

Nickel Chelates of Trithione- and Isotrithionedithiolate — a New Class of 1,2-Dithiolates. Part I. The Crystal Structure of Tetrabutylammonium Bis(isotrithionedithiolato)nickelate(II)

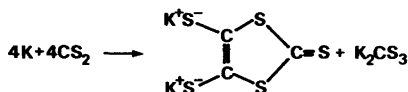
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(N(C₄H₉)₄)₂Ni(C₃S₅)₂, is monoclinic, *P*2₁/*c*, with *a* = 8.382(2), *b* = 14.664(3), *c* = 19.415(3) Å, β = 83.447(6)° and *Z* = 2. The structure was determined from 1446 observed reflections and refined by the block-diagonal least-squares method to *R* = 0.078. The Ni(C₃S₅)₂²⁻ ion is nearly planar and the nickel-sulfur coordination polyhedron is square planar with Ni–S distances of 2.221(6) and 2.211(6) Å.

The crystal and molecular structures of 1,2-dithiolene complexes, well known for their reversible redox behaviour and extensive ground-state π-electron delocalization, have recently been the subject of considerable attention.^{1,2}

The isotrithionedithiolato ion is formed by reaction of CS₂ with alkali metals:



Chelate complexes are formed with transition metal ions.³ These compounds are new derivatives of 1,2-dithiolene. In order to check the reaction mechanism and to investigate the coordination properties we have performed the present structural investigation.

EXPERIMENTAL

Small crystals (~0.1 mm in cross section) are green and transparent while larger crystals appear

to be black and opaque. The crystal selected for data collection had the dimensions 0.05 × 0.18 × 0.05 mm along the *a*, *b* and *c* axes, respectively. The X-ray data were collected with a Syntex *P*2₁ diffractometer, using graphite monochromated CuKα radiation. The settings of 10 reflections were used to calculate the cell dimensions, which are given together with other crystallographic data in Table 1. Three-dimensional data (1472 reflections for which 2θ ≤ 100°) were measured using the ω/2θ scan technique. The scan intervals (1.2° < ω < 1.4°) were chosen to be approximately twice the width of the crystal rocking angle. The intensity of a standard reflection was measured after every 25 reflections; only statistical variations being observed. The background and integrated intensities were obtained from the Lehmann-Larsen profile analysis method.^{4,5} 1446 reflections with *I* > 3σ(*I*) were used for the structure determination and refinement. The intensities were corrected for Lorentz and

Table 1. Crystallographic data.

<i>M</i>	936.36 g/mol
<i>a</i>	8.382(2) Å
<i>b</i>	14.664(3) Å
<i>c</i>	19.415(3) Å
β	83.447(6) °
<i>V</i>	2370.9(2) Å ³
<i>Z</i>	2
<i>D</i> _x	1.31 g cm ⁻³
Space group	<i>P</i> 2 ₁ / <i>c</i>
μ (CuKα)	46.4 cm ⁻¹
Crystal habit	Green rods

Table 2a. Positional parameters with standard deviations, $\times 10^4$, and isotropic thermal parameters.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (isotropic)
Ni	0	0	0	—
S(1)	362(6)	−1016(3)	810(2)	—
S(2)	−1797(6)	750(3)	695(2)	—
S(3)	−982(6)	−1088(3)	2349(2)	—
S(4)	−2952(6)	484(3)	2231(2)	—
S(5)	−3116(6)	450(3)	3608(2)	—
C(1)	−886(19)	−588(10)	1519(7)	—
C(2)	−1801(19)	186(10)	1481(8)	—
C(3)	−2388(19)	−365(9)	2772(7)	—
N(1)	4683(14)	2507(7)	−644(5)	1.66
C(4)	3006(19)	2847(9)	−818(7)	1.65
C(5)	3187(20)	3595(10)	−1406(7)	2.37
C(6)	1483(20)	4068(10)	−1375(8)	2.30
C(7)	127(20)	3443(10)	−1574(7)	2.50
C(8)	4411(20)	1663(10)	−177(8)	2.19
C(9)	3347(20)	1899(10)	513(8)	2.54
C(10)	3390(20)	1004(11)	971(8)	2.69
C(11)	2269(21)	1153(11)	1666(8)	3.13
C(12)	5460(19)	3314(10)	−277(7)	1.42
C(13)	6973(19)	3002(10)	51(7)	1.80
C(14)	7748(19)	3864(10)	304(7)	2.10
C(15)	9389(21)	3580(11)	583(8)	3.19
C(16)	5806(18)	2260(10)	−1294(7)	1.34
C(17)	5130(21)	1457(11)	−1712(8)	3.09
C(18)	6289(22)	1287(11)	−2389(8)	3.71
C(19)	6086(27)	2091(14)	−2916(10)	6.35

Table 2b. Anisotropic temperature factors ($\times 10^4$), $T = \exp[-(h^2\beta_{11} + \dots + kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	52(6)	22(2)	15(1)	3(6)	−6(14)	10(2)
S(1)	90(9)	26(3)	19(2)	26(9)	4(6)	12(4)
S(2)	109(10)	32(3)	16(1)	49(10)	4(7)	11(4)
S(3)	82(9)	29(3)	15(2)	13(9)	−11(7)	9(4)
S(4)	101(10)	27(3)	14(2)	8(9)	5(6)	−7(4)
S(5)	106(10)	41(3)	15(2)	12(10)	−8(7)	2(4)
C(1)	108(36)	14(10)	14(6)	−60(34)	−7(24)	−6(13)
C(2)	83(34)	7(10)	26(7)	−39(33)	−20(25)	27(13)
C(3)	85(34)	10(10)	18(6)	−17(32)	−52(25)	19(12)

polarization effects, using program GECOR of the SYNTEX XTL system modified for a Hewlett-Packard computer,⁶ but not for absorption or extinction.

STRUCTURE DETERMINATION

The positions of the nickel atom, the five sulfur atoms and ten of the carbon atoms were obtained

from *E*-maps based on phases determined by the multi-solution program MULTAN.⁷ The remaining non-hydrogen atoms were located from an electron density calculation (program FOUR).⁶ Since there are only two formula units per unit cell, the nickel atoms ought to occupy one of the two-fold special positions, *e.g.* (0,0,0), (0,1/2,1/2). The scattering from the nickel atoms thus contributes only to reflections with $k+l=2n$. When MULTAN was applied to the

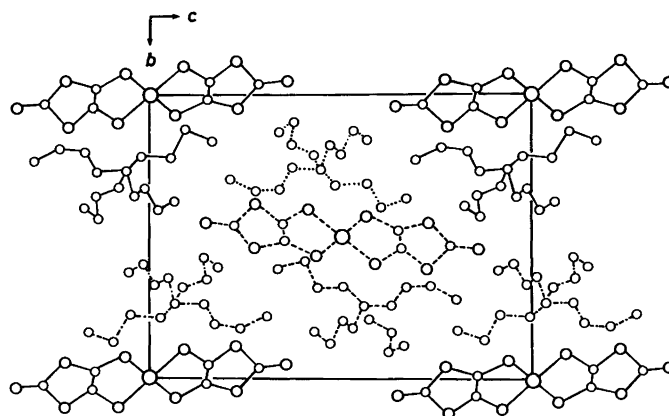


Fig. 1. The unit cell projected along the a axis showing the packing of the ions. The ions are drawn with full, dashed and dotted lines to indicate increasing values of x .

original data set the correct solution was only the third most probable.

The positional and thermal parameters of all 26 non-hydrogen atoms in the asymmetric unit were subjected to several cycles of block-diagonal least-squares refinement.⁶ The final refinement included anisotropic temperature factors for the nickel, sulfur and the C(1)–C(3) atoms, the resulting parameters being given in Table 2. A final R value of 0.078 was obtained. The observations were assigned weights according to counting statistics, *i.e.* $w = 1/\sigma^2(F)$. Atomic scattering factors for Ni^{2+} , S, N and C were those given by Doyle and Turner.⁸ A list of structure factors may be obtained from the authors.

RESULTS AND DISCUSSION

The packing of the $[\text{Ni}(\text{C}_3\text{S}_5)_2]^{2-}$ and $\text{N}(\text{C}_4\text{H}_9)_4^+$ ions is shown in Fig. 1. The anions extend along

the c -axis while the cations occupy the holes between the anions. Contacts between the different ions are of normal van der Waals order. The $\text{Ni}(\text{C}_3\text{S}_5)_2^{2-}$ ion is almost perfectly planar. None of the 9 atoms Ni, S(1)–S(5), C(1)–C(3) deviate by more than one standard deviation from the plane, and the ion has almost mmm symmetry. It is also notable that all non-bonding S–S distances (S(1)–S(2), S(1)–S(3), S(3)–S(5), S(5)–S(4), S(4)–S(2)) are approximately equal (3.20, 3.07, 3.09, 3.03, 3.01, 3.07 Å, respectively).

The atoms in the $[\text{N}(\text{C}_4\text{H}_9)_4]^+$ cation show considerable thermal motion and the standard deviations of the bond lengths are therefore high (Table 4). The C–C distances have values between 1.52(2) and 1.58(2) Å.

The Ni–S distances (Fig. 2) determined in this investigation, 2.221(6) Å and 2.211(6) Å, are the longest found so far in Ni complexes of the dithiolene type (Table 3) and are in better agreement

Table 3. Structural data for Ni complexes with 1,2-dithiolene. The bond distances given are average values.

Compound	Ni–S (Å)	C–S (Å)	C–C (Å)	Ref.
$\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2^{2-}$	2.166(6)	1.75(2)	1.33(2)	10
$\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2^-$	2.146(1)	1.714(4)	1.356(7)	11
$\text{Ni}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2^-$	2.135(4)	1.70(2)	1.40(2)	12
$\text{Ni}(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2$	2.101(2)	1.71(1)	1.37(1)	13
$\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2$	2.113(3)	1.71(1)	1.37(1)	14

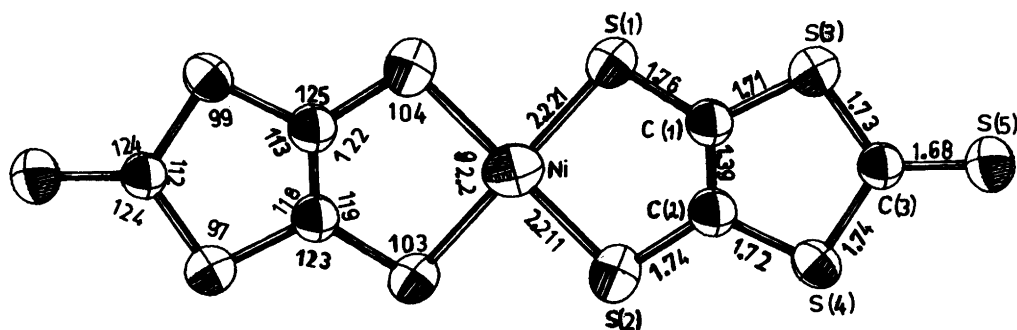


Fig. 2. The planar, centrosymmetric $\text{Ni}(\text{C}_3\text{S}_3)_2^{2-}$ ion. The standard deviations in the Ni-S, C-S and C-C bond distances are 0.004 Å, 0.01–0.02 Å and 0.02 Å, respectively.

Table 4. Bond lengths (Å) with standard deviations, within the tetrabutylammonium cation $[\text{N}(\text{C}_4\text{H}_9)]^+$.

N(1)–C(4)	1.56(2)	N(1)–C(12)	1.56(2)
C(4)–C(5)	1.58(2)	C(12)–C(13)	1.55(2)
C(5)–C(6)	1.58(2)	C(13)–C(14)	1.53(2)
C(6)–C(7)	1.54(2)	C(14)–C(15)	1.58(2)
N(1)–C(8)	1.54(2)	N(1)–C(16)	1.53(2)
C(8)–C(9)	1.56(2)	C(16)–C(17)	1.57(2)
C(9)–C(10)	1.58(2)	C(17)–C(18)	1.56(2)
C(10)–C(11)	1.57(2)	C(18)–C(19)	1.58(2)

with those in double negatively charged nickel dithiolene complexes. It would appear that the electron density of the sulfur ligand atoms is very susceptible to the charge on the complex. The shortest Ni–S distances have been determined for neutral complexes (Table 3). In the present structure the electron density of the coordinating sulfur atoms S(1) and S(2), will be influenced, as compared to the compounds in Table 3, by the sulfur atoms in the isothrithione ring.

The C–S bond distances in the isothrithione part of the ion vary from 1.68 Å to 1.74 Å and are thus close to the value 1.71 Å reported for C–S double bonds.⁹ The remaining C–S bonds are of intermediate character since the usual value for a single bond is 1.81 Å.⁹

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