

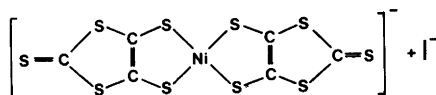
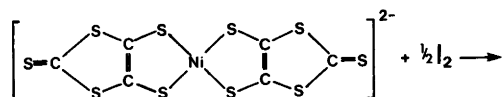
Nickel Chelates of Trithione- and Isotrithionedithiolate — a New Class of 1,2-Dithiolates. Part III. The Crystal Structure of Tetrabutylammonium Bis(isotrithione-dithiolato)nickelate(III)

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When alkali metals react with carbon disulfide in a solution of dimethylformamide (DMF), a new type of sulfur-rich dithiolene ligand is formed: 1,3-dithiole-2-thion-4,5-dithiolate.^{1,2} Its chelate complex with nickel shows characteristic reversible electron-transfer reactions. In a solution of acetone, it is possible to oxidize the nickel(II) complex with iodine to a nickel(III) complex¹ of the composition $[\text{N}(\text{C}_4\text{H}_9)_4]\text{Ni}(\text{C}_3\text{S}_5)_2$:



The structure analysis of the nickel(III) complex should provide information about the change in bonding character compared to the corresponding nickel(II) complex.²

The nickel(III) compound, $[\text{N}(\text{C}_4\text{H}_9)_4]\text{Ni}(\text{C}_3\text{S}_5)_2$, crystallizes in space group $P2_1/c$ with parameters $a = 14.649(3)$ Å, $b = 13.497(3)$ Å, $c = 16.383(4)$ Å, $\beta = 91.14(6)^\circ$, $D_x = 1.42$, $\mu = 1.2$ mm⁻¹, $Z = 4$, and M.W. = 693.8. Small crystals, ≤ 0.1 mm in cross section, are green and transparent, while larger crystals appear to be black and opaque. The x-ray data were collected on a Syntex $P2_1$ diffractometer, using graphite monochromated $\text{MoK}\alpha$ radiation. Three-dimensional data (6848 reflections with $2\theta \leq 100^\circ$) were measured using the $\omega/2\theta$ scan

technique. Integrated intensity values were obtained from the Lehmann-Larsen profile analysis method.^{3,4} Those 2349 reflections having $I > 3\sigma(I)$ were used for the structure determination and refinement. The intensities were corrected for Lorentz and polarization effects, using the program GECOR,⁵ but not for absorption or extinction, since these effects were small. The structure was solved from the Patterson function. Positional and thermal parameters were subjected to several cycles of block-diagonal least squares refinement.⁵ The final refinement included anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms, and the

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

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} Å ²
Ni	1601(1)	1389(1)	1588(1)	3.4(1)
S(1)	1665(2)	2921(2)	1232(2)	4.2(1)
S(2)	132(2)	1353(2)	1551(2)	4.8(1)
S(3)	168(2)	4433(2)	918(2)	5.0(1)
S(4)	-1247(2)	2983(3)	1164(2)	5.3(1)
S(5)	-1779(3)	5008(3)	657(3)	7.7(1)
S(6)	3079(2)	1434(2)	161(2)	4.5(1)
S(7)	1567(2)	-122(2)	2008(2)	5.2(1)
S(8)	4474(2)	-62(2)	2208(2)	5.1(1)
S(9)	3092(2)	-1503(2)	2565(2)	5.5(1)
S(10)	5036(2)	-2022(3)	2872(2)	6.4(1)
C(1)	529(7)	3227(7)	1177(6)	3.6(2)
C(2)	-138(7)	2558(8)	1288(6)	3.8(2)
C(3)	-992(8)	4188(9)	890(6)	5.1(3)
C(4)	3355(7)	286(7)	2005(6)	3.9(2)
C(5)	2707(7)	-389(8)	2186(6)	4.3(2)
C(6)	4259(7)	-1241(9)	2581(6)	4.6(2)
Tetrabutylammonium ion				
N	2368(6)	4151(6)	3739(5)	4.1(2)
C(7)	2916(7)	3216(8)	3558(6)	4.1(2)
C(8)	3149(8)	2568(9)	4266(6)	5.1(3)
C(9)	2708(9)	1707(9)	4013(7)	5.9(3)
C(10)	4025(9)	1091(11)	4706(9)	7.8(4)
C(11)	1461(7)	3903(8)	4137(6)	4.4(2)
C(12)	832(8)	3205(9)	3675(7)	5.3(3)
C(13)	5(9)	2982(12)	4155(7)	6.8(3)
C(14)	-671(10)	2332(10)	3761(8)	7.1(4)
C(15)	2157(7)	4697(8)	2942(6)	4.0(2)
C(16)	2984(8)	5078(8)	2490(6)	4.7(2)
C(17)	2695(8)	5661(9)	1741(8)	5.8(3)
C(18)	3477(10)	6044(9)	1274(7)	7.1(3)
C(19)	2928(8)	4808(7)	4332(6)	4.6(2)
C(20)	2575(9)	5809(10)	4493(7)	7.3(3)
C(21)	3191(12)	6338(12)	5112(9)	8.5(4)
C(22)	4106(11)	6547(17)	4866(13)	12.6(6)

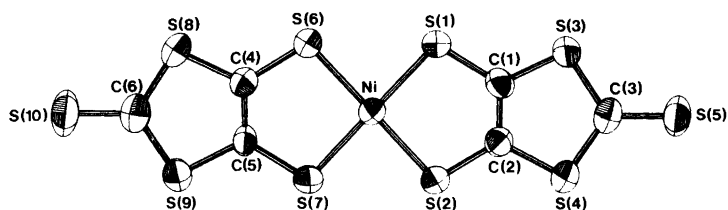


Fig. 1. The $\text{Ni}^{\text{III}}(\text{C}_3\text{S}_3)_2^-$ ion. The notation is in accordance with Tables 1 and 2.

resulting R ($=\Sigma|F_o - |F_c||\Sigma F_o$) value was 0.054. Lists of structure factors, thermal parameters and refined coordinates of the hydrogen atoms are available from the authors on request. The positional parameters of the non-hydrogen atoms are given in Table 1. Bond distances and angles of the $\text{Ni}^{\text{III}}(\text{C}_3\text{S}_3)_2^-$ ion are given in Table 2, and its

Table 2. Bond lengths (Å) and angles ($^\circ$) within the $\text{Ni}^{\text{III}}(\text{C}_3\text{S}_3)_2^-$ ion.

Bond distances		Bond angles	
Ni—S(1)	2.151(3)	S(1)—Ni—S(2)	93.4(1)
Ni—S(2)	2.160(3)	S(6)—Ni—S(7)	93.1(1)
Ni—S(6)	2.158(3)	S(1)—Ni—S(6)	86.1(1)
Ni—S(7)	2.154(3)	S(2)—Ni—S(7)	87.4(1)
S(1)—C(1)	1.72(1)	Ni—S(1)—C(1)	101.6(4)
S(2)—C(2)	1.73(1)	Ni—S(2)—C(2)	102.1(4)
S(3)—C(1)	1.76(1)	Ni—S(6)—C(4)	102.0(4)
S(3)—C(3)	1.73(1)	Ni—S(7)—C(5)	102.7(4)
S(4)—C(2)	1.73(1)		
S(4)—C(3)	1.73(1)	S(1)—C(1)—C(2)	122.5(8)
S(5)—C(3)	1.64(1)	S(1)—C(1)—S(3)	121.5(6)
S(6)—C(4)	1.72(1)	C(2)—C(1)—S(3)	115.9(8)
S(7)—C(5)	1.73(1)	S(2)—C(2)—S(4)	123.4(6)
S(8)—C(4)	1.73(1)	S(2)—C(2)—C(1)	120.2(8)
S(8)—C(6)	1.74(1)	S(4)—C(2)—C(1)	116.4(8)
S(9)—C(5)	1.72(1)	C(1)—S(3)—C(3)	96.9(5)
S(9)—C(6)	1.74(1)	C(2)—S(4)—C(3)	97.8(5)
S(10)—C(6)	1.62(1)	S(3)—C(3)—S(4)	112.9(7)
C(1)—C(2)	1.35(1)	S(3)—C(3)—S(5)	124.3(7)
C(4)—C(5)	1.35(1)	S(4)—C(3)—S(5)	122.8(7)
		S(6)—C(4)—S(8)	122.0(6)
		S(6)—C(4)—C(5)	121.9(8)
		C(5)—C(4)—S(8)	116.1(8)
		S(7)—C(5)—S(9)	123.6(6)
		S(7)—C(5)—C(4)	120.1(8)
		C(4)—C(5)—S(9)	116.2(8)
		C(4)—S(8)—C(6)	98.0(5)
		C(5)—S(9)—C(6)	98.2(5)
		S(8)—C(6)—S(9)	111.4(6)
		S(8)—C(6)—S(10)	124.7(6)
		S(9)—C(6)—S(10)	123.8(7)

structure together with atom identifications is shown in Fig. 1.

The most significant differences between the Ni(II) and the Ni(III) complexes are found for the Ni—S bond distances. In the $\text{Ni}^{\text{II}}(\text{C}_3\text{S}_3)_2^{2-}$ complex, these distances were found to be 2.221(4) and 2.211(4) Å,² while the average value in $\text{Ni}^{\text{III}}(\text{C}_3\text{S}_3)_2^-$ is 2.156(3) Å (cf. Table 2). This difference in ionic radius of Ni shows that the redox process within the nickel-dithiolene complexes has taken place at the central nickel atom. The C—S and the C—C bond lengths are of comparable magnitudes in the two complexes. The C(3)—S(5) and C(6)—S(10) distances of 1.64 and 1.62 Å are slightly shorter than the corresponding value in the $\text{Ni}^{\text{II}}(\text{C}_3\text{S}_3)_2^{2-}$ ion, being 1.68 Å, *i.e.* showing more double bond character in the oxidized form. The ring systems have a high degree of electron delocalization in both complexes, the C—S and C—C bond lengths being intermediate between double and single bond values. The previous structure determination showed that the $\text{Ni}^{\text{II}}(\text{C}_3\text{S}_3)_2^{2-}$ ion is planar,² while the planes containing Ni, S(1)—S(5), C(1)—C(3) and Ni, S(6)—S(10), C(4)—C(6), respectively, in the $\text{Ni}^{\text{III}}(\text{C}_3\text{S}_3)_2^-$ ion have an inclination of 6.1°. Normally, MS_4 complexes should be planar for a d^8 configuration of M, and the present deviation may be due to packing effects.

The bond distances and angles within the tetrabutylammonium ion have normal values.

1. Steimecke, G., Sieler, J., Kirmse, R. and Hoyer, E. *Phosphorus Sulfur* 7 (1979) 49.
2. Sjölin, L., Lindqvist, O., Sieler, J., Steimecke, G. and Hoyer, E. *Acta Chem. Scand. A* 33 (1979) 445.
3. Lehmann, M. S. and Larsen, F. K. *Acta Crystallogr. A* 30 (1974) 580.
4. Lindqvist, O. and Ljungström, E. *J. Appl. Crystallogr.* 12 (1979) 134.
5. Sjölin, L. *Thesis*, University of Göteborg, Göteborg 1979.
6. Mazid, M. A., Razi, T. and Sadler, P. J. *Inorg. Chem.* 20 (1981) 2872.

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