Chelating Behaviour of $S_2O_3^{2-}$ in Thiosulphatotetrathioureanickel(II) Monohydrate

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IT is known that the $S_2O_3^{2-}$ group can behave as a bidentate ligand when co-ordinating to metal atoms,[1] but no direct evidence of this through *X*-ray structural work has yet been given. Chelating behaviour is now reported for $S_2O_3^{2-}$ in the crystals of thiosulphatotetrathioureanickel(II) monohydrate, $Ni[SC(NH_2)_2]_4S_2O_3,H_2O$, in which the metal atom co-ordinates to four sulphur atoms from thiourea molecules and to a sulphur and to an oxygen atom from a thiosulphate group, in a distorted octahedral environment as shown in the Figure.

The Ni–S(thiosulphate) distance is longer than the Ni–S(thiourea) distance, so the co-ordination polyhedron can be considered also as a (distorted) square pyramid with an extra co-ordination site under the base. The two bonding interactions between $S_2O_3^{2-}$ and Ni are different in strength,

a = 2·107 (9) Å
b = 2·396 (4)
c = 2·399 (4)
d = 2·442 (4)
e = 2·469 (4)
f = 2·718 (4)

$\angle bc$ = 87·2 (0·1)°
$\angle bd$ = 101·8 (0·1)
$\angle be$ = 90·6 (0·1)
$\angle ab$ = 96·1 (0·3)
$\angle cd$ = 98·9 (0·1)
$\angle ce$ = 81·2 (0·1)

$\angle cf$ = 106·9 (0·1)°
$\angle df$ = 79·9 (0·1)
$\angle ad$ = 85·6 (0·2)
$\angle ef$ = 88·2 (0·1)
$\angle ae$ = 93·3 (0·3)
$\angle af$ = 69·5 (0·3)

g = 2·01 (1) Å
h = 1·50 (1)
i = 1·46 (1)
l = 1·43 (1)

$\angle hi$ = 110·7 (0·6)°
$\angle hl$ = 110·4 (0·7)
$\angle il$ = 111·6 (0·7)
$\angle gh$ = 104·8 (0·4)
$\angle gi$ = 108·6 (0·5)
$\angle gl$ = 110·6 (0·5)

m = 1·71 (1) Å
n = 1·33 (1)
o = 1·32 (2)
$\angle mn$ = 119·3 (1·1)°
$\angle mo$ = 122·3 (1·2)
$\angle no$ = 118·3 (1·4)

m^1 = 1·71 (2) Å
n^1 = 1·32 (2)
o^1 = 1·32 (2)
$\angle m^1n^1$ = 121·7 (1·0)°
$\angle m^1o^1$ = 121·2 (1·1)
$\angle n^1o^1$ = 117·1 (1·4)

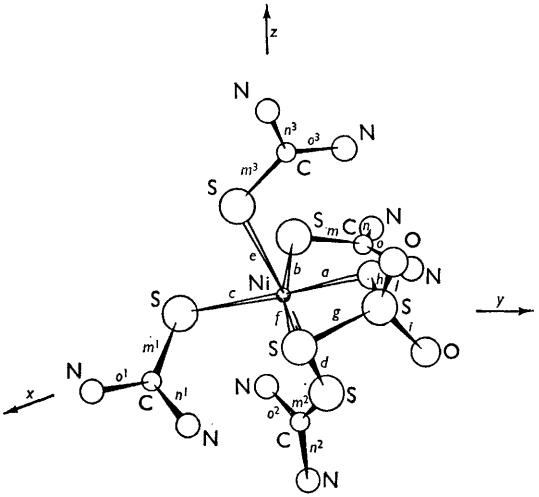
m^2 = 1·69 (1) Å
n^2 = 1·32 (2)
o^2 = 1·35 (2)
$\angle m^2n^2$ = 119·8 (1·2)°
$\angle m^2o^2$ = 121·1 (1·1)
$\angle n^2o^2$ = 119·0 (1·4)

m^3 = 1·70 (1) Å
n^3 = 1·33 (2)
o^3 = 1·33 (2)
$\angle m^3n^3$ = 119·7 (1·0)°
$\angle m^3o^3$ = 124·0 (1·1)
$\angle n^3o^3$ = 116·3 (1·2)

FIGURE. *Structure of the complex in* $Ni[SC(NH_2)_2]_4S_2O_3,H_2O$. *Standard deviations, given in parentheses, are in units of the last decimal place.*

the stronger one being that to the oxygen atom. The dimensions of the thiosulphate group are not significantly different from those found in other compounds;[2] the same can be said for the thiourea molecules when compared with uncomplexed thiourea.[3] The water molecule is hydrogen-bonded to two oxygen atoms of two thiosulphate groups (OH · · · · O = 2·82 and 2·89 Å, ∠O · · · · HOH · · · · O = 91·1°).

The structure was solved by three-dimensional Fourier methods and refined, using Booth's differential synthesis with anisotropic thermal parameters, to R = 9·5% for 1971 independent reflections. Crystal data (from powder diffractometer data, Cu-K_α) are: a = 19·07 ± 0·02, b = 10·42 ± 0·01, c = 8·91 ± 0·01 Å, Z = 4, D_c = 1·77, D_m = 1·82; space group: $P2_12_12_1$. The anhydrous formula previously assigned[4] to this compound is incorrect; the water molecule, which plays the role of "crystallization water," was found from the electron-density distribution.



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