

# Crystal structure of tetramethylformamidium disulfide $\mu$ -Oxo-bis-(trichloroferrate(III))

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Crystal Structure of Tetramethylformamidium disulfide  $\mu$ -oxo-bis-  
[trichloroferrate(III)]

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Oxidation of thioureas has been known to give a variety of reaction products depending on the substituents of the thioureas, the type of the oxidizing agent, the polarity of the reaction medium and other reaction conditions.<sup>1</sup> We have shown that oxidation of 1,1-diphenylthiourea and N-methylthiourea with iron (III) leads to 1,2,4-thiadiazoline derivatives.<sup>2,3</sup> Kinoshita et al. studied the mechanism of oxidation reaction of substituted thioureas with BPO and suggested that 1,2,4-thiazolidine heterocycles are formed through abstraction of thiourea hydrogen and sulfur atoms.<sup>4</sup> In this respect, it is interesting to examine oxidation products of thioureas having no urea hydrogen atoms. In this work we report on the crystal structure of the oxidation product of tetramethylthiourea with iron (III) chloride.

Tetramethylthiourea (1.32 g: 0.01 mol) and anhydrous iron (III) chloride (1.62 g: 0.01 mol) dissolved in absolute ethanol (30 ml) were reacted at room temperature for 1 h. Dark-red gel-like precipitate was formed, which was subsequently separated from the mother liquor by decantation. The residue was re-dissolved in anhydrous acetone dried with molecular sieve (60 ml). The solution was kept at 4 °C in refrigerator for a few days. Precipitated crystals were filtered off and dried in a desiccator. Two different types of crystals were obtained from the same acetone solution: diamond shaped petal-like crystals (Form I) and rhomboid platelet-like crystals (Form II). X-ray analyses were carried out on these two crystal modifications.

The detailed measurement conditions and crystal data are listed in Table 1. The atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, Vol. IV.<sup>5</sup> All calculations were performed using the program TEXSAN crystallographic software package.<sup>6</sup> The final atomic parameters are listed in Table 2. The molecular structure is shown in Fig. 1, together with the atomic labeling scheme. Selected bond distances and bond angles are listed in Tables 3 and 4.

Forms I and II turn out to be polymorphic forms of formamidinium salts of  $\mu$ -oxo-bis-[trichloroferrate(III)] ions where two tetramethylthiourea molecules are linked by a disulfide bond. Similar formamidinium disulfide salts were also derived from thiourea.<sup>7</sup> There are two independent  $\mu$ -oxo-bis-[trichloroferrate(III)] ions in the asymmetric unit of the Form I crystal, whereas only one ion exists in that of Form II. This ion occupies a

special position in the unit cell of the Form I crystal; the O(1) atom is situated on the mirror plane and the O(2) atom on the inversion center. Significant differences are observed in the Fe-O-Fe bond angles (Fe(1)-O(1)-Fe(2) and Fe(3)-O(2)-Fe(3) are  $146.4(2)^\circ$  and  $180^\circ$  for Form I and Fe(1)-O(1)-Fe(2) is  $167.9(1)^\circ$  for Form II). In consistent with variation in the Fe-O-Fe bond angles, the Fe-O-Fe antisymmetric vibrations are observed in IR spectra at  $845\text{ cm}^{-1}$  and  $890\text{ cm}^{-1}$  for Form I crystals and  $875\text{ cm}^{-1}$  for Form II crystals. Molecular geometries of the formamidinium disulfide part are generally similar for Form I and II crystals. The only significant differences are in the torsional angle around the C-S bond as shown in Table 4.

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Table 1 Crystal and experimental data

|                          | Form I                        | Form II                    |
|--------------------------|-------------------------------|----------------------------|
| Formula :                | $C_{10}H_{24}Cl_6Fe_2N_4OS_2$ |                            |
| Formula weight :         | 604.86                        |                            |
| Crystal system :         | orthorhombic                  | monoclinic                 |
| Space group:             | Pnma Z= 8                     | P2 <sub>1</sub> /n Z= 4    |
| Radiation :              | Mo K $\alpha$ (0.71069 Å)     |                            |
| T                        | 296 K                         |                            |
| $2\theta_{max}$          | 55.0 °                        |                            |
| Scan type :              | $\omega/2\theta$              |                            |
| F(000)                   | 2448                          | 1224                       |
|                          | $a=15.209(3)$ Å               | $a= 11.096(1)$ Å           |
|                          | $b=31.741(4)$ Å               | $b= 12.367(3)$ Å           |
|                          | $c=10.360(1)$ Å               | $c= 17.984(1)$ Å           |
|                          |                               | $\beta= 92.761(8)^\circ$   |
| V=                       | 5001(1) Å <sup>3</sup>        | 2465.0(6) Å <sup>3</sup>   |
| D <sub>calc</sub> =      | 1.61 g/cm <sup>3</sup>        | 1.63 g/cm <sup>3</sup>     |
|                          | $R=0.038, R_w=0.043$          | $R=0.027, R_w=0.036$       |
| $\mu$                    | 19.77 cm <sup>-1</sup>        | 20.06 cm <sup>-1</sup>     |
| No. of reflections used  | 3509 (I>3.00 $\sigma$ (I))    | 4222 (I>3.00 $\sigma$ (I)) |
| No. of parameters        | 331                           | 322                        |
| Goodness-of-fit          | 1.58                          | 1.44                       |
| $(\Delta/\sigma)_{max}$  | 0.39                          | 0.24                       |
| $(\Delta/\rho)_{max}$    | 0.58 e/Å <sup>3</sup>         | 0.36 e/Å <sup>3</sup>      |
| Measurement:             | Rigaku AFC-5R                 |                            |
| Program system:          | TEXSAN                        |                            |
| Structure determination: | direct method                 |                            |
| Refinement:              | full-matrix least-squares     |                            |

Table 2 Fractional coordinates of non-hydrogen atoms

| Atom    | x          | y           | z           | $B^{eq}/\text{\AA}^2$ |
|---------|------------|-------------|-------------|-----------------------|
| Form I  |            |             |             |                       |
| Fe(1)   | 0.96061(5) | 1/4         | 0.14384(7)  | 2.74(3)               |
| Fe(2)   | 1.04407(6) | 1/4         | -0.15781(8) | 3.44(4)               |
| Fe(3)   | 0.97319(4) | 0.02566(2)  | 0.64313(6)  | 3.67(3)               |
| Ci(1)   | 1.0349(1)  | 1/4         | 0.3280(2)   | 6.2(1)                |
| Ci(2)   | 0.8777(1)  | 0.19315(5)  | 0.1401(1)   | 7.49(8)               |
| Ci(3)   | 1.1861(1)  | 1/4         | -0.2111(2)  | 5.15(9)               |
| Ci(4)   | 0.9885(1)  | 0.30899(6)  | -0.2323(2)  | 9.4(1)                |
| Ci(5)   | 0.83547(8) | 0.04990(4)  | 0.6283(1)   | 4.95(6)               |
| Ci(6)   | 0.98059(8) | -0.01769(4) | 0.8103(1)   | 4.88(6)               |
| Ci(7)   | 1.0629(1)  | 0.07955(5)  | 0.6699(2)   | 6.99(8)               |
| O(1)    | 1.0332(3)  | 1/4         | 0.0120(4)   | 3.9(2)                |
| O(2)    | 1          | 0           | 1/2         | 7.3(3)                |
| S(1)    | 0.66490(7) | 0.08614(4)  | 0.1491(1)   | 3.78(5)               |
| S(2)    | 0.74706(8) | 0.06971(3)  | 0.2974(1)   | 3.95(5)               |
| N(1)    | 0.8073(2)  | 0.0787(1)   | -0.0038(3)  | 3.0(1)                |
| N(2)    | 0.7223(2)  | 0.1386(1)   | -0.0320(3)  | 3.3(2)                |
| N(3)    | 0.8496(2)  | 0.1279(1)   | 0.3998(3)   | 3.4(2)                |
| N(4)    | 0.7015(2)  | 0.1439(1)   | 0.4048(4)   | 4.9(2)                |
| C(1)    | 0.7400(2)  | 0.1031(1)   | 0.0274(4)   | 2.8(2)                |
| C(2)    | 0.8909(3)  | 0.0951(2)   | -0.0503(5)  | 4.0(2)                |
| C(3)    | 0.8041(4)  | 0.0327(2)   | 0.0070(7)   | 4.8(3)                |
| C(4)    | 0.6659(4)  | 0.1721(2)   | 0.0218(7)   | 5.1(3)                |
| C(5)    | 0.7494(4)  | 0.1463(2)   | -0.1658(5)  | 4.8(3)                |
| C(6)    | 0.7677(3)  | 0.1190(1)   | 0.3738(4)   | 3.3(2)                |
| C(7)    | 0.8757(4)  | 0.1561(2)   | 0.5059(5)   | 5.0(3)                |
| C(8)    | 0.9249(3)  | 0.1074(2)   | 0.3359(6)   | 5.0(3)                |
| C(9)    | 0.7114(6)  | 0.1898(3)   | 0.4034(8)   | 7.8(4)                |
| C(10)   | 0.6139(5)  | 0.1264(5)   | 0.438(1)    | 9.4(6)                |
| Form II |            |             |             |                       |
| Fe(1)   | 0.58611(3) | 0.21469(3)  | 0.40375(2)  | 3.32(2)               |
| Fe(2)   | 0.55387(3) | 0.19665(3)  | 0.20974(2)  | 3.25(1)               |
| Ci(1)   | 0.74734(7) | 0.12469(8)  | 0.44560(5)  | 5.73(4)               |
| Ci(2)   | 0.61482(8) | 0.38895(6)  | 0.42582(5)  | 5.46(4)               |
| Ci(3)   | 0.42753(6) | 0.15610(6)  | 0.46337(4)  | 4.48(3)               |
| Ci(4)   | 0.49272(8) | 0.35674(7)  | 0.16723(4)  | 5.55(4)               |
| Ci(5)   | 0.42852(6) | 0.06832(6)  | 0.16631(4)  | 4.91(3)               |
| Ci(6)   | 0.73310(6) | 0.15340(7)  | 0.16779(4)  | 4.92(3)               |
| O(1)    | 0.5580(2)  | 0.1953(2)   | 0.3075(1)   | 4.8(1)                |
| S(1)    | 0.19234(6) | 0.17084(6)  | 0.31176(4)  | 3.81(3)               |
| S(2)    | 0.01490(6) | 0.16160(5)  | 0.27311(4)  | 3.97(3)               |
| N(1)    | 0.2459(2)  | 0.3501(2)   | 0.3883(1)   | 3.46(9)               |
| N(2)    | 0.1042(2)  | 0.2374(2)   | 0.4407(1)   | 3.8(1)                |
| N(3)    | -0.0881(2) | 0.3477(2)   | 0.2315(1)   | 3.27(8)               |
| N(4)    | 0.0782(2)  | 0.3003(2)   | 0.1652(1)   | 3.8(1)                |
| C(1)    | 0.1792(2)  | 0.2624(2)   | 0.3881(1)   | 3.1(1)                |
| C(2)    | 0.3061(3)  | 0.3895(3)   | 0.3227(2)   | 4.4(1)                |
| C(3)    | 0.2793(3)  | 0.4094(3)   | 0.4568(2)   | 4.6(1)                |
| C(4)    | 0.0379(3)  | 0.3198(4)   | 0.4812(2)   | 5.2(2)                |
| C(5)    | 0.0783(4)  | 0.1246(3)   | 0.4605(2)   | 5.5(2)                |
| C(6)    | 0.0015(2)  | 0.2826(2)   | 0.2182(1)   | 3.1(1)                |
| C(7)    | -0.1435(3) | 0.4183(3)   | 0.1737(2)   | 4.5(1)                |
| C(8)    | -0.1499(3) | 0.3503(3)   | 0.3020(2)   | 4.4(1)                |
| C(9)    | 0.1127(3)  | 0.4093(3)   | 0.1419(2)   | 4.8(1)                |
| C(10)   | 0.1398(5)  | 0.2138(4)   | 0.1261(2)   | 6.2(2)                |

$$B^{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i a_j$$

Table 3 Selected bond lengths (Å)

| Atom  | Atom  | Distance  |          |
|-------|-------|-----------|----------|
|       |       | Form I    | Form II  |
| Fe(1) | O(1)  | 1.757(4)  | 1.760(2) |
| Fe(2) | O(1)  | 1.767(4)  | 1.757(2) |
| Fe(3) | O(2)  | 1.7402(6) |          |
| S(1)  | S(2)  | 2.048(2)  | 2.059(1) |
| S(1)  | C(1)  | 1.784(4)  | 1.792(2) |
| S(2)  | C(6)  | 1.780(4)  | 1.795(2) |
| N(1)  | C(1)  | 1.323(5)  | 1.313(3) |
| N(1)  | C(2)  | 1.457(5)  | 1.468(4) |
| N(1)  | C(3)  | 1.465(6)  | 1.466(3) |
| N(2)  | C(1)  | 1.312(5)  | 1.325(3) |
| N(2)  | C(4)  | 1.476(6)  | 1.471(4) |
| N(2)  | C(5)  | 1.467(6)  | 1.471(4) |
| N(3)  | C(6)  | 1.306(5)  | 1.310(3) |
| N(3)  | C(7)  | 1.471(6)  | 1.470(4) |
| N(3)  | C(8)  | 1.474(6)  | 1.472(4) |
| N(4)  | C(6)  | 1.319(5)  | 1.326(3) |
| N(4)  | C(9)  | 1.464(9)  | 1.468(4) |
| N(4)  | C(10) | 1.48(1)   | 1.467(4) |

Estimated standard deviations in the least significant figure are given in parentheses.

Table 4 Selected bond angles (°) and torsion angles (°).

| Atom   | Atom | Atom  | Atom    | Atom | Atom  | Atom      | Atom      |
|--------|------|-------|---------|------|-------|-----------|-----------|
| Form I |      |       | Form II |      |       | Angle     |           |
| Fe(1)  | O(1) | Fe(2) | Fe(2)   | O(1) | Fe(1) | 146.4(2)  | 167.9(1)  |
| Fe(3)  | O(2) | Fe(3) | Fe(3)   | O(2) | Fe(3) | 180.00    |           |
| S(2)   | S(1) | C(1)  | C(1)    | S(1) | S(2)  | 102.5(1)  | 100.47(8) |
| S(1)   | S(2) | C(6)  | C(6)    | S(2) | S(1)  | 102.6(1)  | 101.05(8) |
| C(1)   | N(1) | C(2)  | C(2)    | N(1) | C(1)  | 123.2(3)  | 123.5(2)  |
| C(1)   | N(1) | C(3)  | C(3)    | N(1) | C(1)  | 122.6(4)  | 122.4(2)  |
| C(2)   | N(1) | C(3)  | C(3)    | N(1) | C(2)  | 114.2(4)  | 113.7(3)  |
| C(1)   | N(2) | C(4)  | C(4)    | N(2) | C(1)  | 124.2(4)  | 122.5(3)  |
| C(1)   | N(2) | C(5)  | C(5)    | N(2) | C(1)  | 121.9(4)  | 122.1(3)  |
| C(4)   | N(2) | C(5)  | C(5)    | N(2) | C(4)  | 113.6(4)  | 115.4(3)  |
| C(6)   | N(3) | C(7)  | C(7)    | N(3) | C(6)  | 122.9(4)  | 122.1(2)  |
| C(6)   | N(3) | C(8)  | C(8)    | N(3) | C(6)  | 123.5(4)  | 124.1(2)  |
| C(7)   | N(3) | C(8)  | C(8)    | N(3) | C(7)  | 113.2(4)  | 113.5(2)  |
| C(6)   | N(4) | C(9)  | C(9)    | N(4) | C(6)  | 121.1(5)  | 122.8(2)  |
| C(6)   | N(4) | C(10) | C(10)   | N(4) | C(6)  | 121.1(7)  | 123.6(3)  |
| C(9)   | N(4) | C(10) | C(10)   | N(4) | C(9)  | 117.8(7)  | 113.5(3)  |
| S(1)   | C(1) | N(1)  | N(1)    | C(1) | S(1)  | 119.5(3)  | 117.2(2)  |
| S(1)   | C(1) | N(2)  | N(2)    | C(1) | S(1)  | 117.3(3)  | 118.4(2)  |
| N(1)   | C(1) | N(2)  | N(2)    | C(1) | N(1)  | 123.1(4)  | 124.4(2)  |
| S(2)   | C(6) | N(3)  | N(3)    | C(6) | S(2)  | 116.8(3)  | 117.1(2)  |
| S(2)   | C(6) | N(4)  | N(4)    | C(6) | S(2)  | 120.1(3)  | 119.7(2)  |
| N(3)   | C(6) | N(4)  | N(4)    | C(6) | N(3)  | 123.1(4)  | 123.2(2)  |
| S(1)   | S(2) | C(6)  | N(3)    | S(2) | S(1)  | -132.0(3) | -128.1(2) |
| S(1)   | S(2) | C(6)  | N(4)    | S(2) | S(1)  | 49.9(4)   | 54.3(2)   |
| S(2)   | S(1) | C(1)  | N(1)    | S(1) | S(2)  | 50.2(3)   | -124.4(2) |
| S(2)   | S(1) | C(1)  | N(2)    | S(1) | S(2)  | -133.4(3) | 56.2(2)   |

Estimated standard deviations in the least significant figure are given in parentheses.



## Figure Captions

Fig. 1 Molecular structure with the numbering of the atoms, (a) Form I and (b) Form II. Primed atoms are symmetrically related either via the mirror or the inversion center. Thermal ellipsoids of the non-hydrogen atoms scaled to enclose 50 % probability.

