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Short Communications

Nickel Chelates of Trithione- and Isotrithionedithiolate – A New Class of 1,2-Dithiolates. Part II.* The Crystal Structure of Tetramethylammonium Bis(isotrithionedithiolato)nickelate(II)

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A mixture of dimethylformamide (DMF), alkali metals and carbondisulfide reacts to give 1,3-dithiole-2-thion-4,5-dithiolate:[1,2]

$$4K + 4CS_2 \rightarrow C_3S_5^{2-} + CS_3^{2-} + 4K^+$$

On heating the products to 120–140 °C in the presence of dimethylformamide, the "isotrithionedithiolate" ion rearranges to form an isomeric $C_3S_5^{2-}$ ion which has different physical and chemical properties. A nickel chelate complex of this ion with the composition $[N(C_4H_9)_4]_2[Ni(C_3S_5)_2]$, has been isolated.[3] The structure analysis of this compound will provide valuable information concerning the nature of the rearrangement within the $C_3S_5^{2-}$ ion and of the coordination properties of the new isomer system. The compound crystallizes in space group $P2_1/n$ with parameters: $a = 14.670(3)$ Å, $b = 8.611(2)$ Å,** $\beta = 105.15(6)°$, $D_x = 1.31$ g cm^{-3}, $\mu = 4.6$ mm^{-1}, $Z = 2$ and M.W. = 936.4.

The intensity data were collected on a Syntex $P2_1$ four-circle diffractometer using graphite monochromatized Cu$K\alpha$ radiation to $2\theta = 100°$. A total of 1346 reflexions were collected, and those 937 reflexions with $I > 3\sigma(I)$ were considered significant and used in the subsequent calculations. The background and integrated intensities were obtained from the Lehmann-Larsen profile analysis method.[4] The intensities were corrected for Lorentz and polarisation effects, but not for absorption or extinction. The full-matrix least squares refinement of an overall scale factor, positional and anisotropic thermal parameters for all non-hydrogen atoms, isotropic thermal parameters for the hydrogen atoms gave a final $R = 0.054$. A list of structure factors, thermal parameters and coordinates of the hydrogen atoms is available from the authors on request. The positional parameters of the non-hydrogen atoms are given in Table 1.

Table 1. Positional parameters with standard deviations, $\times 10^4$, and isotropic thermal parameters.

	x/a	y/b	z/c	B Å^{-2}
Ni(1)	0	0	0	3.7(1)
S(1)	1346(3)	−44(6)	−779(2)	6.3(1)
S(2)	658(3)	800(5)	−801(2)	4.7(1)
S(3)	3316(3)	596(6)	736(2)	7.4(1)
S(4)	3696(3)	1379(7)	−120(2)	8.2(1)
S(5)	2455(3)	1940(6)	−1481(2)	6.0(1)
C(1)	2126(10)	476(8)	339(7)	4.9(4)
C(2)	1839(11)	894(9)	−364(7)	5.2(4)
C(3)	2534(10)	1349(6)	−678(7)	4.5(4)
N(1)	5718(8)	−1178(3)	3175(5)	4.2(4)
C(4)	5700(10)	−1361(7)	3937(7)	4.3(4)
C(5)	6254(10)	−179(20)	4403(7)	5.5(5)
C(6)	6395(12)	−755(22)	5156(9)	7.5(6)
C(7)	6879(12)	489(20)	5657(8)	6.6(5)
C(8)	5302(10)	385(17)	2907(7)	4.5(5)
C(9)	4255(10)	607(18)	2873(7)	5.6(5)
C(10)	3926(10)	2194(18)	2601(7)	5.2(5)
C(11)	2895(12)	2471(23)	2522(9)	7.6(6)
C(12)	6747(10)	−1088(18)	3102(7)	4.4(4)
C(13)	7279(13)	−2526(24)	3402(9)	8.2(5)
C(14)	8353(14)	−2070(24)	3391(10)	9.4(5)
C(15)	9117(17)	−2977(31)	3833(12)	13.5(6)
C(16)	5169(10)	−2546(17)	2770(7)	4.6(4)
C(17)	5064(10)	−2463(19)	2016(7)	5.6(5)
C(18)	4555(13)	−3913(22)	1670(9)	7.7(5)
C(19)	4438(15)	−3855(26)	886(10)	10.6(6)

* For part I, see Ref. 2.
** $c = 20.140(3)$ Å.

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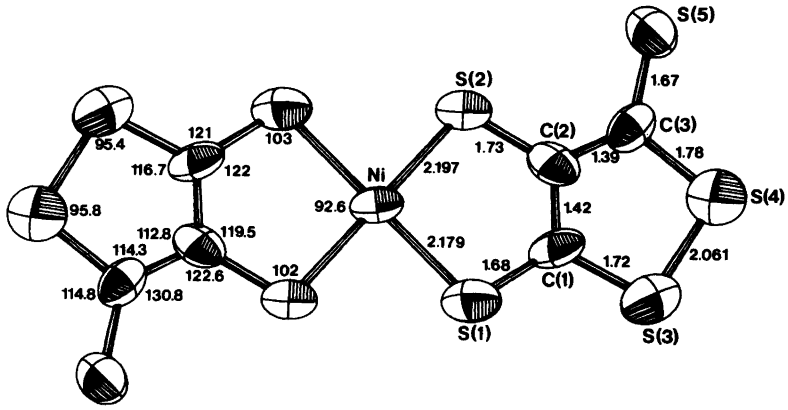
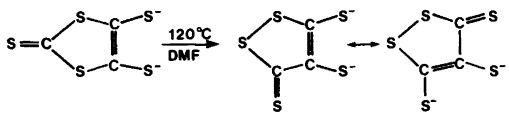


Fig. 1. The planar $Ni(C_3S_5)_2^{2-}$ ion. The standard deviations in the Ni – S, C – S and C – C bond distances are 0.004, 0.01 and 0.02 Å, respectively.

The structure of the $[Ni(C_3S_5)_2]^{2-}$ ion is shown in Fig. 1. The structure analysis shows that the 1,3-dithiole-2-thion-4,5-dithiolate has transformed to the thermodynamically more stable 1,2-dithiole-3-thion-4,5-dithiolate (trithionedithiolate) by heating. The trithionedithiolate ion is stabilized in relation to the isotrithionedithiolate by resonance in the ring system:



As expected the $[Ni(C_3S_5)_2]^{2-}$ anion is planar. None of the atoms deviates by more than one standard deviation from the plane. The two Ni – S distances (Fig. 1) are significantly shorter than the corresponding distances, 2.211(4) and 2.221(4) Å, in the nickel(II) isotrithionedithiolate compound,[2] but are comparable with the distances found in other 1,2-ditriolates.[5,6] The S(3) – S(4) distance corresponds to a single bond which is also consistent with the C(1) – S(3) – S(4) and S(3) – S(4) – C(3) angles of 95.4 and 95.8°, respectively.

The atoms in the $[N(C_4H_9)_4]^+$ cation show considerable thermal motions and the standard deviations of the bond lengths are therefore high. Two $[N(C_4H_9)_4]^+$ cations are centrosymmetrically arranged around the $Ni[(C_3S_5)_2]^{2-}$ anion. The shortest contact between the ions are S – H bridges with distances of 2.8 – 2.9 Å. Similar S – H contacts have been observed previously in nickel-1,1 dithiolate structures.[7]

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