

## *Short Communication*

# **Crystal and molecular structure of tetraethyl-ammonium bis (stilbene 1,2-dithiolato) nickelate(III)**

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### *Crystal structure | Stilbene 1,2-dithiolene complex | One-dimensional complex*

**Abstract.** The crystals of the title compound are orthorhombic, space group  $Pca2_1$  with the following parameters:  $a = 16.387(4)$ ,  $b = 7.507(2)$ ,  $c = 28.612(8)$  Å,  $V = 6343.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.35$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 0.753$  mm<sup>-1</sup>, Final  $R = 0.11$ ,  $R_w = 0.12$  with  $1.00/[\sigma^2(F_o) + 0.0005 |F_o|^2]$  for 1073 unique reflections [ $I > 3\sigma(I)$ ].

The nickel atom has an approximate square planar configuration. The nitrogen atom of the cation exhibits a tetrahedral configuration. The anions are arranged along the  $a$ -axis at  $Z = 0.25$  and  $0.75$  with the Nickel atoms nearly collinear.

## **Introduction**

The ligands of 1,2-dithiolenes are very interesting as they form organometallic adducts and exhibit rare structural forms in their complexes. They form stable complexes with transition metal atoms. The stilbene 1,2-

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**Table 1.** Final fractional coordinates of non-hydrogen atoms and equivalent isotropic thermal parameters ( $\times 10^3 \text{ \AA}^2$ ) with estimated standard deviations in parentheses,

$$U_{\text{eq}} = \frac{1}{3} \sum_{i=1}^3 U_{ii}.$$

Atom	x	y	z	$U_{\text{eq}}$
Ni	0.3647(2)	0.4904(6)	0.2500(0)	46(2)
S(1)	0.4451(7)	0.4152(15)	0.1903(4)	60(5)
S(2)	0.3313(7)	0.7201(14)	0.2151(5)	62(5)
S(3)	0.4232(7)	0.2623(15)	0.2852(6)	71(5)
S(4)	0.3118(8)	0.5675(16)	0.3114(5)	74(5)
C(1)	0.423(3)	0.577(5)	0.147(2)	58(7)
C(2)	0.379(2)	0.699(4)	0.158(1)	23(7)
C(3)	0.373(3)	0.260(5)	0.338(2)	89(6)
C(4)	0.343(2)	0.408(4)	0.352(1)	51(6)
C(11)	0.471(2)	0.564(4)	0.103(1)	49(6)
C(12)	0.505(3)	0.723(4)	0.081(2)	76(6)
C(13)	0.548(3)	0.622(5)	0.041(2)	132(6)
C(14)	0.566(2)	0.569(4)	0.024(1)	66(6)
C(15)	0.545(2)	0.404(4)	0.042(1)	49(6)
C(16)	0.488(2)	0.401(4)	0.088(2)	69(6)
C(21)	0.342(2)	0.845(4)	0.128(1)	63(6)
C(22)	0.337(2)	1.041(4)	0.143(1)	63(6)
C(23)	0.292(2)	1.155(4)	0.110(1)	59(6)
C(24)	0.253(2)	1.086(4)	0.070(1)	60(6)
C(25)	0.256(2)	0.931(4)	0.060(1)	62(6)
C(26)	0.281(2)	0.798(4)	0.091(1)	65(6)
C(31)	0.419(2)	0.150(4)	0.379(1)	52(6)
C(32)	0.405(2)	-0.038(4)	0.367(1)	53(6)
C(33)	0.439(3)	-0.169(4)	0.392(2)	73(6)
C(34)	0.497(3)	-0.135(5)	0.430(2)	85(6)
C(35)	0.512(4)	0.052(5)	0.447(3)	166(6)
C(36)	0.460(2)	0.206(4)	0.416(1)	58(6)
C(41)	0.282(3)	0.411(5)	0.396(2)	107(6)
C(42)	0.254(2)	0.258(4)	0.419(2)	64(6)
C(43)	0.202(3)	0.293(4)	0.458(2)	77(6)
C(44)	0.176(2)	0.466(4)	0.478(2)	69(6)
C(45)	0.197(3)	0.618(5)	0.453(2)	107(6)
C(46)	0.255(2)	0.598(4)	0.415(1)	71(6)
N	0.624(2)	0.853(4)	0.249(2)	79(6)
C(5)	0.061(2)	0.038(4)	0.218(2)	63(6)
C(51)	0.092(3)	-0.068(5)	0.178(2)	117(6)
C(6)	0.688(3)	0.740(5)	0.224(2)	91(6)
C(61)	0.648(3)	0.613(5)	0.189(2)	112(6)
C(7)	0.062(3)	0.275(4)	0.276(2)	81(6)
C(71)	0.033(3)	0.132(5)	0.300(2)	107(6)
C(8)	0.170(3)	0.045(5)	0.288(2)	75(7)
C(81)	0.634(3)	1.072(5)	0.316(2)	82(7)

**Table 2.** Bond lengths (Å) for the central part of the anion and the cation with estimated standard deviations in parentheses.

Ni–S(1)	2.23(1)	Ni–S(2)	2.07(1)
Ni–S(3)	2.21(1)	Ni–S(4)	2.04(1)
S(1)–C(1)	1.77(4)	S(2)–C(2)	1.82(4)
S(3)–C(3)	1.73(5)	S(4)–C(4)	1.75(4)
N–C(5)	1.59(6)	N–C(6)	1.53(6)
N–C(7)	1.60(6)	N–C(8)	1.53(5)
C(5)–C(51)	1.48(6)	C(6)–C(61)	1.53(6)
C(7)–C(71)	1.36(6)	C(8)–C(81)	1.33(6)

**Table 3.** Bond angles (°) for the central part of the anion and the cation with estimated standard deviations in parentheses.

S(1)–Ni–S(2)	89.9(5)	S(1)–Ni–S(3)	84.1(6)
S(1)–Ni–S(4)	168.9(6)	S(2)–Ni–S(3)	169.6(7)
S(2)–Ni–S(4)	93.8(6)	C(1)–S(1)–Ni	104(1)
S(3)–Ni–S(4)	90.7(6)	N–C(8)–C(81)	113(2)
C(2)–S(2)–Ni	104(3)	C(3)–S(3)–Ni	102(2)
C(4)–S(4)–Ni	105(1)	C(2)–C(1)–S(1)	118(3)
C(5)–N–C(6)	106(3)	C(5)–N–C(7)	109(2)
C(5)–N–C(8)	109(3)	C(6)–N–C(7)	116(5)
C(6)–N–C(8)	110(3)	C(7)–N–C(8)	109(2)
N–C(5)–C(51)	109(3)	N–C(6)–C(61)	111(3)
N–C(7)–C(71)	112(3)		

dithiolene ligand is analysed in the present paper, which is also inert to substitution by most common ligands.

## Experimental

The compound was prepared according to the procedure given by Schrauzer and Mayweg (1965) and Davison et al. (1963). Purple red crystals were obtained by slow evaporation of an acetonitrile solution at 20°C. Chemical analysis gave the following percentage compositions for the various elements.

Calculated (%)	C 64.19	N 2.08	H 5.94
Found (%)	C 63.97	N 1.96	H 5.77

The density of the crystal was measured to be 1.35 g cm<sup>-3</sup> by floating technique. An Enraf-Nonius CAD-4 diffractometer was employed for data collection with graphite-monochromated MoK $\alpha$  ( $\lambda = 0.71069$  Å). The cell constants were determined from least squares refinement of 23-high angle reflections. The intensity data were collected by  $\omega$ -2 $\theta$  scan technique with  $2^\circ < \theta < 24^\circ$ . Of the 3408 reflections collected, 1073 unique reflections

with  $I > 3\sigma(I)$  were used for structure determination. The crystal data are given in the Abstract.

Based on the systematic absence the space group could be *Pcam* or *Pca2<sub>1</sub>*. The intensity statistics revealed a non-centro-symmetric space group, which was tried along with the centric space group *Pcam*. No progress in structure elucidation could be attained in *Pcam* while in *Pca2<sub>1</sub>* all the atoms appeared in the difference Fourier maps. During refinements no correlation between parameters appeared, which rules out the centric space group *Pcam*. The structure was solved by Patterson synthesis.

Since the phenyl carbon atoms moved considerably on refinement, the four phenyl groups were fixed geometrically. The atoms in these groups were then refined with damping. Final anisotropic refinement of all atoms (giving damping to the phenyl carbon atoms) led to a *R*-value of 0.11. A weighting scheme of the form  $1/[\sigma^2(F_o) + 0.0005 |F_o|^2]$  was used in the final stages of refinement.

The ratio of the number of reflections to the number of parameters to be refined is small (2.5). This may be the reason for the poor refinement and the probable cause for the requirement to fix the phenyl rings geometrically in the initial step. All the above analysis was done using the program SHELX-76 (Sheldrick, 1976).

## Discussion

The fractional coordinates of all the nonhydrogen atoms are listed in Table 1<sup>1</sup>. The bond lengths and bond angles involving Ni and cation nitrogen atom are listed in Tables 2 and 3 respectively. The ORTEP plots (Johnson, 1965) of the anion and cation are shown in Figures 1 and 2.

The nickel atom has an approximate square planar coordination. The Ni–S distances are all not equal, two of them are larger [Ni–S(1) 2.23(1), Ni–S(3) 2.21(1) Å], than the other two [Ni–S(2) 2.07(1) and Ni–S(4) 2.04(1) Å] which are in agreement with those reported for similar stilbene 1,2-dithiolato nickelate (III) complexes (Mahadevan, 1984). The average S–Ni–S angle is 89.6 (6°). The conformation of the phenyl rings in this structure about the C–C bond is similar to the one reported in the case of [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][Ni(S<sub>2</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>)<sub>2</sub>] (Sartain and Truter, 1967), and unlike in [Ni(S<sub>2</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>)<sub>2</sub>] (Mahadevan, 1984).

The nitrogen atom of the cation has an approximate tetrahedral configuration around it with all N–C and C–C lengths being normal. C–N–C angles range between 105° and 112°, which is as observed in other [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sup>+</sup> moieties (Kobayashi and Sasaki, 1977).

<sup>1</sup> The structure factor tables of this paper can be ordered referring to the No. CSD 52549, names of the authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

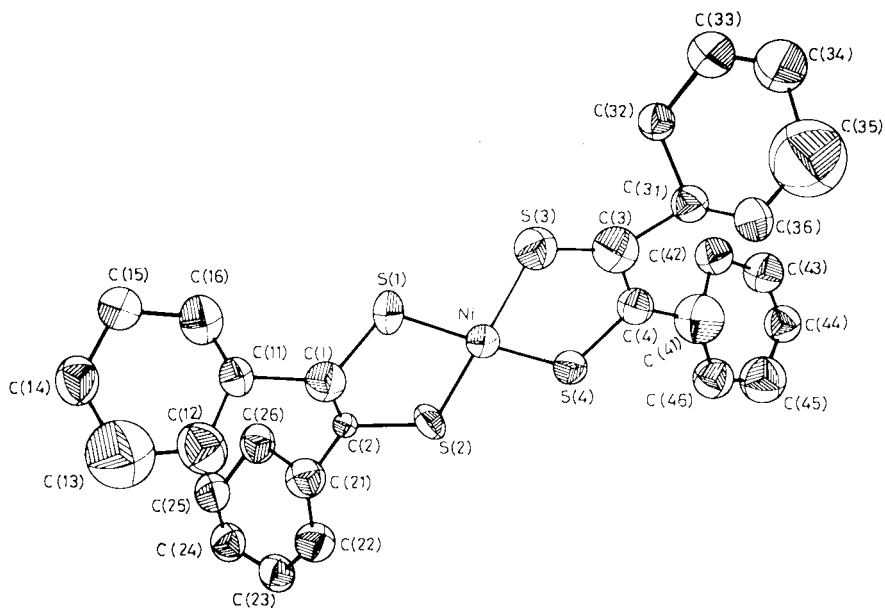


Fig. 1. ORTEP plot of the anion.

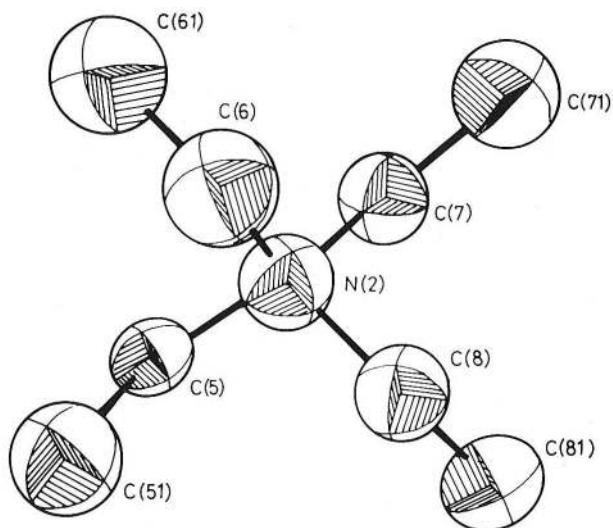


Fig. 2. ORTEP plot of the cation.

### Intermolecular features

The anions form a chain along the *a*-axis. The nearest Ni ... Ni contact along the chain is 8.19(1) Å and the interchain Ni ... Ni distance is 14.79(5) Å, with the Ni atoms nearly collinear. Such a packing imparts a one-dimensional nature to this compound.

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