1) Å; Kiers & Vos, 1972],  $S_2O_6^{2-}$  in  $Na_2S_2O_6 \cdot 2H_2O$  [2.141 (1) Å; Kiers, Piepenbroek & Vos, 1978] and  $^-O_2S-SO_3^-$  in  $(NH_4)_2S_2O_5$  [2.170 (4) Å; Baggio, 1971]. This suggests that the  $S_2O_4^{2-}$  ion can be thought of as two  $SO_2^-$  radicals weakly linked together. In this respect it is noteworthy that, in general, sulfinates of the type  $Q-SO_2^-$  (see Table 5) have longer  $Q-S$  bonds than the corresponding sulfonates  $Q-SO_3^-$ , and that, especially, a strong increase in bond length is observed when going from  $^-O_2S-SO_3^-$  to  $^-O_2S-SO_2^-$ . It is further interesting to note that the isoelectronic radicals  $PF_2$ ,  $SO_2^-$  and  $ClO_2$ , in which the central atoms (P, S and Cl) are consecutive atoms in the periodic table, have in common that they do not unite to molecules with strong central bonds. Two  $PF_2$  radicals form a (staggered) molecule  $P_2F_4$  with P—P [2.281 (6) Å; Hodges, Su & Bartell, 1975] *ca* 0.1 Å longer than those in  $P_2(CF_3)_4$  [2.182 (16) Å; Hodges *et al.*, 1975] and  $P_2(CH_3)_4$  [2.192 (9) Å; McAdam, Beagley & Hewitt, 1970]. As we have seen above, in the (eclipsed)  $S_2O_4^{2-}$  ion the bond between the two  $SO_2^-$  units is extraordinarily long (2.39 Å). The stable  $ClO_2$  radicals, finally, do not dimerize to 'Cl<sub>2</sub>O<sub>4</sub>' molecules. It thus appears that the tendency to bond formation decreases in the order  $PF_2$ ,  $SO_2^-$ ,  $ClO_2$ . This difference and the difference in conformation between  $P_2F_4$  and  $S_2O_4^{2-}$  can be explained qualitatively by considering the valency structures given in Fig. 4. In drawing these valency structures it has been assumed that 3*d* orbitals do not take part in the bonding, in agreement with the fact that from EPR spectra of  $SO_2^-$  and  $ClO_2$  (Atkins & Symons, 1967) no evidence of *d*-orbital participation was found. If we further suppose that valency structures without formal charge at the central atoms are favoured, structure β is more favourable for  $S_2O_4^{2-}$  than for  $P_2F_4$ , implying that for  $S_2O_4^{2-}$  the tendency to have an eclipsed conformation and a long central bond is greater than that for  $P_2F_4$ . For the unstable 'Cl<sub>2</sub>O<sub>4</sub>' molecule both the α and

β structures are unfavorable. The qualitative explanation given above should be rationalized by quantum-mechanical calculations. We have not been able, however, to describe the  $S_2O_4^{2-}$  structure by *ab initio* calculations with single-determinant wave functions. In this context we note that with single-determinant wave functions low-lying triplet states were calculated for  $S_2O_4^{2-}$ , which might indicate that we are indeed dealing with two almost isolated  $SO_2^-$  radicals. As is well known, a single-determinant wave function is not appropriate to describe such structures. A similar situation occurs for  $N_2O_4$  which has a long N—N bond of 1.75 Å and a planar rather than a *gauche* conformation (Smith & Hedberg, 1956). Ahlrichs & Keil (1974) explicitly mentioned the important effects of electron correlation in the rationalization of the  $N_2O_4$  structure. In the near future we will use a many-determinant approach for  $S_2O_4^{2-}$  to check whether we can explain the eclipsed conformation in this way. Moreover, account may have to be taken of the fact that the  $S_2O_4^{2-}$  species bears a double negative charge.

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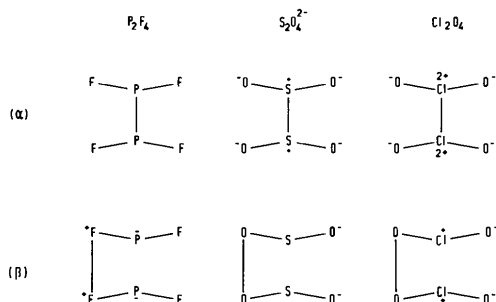


Fig. 4. Valency structures (α and β) of  $P_2F_4$ ,  $S_2O_4^{2-}$  and 'Cl<sub>2</sub>O<sub>4</sub>'.

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## Structure Cristalline du Méthanesulfonate de Cadmium Dihydraté: $\text{Cd}(\text{CH}_3\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$

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Crystals of cadmium methanesulphonate dihydrate are triclinic, space group  $P\bar{1}$ , with  $a = 4.777$  (1),  $b = 6.098$  (1),  $c = 9.993$  (2) Å,  $\alpha = 124.71$  (1),  $\beta = 91.90$  (2),  $\gamma = 94.35$  (2)° and  $Z = 1$ . Mo  $K\bar{\alpha}$  intensities were collected on an automatic four-circle diffractometer and the structure was determined by means of Fourier syntheses. An anisotropic full-matrix least-squares refinement was performed yielding a final  $R$  of 0.065 for the 1172 reflexions actually measured. The Cd atom is located at the inversion centre of an octahedron constituted by two aqueous O atoms and four sulphonic O atoms belonging to four methanesulphonato groups. All the Cd—O bond lengths are between 2.261 (4) and 2.295 (4) Å and the O—Cd—O angles are close to 90°. The Cd atoms are bridged by the methanesulphonato groups so forming parallel infinite chains.

### Introduction

Dans les méthanesulfonates métalliques cristallisés l'anion  $\text{CH}_3\text{SO}_3^-$  peut être mono-, tri- ou pentacoordinant selon le métal concerné (Charbonnier, Faure & Loiseleur, 1977*a,b,c*). La détermination de la structure du méthanesulfonate de cadmium dihydraté montre la bicoordination de ce groupement vis à vis du cadmium(II).

1172 répondant aux critères classiques de validité, ont été mesurées sur diffractomètre CAD-4 Nonius (Centre de Diffractométrie de l'Université Claude Bernard) à partir d'un cristal taillé en parallélépipède (0,15 × 0,17 × 0,20 mm). Les corrections de Lorentz et de polarisation ont été effectuées; l'absorption a été négligée.

### Résultats expérimentaux

La méthode d'obtention du composé et l'indexation du cliché de poudre ont été publiées précédemment (Charbonnier, Faure & Loiseleur, 1975). La symétrie est triclinique; le groupe  $P\bar{1}$  s'est imposé en cours de détermination de la structure. Les paramètres ont pour valeur:  $a = 4,777$  (1),  $b = 6,098$  (1),  $c = 9,993$  (2) Å,  $\alpha = 124,71$  (1),  $\beta = 91,90$  (2),  $\gamma = 94,35$  (2)°;  $V = 237,6$  Å<sup>3</sup>;  $M_r = 338,5$ ;  $D_m = 2,31$ ,  $D_c = 2,37$  g cm<sup>-3</sup>,  $Z = 1$ ;  $F(000) = 166$ ,  $\mu = 27,2$  cm<sup>-1</sup> pour  $\lambda(\text{Mo } K\bar{\alpha})$ .

Les intensités de 1225 réflexions indépendantes, dont

### Détermination de la structure

L'atome de cadmium étant placé à l'origine, l'indice  $R = \sum |F_o| - |F_c| / \sum |F_o|$  vaut 0,40. La synthèse Fourier consécutive permet de localiser tous les atomes sauf ceux d'hydrogène. Les positions atomiques ainsi déterminées révèlent la centrosymétrie de la maille: le groupe  $P\bar{1}$  a donc été retenu.

L'affinement de l'agitation thermique isotrope conduit en six itérations à un indice de 0,11. L'affinement d'agitation thermique anisotrope en quatre itérations a permis d'obtenir la valeur 0,086. La pondération était du type  $w = (\Delta F)^{-2}$  calculée d'après la courbe de variation de la moyenne des différences  $\Delta F = |F_o| -$