The Synthesis and Crystal Structure of $[K(18\text{-crown-}6)]^+$-$[NCS{\cdot}SO_2]^-$ (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane)†

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Reaction of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) with potassium thiocyanate in liquid sulfur dioxide gives, on recrystallisation from diethyl ether–sulfur dioxide, yellow crystals of the complex $[K(18\text{-crown-}6)]^+[NCS{\cdot}SO_2]^-$ in 98% yield. Vibrational spectroscopy points to the formation of a weak donor–acceptor complex anion $[NCS{\cdot}SO_2]^-$, and this was confirmed by X-ray crystallography: triclinic, $P\bar{1}$ (no. 2), $a = 7.635(2)$, $b = 9.595(2)$, $c = 8.171(1)$ Å, $\alpha = 102.95(2)$, $\beta = 95.68(2)$, $\gamma = 111.91(2)°$, $Z = 1$. The centrosymmetric $[K(18\text{-crown-}6)]^+$ cations are centred on special positions on the corners of the unit cell, and the complex anion is disordered about the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The nature of the disorder makes it difficult to locate the positions of some light atoms in the $[NCS{\cdot}SO_2]^-$ anion, although the S–S bond length, 2.736(9) Å, is consistent with the lability of the complex. Dissociation pressure measurements at different temperatures were used to determine a binding energy for gaseous $[NCS{\cdot}SO_2]^-$ of 66 kJ mol^{-1}, a value which is compared with those of related sulfite complexes in relation to Pearson's concept of 'absolute hardness'.

The ability of sulfur dioxide to form sulfite complexes of the type $[X{\cdot}SO_2]^-$ with halides and pseudohalides has been recognised since Jander's classic studies during the early years of this century.[1] The fluorosulfite ion, FSO_2^-, is the most stable halogenosulfite in the solid state, and the potassium salt is a colourless, crystalline compound with a dissociation pressure of sulfur dioxide of less than 1 mmHg at 100 °C.[2] Other alkali-metal halogeno- and pseudohalogeno-sulfites are subject to widely varying stoichiometries. They are appreciably less stable with respect to dissociation, and evolve SO_2 on standing at room temperature. Thus, potassium thiocyanate dissolves readily in liquid sulfur dioxide (solubility 502.0 mmol per 1000 g at 273 K)[1] to form a yellow solution; several investigations of this system have been performed since 1916, identifying three complexes, $K^+NCS^-{\cdot}nSO_2$, where $n = 0.5$,[3] 1[3,4] and 2.[5] Well-defined and relatively more stable 1 : 1 halogenosulfite salts are formed in the presence of large counter-cations such as $[P(CH_2Ph)Ph_3]^+$ and $[Na(18\text{-crown-}6)]^+$ (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane), and the crystal structure of $[P(CH_2Ph)Ph_3]^+$-$[I{\cdot}SO_2]^-$ has been determined, in the only structural investigation of a halogenosulfite salt to be reported to date.[6]

Halogeno- and pseudohalogeno-sulfites are of chemical interest because they exhibit a range of bonding regimes, from the relatively strong covalent bonding of the FSO_2^- anion to the much weaker donor–acceptor interactions of complexes like $[I{\cdot}SO_2]^-$, depending on the 'hardness' of the donor anion.[7] Most previous studies have probed the nature of the $X^-\cdots SO_2$ interaction by reference to spectroscopic properties, such as the perturbation of the SO_2 stretching frequencies, or to thermochemical parameters associated with the transformations (1) and (2).[1–8] However, with the exception of $[P(CH_2Ph)Ph_3]^+[I{\cdot}SO_2]^-$, structural details about halogeno- and pseudohalogeno-sulfites are lacking, and structures have been deduced mainly on qualitative rather than quantitative grounds.

$$M^+[X{\cdot}SO_2]^-(s) \longrightarrow M^+X^-(s) + SO_2(g) \qquad (1)$$

$$[X{\cdot}SO_2]^-(solv) \longrightarrow X^-(solv) + SO_2(solv) \qquad (2)$$

Eller and Kubas[6] have reported previously the formation of $[Na(18\text{-crown-}6)]^+[NCS{\cdot}SO_2]^-$, although they were unable to obtain either thermochemical details or crystals suitable for X-ray diffraction. We now report the characterisation and X-ray crystal structure of $[K(18\text{-crown-}6)]^+[NCS{\cdot}SO_2]^-$, as derived from the reaction of sulfur dioxide, 18-crown-6 and potassium thiocyanate [equation (3)]. The vibrational, thermochemical and crystallographic properties all point to the formation of a weak donor–acceptor adduct, $NCS^-\cdots SO_2$, and we discuss our results in terms of Pearson's concept of 'absolute hardness'.[9]

$$18\text{-crown-}6 + K^+NCS^- + SO_2 \xrightarrow{SO_2(l)} [K(18\text{-crown-}6)]^+[NCS{\cdot}SO_2]^- \qquad (3)$$

Experimental

Potassium thiocyanate (BDH) and 18-crown-6 (Aldrich) were recrystallised from ethanol and acetonitrile, respectively, and authenticated by their IR spectra. Sulfur dioxide (BDH) was dried over calcium hydride. All other solvents (ethanol, acetonitrile and diethyl ether) were dried according to standard procedures.[10] Solutions of sulfur dioxide were handled using conventional vacuum-line techniques.

Infrared spectra were recorded between 400 and 4000 cm^{-1} on a Mattson Galaxy FT-IR spectrometer at a resolution of 4 cm^{-1}. Raman spectra were measured on a Spex Ramalog 5 spectrophotometer, being excited with 514.5 nm radiation from a Spectra Physics model 165 Ar$^+$ laser; the GaAs detector was interfaced with a SCADAS data acquisition system (Glen Creston). Chemical analyses were performed by the departmental service in the Laboratory.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: mm Hg ≈ 133 Pa, eV ≈ 1.60 × 10^{-19} J.

Preparation of $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$.—In a typical experiment, equimolar amounts (2.5 mmol) of 18-crown-6 and potassium thiocyanate were dissolved in liquid sulfur dioxide (5 cm^3) to form a yellow solution. Diethyl ether (15 cm^3) (in which the product was insoluble) was then added, followed, if necessary, by more sulfur dioxide to dissolve any precipitate that formed, and the solution was filtered through a chilled sinter funnel. Yellow, block-like crystals of $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$ were grown by slow evaporation of the SO_2 from the solvent mixture over several hours. After the ether had been decanted, the crystals were dried by passing a stream of nitrogen and sulfur dioxide over them. The yield was typically 98% of that expected on the basis of equation (3) and the amount of potassium thiocyanate used.

To prevent loss of sulfur dioxide, the crystals were stored in a small Schlenk tube under an atmosphere of SO_2. The solid decolourised rapidly to give $[K(18\text{-crown-6})]^+[NCS]^-$ when allowed to stand in the air at room temperature, although it was stable under continuous pumping at 195 K. The salt $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$ (0.187 g) was regenerated quantitatively by exposure of $[K(18\text{-crown-6})]^+[NCS]^-$ (0.160 g) to an atmosphere of SO_2 for 2 min, followed by pumping at 195 K.

The IR spectrum, recorded on a powdered sample of $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$ between CsI discs, showed bands at the following wavenumbers (in cm^{-1}): 449m, 523m, 667w, 837ms, 961s, 1101vs, 1235m, 1248ms, 1277s, 1350s, 1364 (sh), 1375m, 1456vs, 2857vs, 2874vs, 2918vvs (18-crown-6); 725m [ν(CS)] and 2090s [ν(CN)]. IR bands due to complexed SO_2 were either very weak or obscured by 18-crown-6 absorptions. The Raman spectrum, recorded for a sample of the solid in a sealed melting-point tube under an atmosphere of sulfur dioxide, showed bands at the following wavenumber shifts (in cm^{-1}): 608, 635, 698, 777, 873, 932, 950, 1064, 1136, 1243, 1271, 1471, 2807, 2843, 2896 (all weak) (18-crown-6); 2089m [ν(CN)] and 1107s [$\nu_{sym}(SO_2)$].

Chemical Analysis.—The salt $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$ (0.188 g) was exposed to continuous pumping at room temperature until constant weight was attained (0.160 g). The SO_2 content was thus found to be 14.9% {calc. for $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$ 15.1%}. The colourless residue also analysed well for the expected formulation {Found: C, 44.30; H, 6.90; K, 10.35; N, 4.05; S, 8.65. Calc. for $[K(18\text{-crown-6})]^+[NCS]^-$: C, 43.20; H, 6.70; K, 10.80; N, 3.85; S, 8.85%}.

Results

Determination of ΔH *for the Complexation Reaction*.—A sample of $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$ was dissolved in a small amount of sulfur dioxide to give a viscous solution in a 500 cm^3 round-bottomed flask attached *via* a side-arm to a Baratron pressure gauge operating between 1 and 760 mmHg. The inside of the flask was coated with the solution, and all the SO_2 (from the solvent *and* the complex) was removed under continuous pumping, leaving a thin layer of $[K(18\text{-crown-6})]^+[NCS]^-$. The apparatus was filled with sulfur dioxide to a pressure between 500 and 700 mmHg to regenerate the $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$, and the excess of SO_2 was pumped away while the flask was cooled to 195 K. The cold-bath was then replaced with a water-bath at the desired temperature and the system allowed to equilibrate for 30 min. This process was repeated at different temperatures to obtain six dissociation pressures: temperature (T/K), vapour pressure (p/mmHg): 273.2, 17.1; 278.0, 25.0; 282.5, 34.5; 286.0, 46.5; 291.7, 75.1; 297.0, 109.2. A plot of ln p against $1/T$ (K^{-1}) yielded a value of ΔH for reaction (4) between 273 and 297 K of +50 ± 2 kJ mol^{-1}.

$$[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-(s) \longrightarrow [K(18\text{-crown-6})]^+[NCS]^-(s) + SO_2(g) \quad (4)$$

X-Ray Crystal Structure of $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$.—Several crystals of $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$ were mounted and sealed in hand-drawn Pyrex capillaries, which had been previously flushed with sulfur dioxide in order to stabilise the complex. Investigation of approximately ten such crystals by oscillation photography revealed a marked tendency towards twin or clump formation, but a weakly diffracting single crystal was eventually obtained, although its quality placed severe restrictions on the structure solution (see below). Following initial study by zero- and first-layer Weissenberg photography, which established a triclinic cell in addition to approximate cell dimensions, the crystal was transferred to a diffractometer.

Crystal data. $C_{13}H_{24}KNO_8S_2$, M = 425.5, triclinic, a = 7.635(2), b = 9.595(2), c = 8.171(1) Å, α = 102.95(2), β = 95.68(2), γ = 111.91(2)°, U = 528.4 Å^3, λ = 1.5418 Å, space group $P\bar{1}$ (no. 2), Z = 1, D_c = 1.359 g cm^{-3}, $F(000)$ = 224. Yellow, block-like crystals, dimensions 0.9 × 0.15 × 1.1 mm.

Data collection. CAD-4 diffractometer, ω–2θ mode with ω scan width (0.9 + 0.15 tan θ)°. Graphite-monochromated Cu-Kα radiation. 1668 Reflections measured (θ_{max} = 55°, ranges of h, k and l: −8 to 8, −1 to 10 and −8 to 8), 1305 unique, giving 428 observed with $I > 3\sigma(I)$. Intensity controls were monitored every 3600 s of X-ray exposure time. An empirical absorption correction (DIFABS)[11] max. 1.862, min. 0.625 was applied during refinement.

Structure solution and refinement. The data were reduced to a standard scale, and corrected for Lorentz and polarisation effects. Attempts to solve the structure in $P\bar{1}$ were unsuccessful, and it was solved initially in space group $P1$ (no. 1) by direct methods (SIR92),[12] which located the positions of the K, C and O atoms of the $[K(18\text{-crown-6})]^+$, although correlations within the ring, the rarity of structures in space group $P1$, and the centrosymmetric nature of related 18-crown-6 crystal structures {*e.g.* $[M(18\text{-crown-6})]^+[NCS]^-$, M = Na, K, Rb or Cs}[13] implied the presence of an inversion centre on the potassium atom. The volume of the unit cell (528.4 Å^3) implied the presence of only one formula unit per cell and accordingly the space group was changed to $P\bar{1}$ with the potassium atom at the origin. The sulfur atoms and one oxygen atom [O(1)] were located in Fourier (F_o) electron density maps, and the nitrogen atom was located in a subsequent difference map (CRYSTALS).[14] Following several cycles of isotropic least-squares refinement, with restraints placed on the geometry of the 18-crown-6 ring, the residual (R factor) stood at 0.11.

Some difficulty was encountered in establishing the positions of the remaining light atoms in the $[NCS{\cdot}SO_2]^-$ unit, and electron density maps were ultimately interpreted in terms of two half-occupied $[NCS{\cdot}SO_2]^-$ units in orientations related by the inversion centre at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). Some light atoms in one half-occupied orientation lie very close to the positions of the sulfur atoms in the alternative half-occupied orientation. Thus, in Fourier maps, for example, the central carbon atom of the S–C–N unit in one orientation could not be resolved from the sulfur atom of the SO_2 unit in the alternative orientation. At this stage the highest peak in the difference map was 0.5 e Å^{-3}, and so the remaining carbon and oxygen atoms were placed in calculated positions, and chemically reasonable restraints placed on the geometry of the NCS and SO_2 units. Least-squares refinement led the oxygen atom to develop an unacceptably large isotropic thermal parameter, which was interpreted as being due to further disorder, and so this atom was split over two positions [O(2) and O(3)], and the occupancies were refined. Prior to final refinement, an empirical absorption correction (DIFABS)[11] was applied, and a four-term Chebychev polynomial weighting scheme was optimised.[15] In the final cycles of least-squares refinement the model included positional and isotropic thermal parameters for all non-hydrogen atoms, except K and S, for which anisotropic thermal parameters were employed. Hydrogen atoms were placed at calculated positions and the refinement continued to convergence, to give a final R factor of 0.076 (R' = 0.066). The resulting picture of the unit cell is reproduced in Fig. 1. Fractional atomic coordinates for non-hydrogen atoms are given in Table 1; bond distances and angles are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

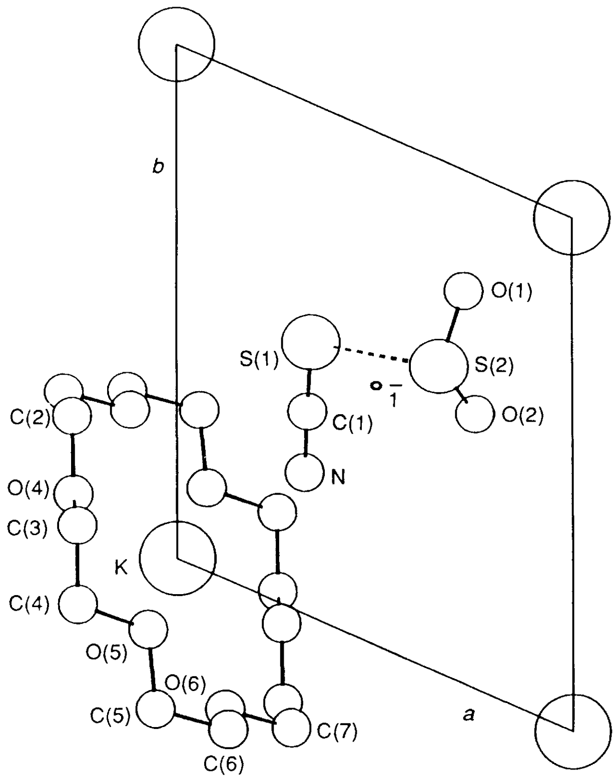

Fig. 1 The unit cell of $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$ viewed along the c axis, showing the position of the inversion centre at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and *one* orientation (occupancy 0.5) of the $[NCS{\cdot}SO_2]^-$ anion. Only one 18-crown-6 ring is shown for the purposes of clarity. The occupancies of O(2) and O(3) are 0.33 and 0.17, respectively; only the former is illustrated here, also in the interests of clarity. Diagrams illustrating the alternative orientation of the $[NCS{\cdot}SO_2]^-$ anion and the position of O(3) have been deposited

Table 1 Fractional atomic coordinates for $[K(18\text{-crown-6})]^+$-$[NCS{\cdot}SO_2]^-$; atoms O(2) and O(3) have occupancies of 0.33(1) and 0.17(1) respectively

Atom	x	y	z
S(1)	0.660(1)	0.4625(9)	0.5485(9)
C(1)	0.670(1)	0.605(2)	0.675(2)
N	0.678(2)	0.727(2)	0.781(2)
S(2)	0.3375(9)	0.404(1)	0.3188(9)
O(1)	0.275(1)	0.233(1)	0.271(1)
O(2)	0.246(2)	0.470(2)	0.429(2)
O(3)	0.424(2)	0.481(2)	0.206(2)
O(4)	−0.263(1)	0.0373(8)	0.2034(8)
O(5)	−0.074(1)	−0.1613(8)	0.2470(9)
O(6)	0.119(1)	−0.2496(9)	−0.0092(9)
C(2)	−0.2660(9)	0.1883(8)	0.2399(8)
C(3)	−0.2534(9)	−0.0202(8)	0.3505(9)
C(4)	−0.2528(9)	−0.1729(8)	0.3016(9)
C(5)	−0.0564(9)	−0.3073(8)	0.2043(9)
C(6)	0.1268(9)	−0.2858(9)	0.1492(9)
C(7)	0.2873(9)	−0.2295(9)	−0.0815(9)
K	0.0000	0.0000	0.0000

Discussion

The compound $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$ has been prepared as a yellow crystalline solid in essentially quantitative yield by the reaction of 18-crown-6 and potassium thiocyanate in liquid sulfur dioxide, followed by recrystallisation from SO_2–diethyl ether [equation (3)]. The dissociation pressure of the solid at 297 K was 109.2 mmHg, and it decolourised rapidly on exposure to air at room temperature, with the formation of $[K(18\text{-crown-6})]^+[NCS]^-$ and free SO_2, although samples could be conveniently stored in a Schlenk tube under an atmosphere of SO_2.

The lowest unoccupied molecular orbital of sulfur dioxide is a π* molecular orbital residing principally on the sulfur atom (**I**), and, when the molecule acts as an acid, it accepts electrons *via* this atom. By contrast, the terminal sulfur and nitrogen atoms of the thiocyanate ion are both potential basic sites, and whether donation occurs *via* the sulfur atom {to form a thiocyanato complex analogous to $[Pd(SbPh_3)_2(SCN)_2]$} or the nitrogen atom {to form an isothiocyanato complex analogous to $[Pd(PPh_3)_2(NCS)_2]$} is not easy to predict;[16] $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$ may therefore be formulated as either a thiocyanate or an isothiocyanate complex.

There are only small differences between the vibrational frequencies of the $[NCS{\cdot}SO_2]^-$ unit and those of uncomplexed NCS^- and SO_2, implying that the interaction between the two components on formation of the complex is weak, a result consistent with its observed lability. The fundamental $\nu_{sym}(SO_2)$ decreases on complexation from 1151 to 1107 cm^{-1}, in keeping with the behaviours of other halogeno- and pseudohalogenosulfites.[8] The CN stretching frequency at 2090 cm^{-1} is higher than in $[K(18\text{-crown-6})]^+[NCS]^-$ (2052 cm^{-1}), while ν(CS), at 725 cm^{-1}, is slightly lower than in the parent salt (732 cm^{-1}). On this evidence we are led, by analogies with related transition-metal complexes, to favour thiocyanato co-ordination [ν(CS) 690–720 cm^{-1}] over isothiocyanato co-ordination [ν(CS) 780–860 cm^{-1}].[17]

This conclusion is confirmed by the X-ray crystal structure of $[K(18\text{-crown-6})]^+[NCS{\cdot}SO_2]^-$, which consists of

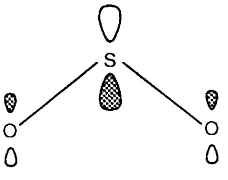

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Table 2 Bond distances (Å) and angles (°) for $[K(18\text{-crown-6})]^+$-$[NCS{\cdot}SO_2]^-$

S(1)–C(1)	1.49(2)	O(4)–K	2.802(7)
N–C(1)	1.26(2)	O(5)–C(4)	1.450(9)
S(2)–S(1)	2.736(9)	O(5)–C(5)	1.42(1)
S(2)–O(1)	1.47(1)	O(5)–K	2.783(8)
S(2)–O(2)	1.37(2)	O(6)–C(6)	1.41(1)
S(2)–O(3)	1.37(2)	O(6)–C(7)	1.432(9)
K–O(1)	2.77(1)	O(6)–K	2.844(7)
K–N	2.89(1)	C(2)–C(7)	1.45(1)
O(4)–C(2)	1.42(1)	C(4)–C(3)	1.43(1)
O(4)–C(3)	1.44(1)	C(5)–C(6)	1.468(9)
S(2)–S(1)–C(1)	99.1(5)	C(3)–O(4)–C(2)	114.2(6)
S(1)–C(1)–N	179.5(9)	C(4)–O(5)–C(5)	113.2(6)
K–N–C(1)	131.6(8)	C(6)–O(6)–C(7)	115.0(6)
S(1)–S(2)–O(1)	94.3(6)	O(4)–C(2)–C(7)	109.1(6)
S(1)–S(2)–O(2)	98.8(6)	O(4)–C(3)–C(4)	110.3(6)
O(1)–S(2)–O(2)	118.5(8)	O(5)–C(4)–C(3)	109.3(6)
S(1)–S(2)–O(3)	99.1(6)	O(5)–C(5)–C(6)	109.8(6)
O(1)–S(2)–O(3)	117.0(8)	O(6)–C(6)–C(5)	108.8(6)
O(2)–S(2)–O(3)	119.5(9)	O(6)–C(7)–C(2)	110.2(6)

centrosymmetric 18-crown-6 rings interacting with potassium ions located on the corners of the unit cell, and weakly interacting NCS^- and SO_2 units disordered about the inversion centre at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) (Fig. 1). The cations form channels in the structure which contain the pyramidal $[NCS{\cdot}SO_2]^-$ anions; under these circumstances one anionic orientation is unlikely to be energetically favoured over spatially similar alternatives, and this may be the source of the observed disorder. Centrosymmetric 18-crown-6 rings are also observed, amongst others, in the crystal structures of $[M(18\text{-crown-6})]^+[NCS]^-$ (M = Na, K, Rb or Cs), which have been discussed in detail by Dunitz *et al.*[13] The nature of the disorder led to difficulties in locating the positions of C(1) and O(2)/O(3), and it was necessary to place these atoms in chemically reasonable positions, and to restrain the geometry of the $[NCS{\cdot}SO_2]^-$ unit during refinement. Although it would be inappropriate to enter into a detailed discussion of the structure, the orientation of the $[NCS{\cdot}SO_2]^-$ unit is such that the partially negatively charged O(1) and N point along a body diagonal of the unit cell towards positively charged potassium ions, while the weakness of the NCS–SO_2 interaction implied by the spectroscopic results is reflected in the relatively long S–S bond length, 2.74(1) Å. This is considerably longer than the formal S–S single bond in α-S_8 [2.055(2) Å][18] but much shorter than twice the van der Waals radius of sulfur (4.06 Å for interactions made perpendicular to primary bonds),[19] and comparable with the transannular S–S interactions in $S_8{}^{2+}$ [2.86(1) Å][20] and S_4N_4 [2.66(1) Å].[21]

Both the spectroscopic properties and the structure of the $[NCS{\cdot}SO_2]^-$ complex point to the presence of a weak donor–acceptor-type interaction. A measure of the strength of the interaction is provided by the enthalpy change of +50 ± 2 kJ mol^{-1} estimated for the dissociation reaction (4). The difference between the lattice energies of $[K(18\text{-crown-6})]^+$-$[NCS{\cdot}SO_2]^-$ and $[K(18\text{-crown-6})]^+[NCS]^-$ was estimated to be 16 kJ mol^{-1} on the basis of Bartlett's equation,[22] which relates the lattice energy of an A^+B^- salt (U in kJ mol^{-1}) to the volume of one formula unit in the unit cell (V_m in Å^3) through equation (5). It follows that the binding energy of the

$$U = 2336.5V_m{}^{-\frac{1}{3}} + 110.5 \qquad (5)$$

$[NCS{\cdot}SO_2]^-$ complex in the gas phase (*i.e.* $\Delta H\{[NCS{\cdot}SO_2]^-(g) \rightarrow NCS^-(g) + SO_2(g)\}$) is 66 kJ mol^{-1}.

The binding energy of the $[NCS{\cdot}SO_2]^-$ complex is of a magnitude similar to that of $Me_3B{\cdot}NMe_3$ (74 kJ mol^{-1}),[23] although more meaningful comparisons can be made with related sulfite complexes, $[X{\cdot}SO_2]^-$, by the application of Pearson's concept of 'absolute hardness' to the donor anion X^-.[9] In general, the absolute hardness (η_X) of a species X has been defined as (i.p. − e.a.)/2, where i.p. is the ionisation potential and e.a. the electron affinity of X, both measured in eV. Pearson has pointed out that the derivation of η for an anion poses special problems since the electron affinity is unlikely to be available, although the hardness of the anion X^- can be approximated by using the ionisation potential and electron affinity of the corresponding neutral radical $X^{\bullet}$. Larson and McMahon[7] have demonstrated that the binding energy of a gaseous $[X{\cdot}SO_2]^-$ complex varies linearly with the hardness of the anion X^- estimated in this way. A value of $\eta_{NCS} = 4.1$ eV can be derived from the ionisation potential (10.4 eV)[24] and electron affinity (2.15 eV)[25] of $NCS^{\bullet}$; on this basis the binding energy determined for $[NCS{\cdot}SO_2]^-$ is pleasingly consistent with Larson and McMahon's correlation (Fig. 2, *cf.* ref. 7). The correlation presents a means by which halogenosulfite complexes may be systematically classified, and is clearly of value for predicting the stabilities of other, hitherto unknown halogeno- and pseudohalogeno-sulfites.

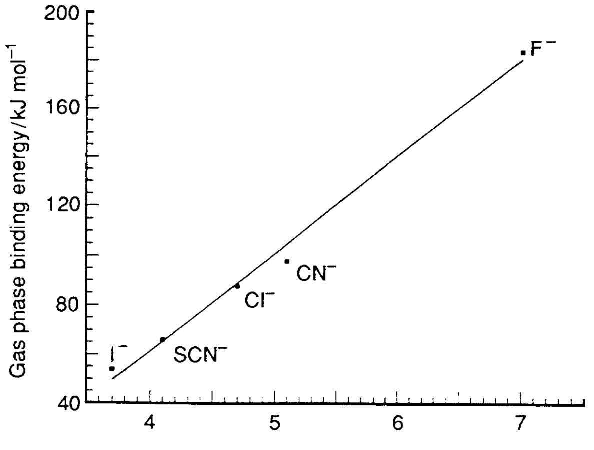

Fig. 2 Correlation of the binding energies of gaseous complex ions of the type $[X{\cdot}SO_2]^-$ (kJ mol^{-1}) with the 'absolute hardness' of the anion X^- (in eV), as estimated by the method of Pearson[9]

The present study illustrates the well known ability of a large cation to stabilise an otherwise labile complex anion by attenuation of the dissociative driving force arising from the difference in lattice energies between the complex and its solid dissociation product. This principle was first applied to halogenosulfite complexes by Eller and Kubas[6] in their work on the $[I{\cdot}SO_2]^-$ anion, although many other examples are well documented, *e.g.* $[NaL]^+Na^-$ (L = cryptand-222, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane).[26] The same strategy will surely allow other anionic complexes of SO_2 and SeO_2 to be isolated and structurally characterised.

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