

## Selective Reduction of Sulfuric Chloride: the Structure of the Chlorosulfite Ion

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The stable salt **2** is obtained from the reaction of SO<sub>2</sub>Cl<sub>2</sub> with the imidazol-2-ylidene **1**; the pyramidal structure of the chlorosulfite anion is confirmed both by X-ray structure and MO calculation.

The existence of stable salts of the chlorosulfite ion remains debatable, although they have been mentioned occasionally.<sup>1</sup> The reason for this may be the incomplete characterisation of the chlorosulfite ion and the lability of its S-Cl bond,<sup>2</sup> well known from decomposition of organic sulfites.<sup>3</sup> Reacting the imidazol-2-ylidene **1**<sup>†</sup> with sulfuric chloride results in the formal abstraction of a Cl<sup>+</sup> ion to give salt **2**.<sup>†</sup> This is different from the nucleophilic attack of the carbene at the centres of the two- and four-valent sulfur atoms which results in the formation of a stable carbon-sulfur bond.<sup>5</sup> **2** is moderately air-stable and eliminates SO<sub>2</sub> above 60 °C.

The X-ray structure analysis<sup>‡</sup> of **2** (Fig. 1) confirms the presence of the chlorosulfite ion with its expected pyramidal coordination geometry at the sulfur atom. The significant modification of the sulfur-oxygen distances [S-O(1) 1.321(9), S-O(2) 1.430(10) Å], the mean values are in the range of expectation, is probably attributed to weak interionic interactions [O(2)⋯H(4) 2.51 Å]. The chlorine-sulfur bond is significantly elongated [S-Cl(2) 2.492(5) Å] on comparison with the standard value of *ca.* 2.05 Å, which corresponds to its lability, mentioned above. The bond angles at the sulfur atom [O(1)-S-O(2) 114.2(5), O(1)-S-Cl(2) 103.6(4), O(2)-S-Cl(2) 99.7(5)°] agree with the prediction of the VSEPR concept.<sup>6</sup> No significant geometric deviations of the chloroimidazolium ion (Fig. 1) can be detected on comparison with other imidazolium compounds.<sup>7,8</sup>

It would be useful to confirm the geometry of the free chlorosulfite ion structure in **2** by a geometry optimization calculation<sup>9</sup> [in a calculation at MP2/6-31G(d)-niveau<sup>3</sup> the geometry was not presented]. Our calculations of the anion in C<sub>v</sub>-symmetry<sup>10</sup> are in good agreement with the experimental results for the S-O distance and angles (Table 1 and Fig. 1). There is a remarkable effect of the added set of *f*-functions to the basis set and of the consideration of electron correlations to the S-Cl distance which only agrees with the experimental results in the given method/basis set combination MP2/6-31 + G(3df). The geometry was characterised as a minimum at the potential hypersurface with the help of a frequency calculation [HF/6-31+G(3df)]. The relatively large S-Cl distance is

achieved by a donor-acceptor bond in which the chlorine atom donates into symmetry-adapted unoccupied orbitals of the sulfur atom. This is reflected in the calculated natural charges<sup>11</sup> (S: +1.86, Cl: -0.75, O: -1.06) as well as the calculated bond orders<sup>12</sup> (S-Cl: 0.32, S-O: 1.31).

From our calculations it is probable that the geometry of the free chlorosulfite ion is similar to that in the crystal lattice with the surrounding positive charge. The surprisingly mild and selective reduction of sulfuric chloride by an imidazol-2-ylidene offers a promising new application of these stable carbenes<sup>4,13</sup> in addition to their well-known interesting chemistry.

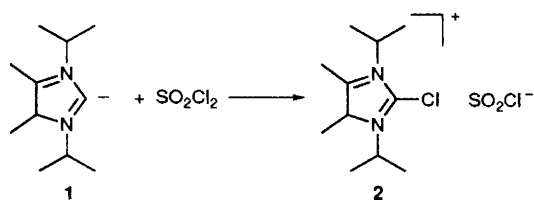
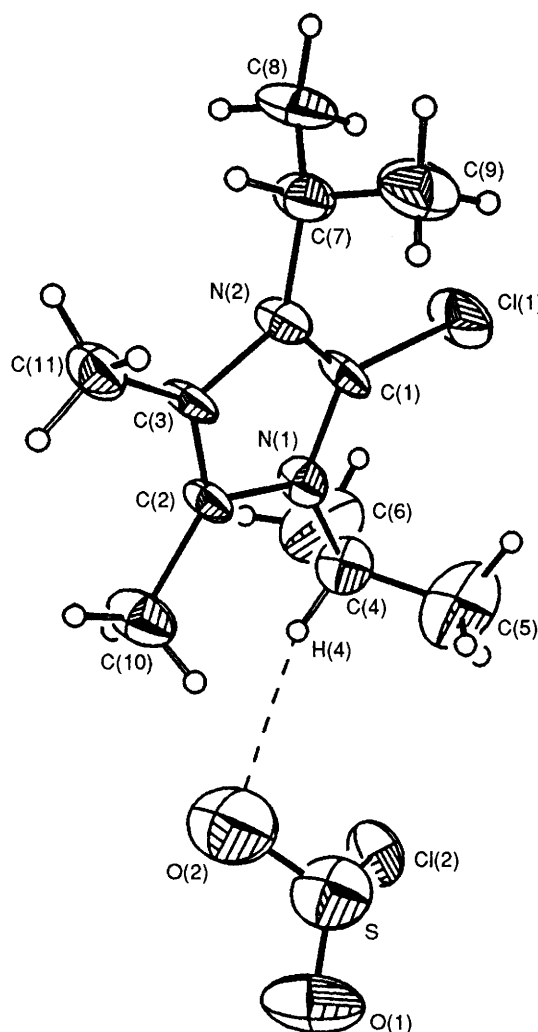


Table 1 Calculated parameters of the SO<sub>2</sub>Cl anion

	HF/ 6-31 + G(3d)	HF/ 6-31 + G(3df)	MP2/ 6-31 + G(3df)
S-Cl/Å	2.712	2.656	2.533
S-O/Å	1.414	1.411	1.464
O-S-O/°	115.6	115.4	115.3
O-S-Cl/°	102.0	101.7	101.7
E <sub>tot</sub> [H]	-1006.784535	-1006.805310	-1007.639215

Fig. 1 View of C<sub>11</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S **2** in the crystal lattice. Selected bond distances (Å) and angles (°): Cl(1)-C(1) 1.696(9), C(1)-N(1) 1.336(10), N(1)-C(2) 1.378(12), C(2)-C(3) 1.347(11), C(3)-N(2) 1.406(10), N(2)-C(1) 1.322(12), Cl(2)-S 2.492(5), S-O(1) 1.321(9), S-O(2) 1.430(10); N(1)-C(1)-N(2) 110.1(7), C(1)-N(1)-C(2) 107.6(7), N(1)-C(2)-C(3) 108.1(7), C(2)-C(3)-N(2) 106.6(7), C(3)-N(2)-C(1) 107.5(7), Cl(2)-S-O(1) 103.6(4), Cl(2)-S-O(2) 99.7(5), O(1)-S-O(2) 114.2(5).

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### Footnotes

† A solution of 0.72 g (4 mmol) **1**<sup>+</sup> in diethyl ether (30 ml) is added dropwise at  $-78^{\circ}\text{C}$  to 0.32 ml (4 mmol)  $\text{SO}_2\text{Cl}_2$  and warmed during 14 h to room temp. Yield after recrystallization of the resulting precipitate in pyridine-diethyl ether: 0.73 g (58%) **2**, colourless crystals.  $^1\text{H}$  NMR (300 MHz,  $[\text{D}_5]\text{pyridine}$ ,  $\text{Me}_4\text{Si}$  ext.):  $\delta$  4.78 [sept., 2H  $\text{CH}(\text{CH}_3)_2$ ;  $^3J$  7.0 Hz], 2.21 (s, 6 H, C-4, C-5- $\text{CH}_3$ ), 1.36 [d, 12H,  $\text{CH}(\text{CH}_3)_2$ ].  $^{13}\text{C}$  NMR (75.43 MHz,  $[\text{D}_5]\text{pyridine}$ ,  $\text{Me}_4\text{Si}$  ext.):  $\delta$  133.05 (C-2), 128.00 (C-4, C-5), 52.59 [ $\text{CH}(\text{CH}_3)_2$ ], 20.06 [ $\text{CH}(\text{CH}_3)_2$ ], 9.80 (C-4, C-5- $\text{CH}_3$ ). IR/ $\text{cm}^{-1}$  (Nujol):  $\nu_{\text{as}}$  (SO) 1248,  $\nu_{\text{s}}$  (SO) 1105,  $\nu$  ( $\text{SO}_2$ ) 530.

‡ The structure determination of **2** was performed with a weak reflecting crystal with dimensions ca.  $0.42 \times 0.22 \times 0.13 \text{ mm}^3$  with a R3m/V Nicolet four circle diffractometer (Mo-K $\alpha$ -radiation, graphite monochromator) at 163 K; with further cooling below 160 K the crystal was destroyed. Monoclinic, cell dimensions, from diffractometer angles of only 10 centred reflections in the  $2\theta$ -range  $4$ – $20^{\circ}$  gave  $a = 8.703(16)$ ,  $b = 18.830(21)$ ,  $c = 9.569(17)$  Å,  $\beta = 98.35(14)^{\circ}$ ,  $V = 1551.4(42)$  Å $^3$ ,  $P2_1/n$ ,  $Z = 4$ ,  $D_c = 1.350 \text{ g cm}^{-3}$ ,  $\mu = 0.55 \text{ mm}^{-1}$ . Data collection  $2\theta_{\text{max}} = 40^{\circ}$ , 1327 independent intensities, of which 1137 observed [ $F_o \geq 4\sigma(F)$ ]. Direct methods and structure refinement with SHELXTL-Plus program package (Vers. 4.11, Iris Indigo). 164 parameters, anisotropic ADPs for all atoms except hydrogen these were treated as riding groups,  $R = 0.085$ ,  $R_w = 0.090$ ,  $w^{-1} = \{\sigma^2(F_o) + 0.0005F_o^2\}$ , maximum residual electron density  $0.53 \text{ e \AA}^{-3}$ . Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 380071, the authors names, and the full citation of the journal.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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