$Cl_2\{N(SiMe_3)_2\}]$, space group $P2_1/n$ at room temperature. Our results indicate the existence of a triclinic form at 185 and 295 K. This polymorphism may result from the crystallization method: the monoclinic form was obtained by sublimation while the triclinic form was crystallized from toluene solution; other details of the synthesis are quite similar in both cases. No significant difference is noticed between the two molecular structures. However, the bond lengths are systematically longer (by a mean of 0.020 Å) in the low-temperature triclinic structure than in the room-temperature monoclinic structure. This difference (Δl) results from the reduction of libration motion upon cooling (Willis & Pryor, 1975); it is much more pronounced for the Cp group (mean Δl for C—C 0.048 Å, mean Δl for Ti—C 0.021 Å) than for other atoms (mean Δl excluding Cp 0.007 Å).

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Bis(tetraethylammonium) Nickel Tetrakisthiophenolate: a New Polymorph

BY ARNOLD L. RHEINGOLD,* KEVIN S. BEALL, PATRICIA J. RIGGS AND SUSAN E. GROH

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

Abstract. Tetraethylammonium tetrakisbenzenethiolatonickelate(2−), $[(C_2H_5)_4N]_2[Ni(C_6H_5S)_4]$, $M_r = 755.86$, orthorhombic, $P2_12_12_1$, $a = 14.145\,(7)$, $b = 16.482\,(8)$, $c = 17.589\,(8)$ Å, $V = 4101\,(3)$ Å^3, $Z = 4$, $D_x = 1.224$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.71073$ Å, $\mu = 6.98$ cm^{-1}, $F(000) = 1624$, $T = 296$ K, $R_F = 0.0509$ for 2675 observed reflections and 377 least-squares parameters. As expected, the anion contains four thiophenolate ligands tetrahedrally coordinated to the Ni atom. The average Ni—S bond distance is 2.296 (4) Å. The structure is similar to a previously reported monoclinic form [Yamamura, Miyamae, Katayama & Sasaki (1985). *Chem. Lett.* pp. 269–272] for which $R = 0.088$.

Experimental. Violet crystals were grown from acetonitrile (0.40 × 0.40 × 0.40 mm). Data were collected on a Nicolet *R3m* diffractometer with graphite monochromator, using ω scans. Lattice parameters were determined from least-squares fit of 25 reflections ($20 \leq 2\theta \leq 25°$). An absorption correction was required ($T_{max}/T_{min} = 0.847/0.633$; $\mu = 6.98$ cm^{-1}). $2\theta_{max} = 50°$ ($h = \pm18$, $k = \pm21$, $l = +22$). Three standard reflections (703, 194 and 039), for 4202 reflections collected, showed less than 2% decay. Of 4176 unique reflections, 2678 were observed with $F_o > 5\sigma(F_o)$ (1498 unobserved reflections). Direct methods (*SOLV*; Sheldrick, 1983) were used for structure solution. Least-squares refinement of 377 parameters, with all non-H atoms anisotropic, all H atoms calculated (C—H = 0.960 Å, $U = 1.2U$ for attached C) and phenyl rings constrained as rigid planar hexagons (C—C = 1.395 Å), converged at $R_F = 5.09\%$, $wR_F = 5.17\%$ $[w^{-1} = \sigma^2(F_o) + gF_o^2$, $g = 0.001]$, $S = 1.231$; $(\Delta/\sigma)_{max} = 0.045$; $(\Delta\rho)_{max} = 0.579$, $\Delta\rho_{min} = -0.265$ e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). *SHELXTL* computer programs (Sheldrick, 1983) were used in the structure determination.

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. Selected bond lengths and bond angles are given in Table 2.† The anion is shown in Fig. 1 and the packing in Fig. 2.

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* To whom correspondence should be addressed.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ni	1909.8 (6)	4347.0 (5)	1178.8 (5)	40.7 (3)
S(1)	1918 (2)	5665 (1)	1528 (1)	50.8 (6)
S(2)	1362 (1)	3808 (1)	2322 (1)	46.9 (6)
S(3)	1363 (2)	3906 (1)	23 (1)	54.0 (7)
S(4)	3338 (1)	3698 (1)	1024 (1)	56.7 (7)
C(11)	2461 (3)	6041 (2)	56 (3)	49 (3)
C(12)	2761	6576	−509	59 (3)
C(13)	2834	7403	−353	54 (3)
C(14)	2608	7695	369	61 (3)
C(15)	2308	7160	934	46 (3)
C(16)	2234	6333	778	39 (2)
C(21)	−432 (4)	4362 (3)	1962 (2)	52 (3)
C(22)	−1367	4549	2143	65 (3)
C(23)	−1695	4440	2884	72 (3)
C(24)	−1087	4145	3444	65 (3)
C(25)	−152	3958	3263	53 (3)
C(26)	176	4067	2522	46 (3)
C(31)	−474 (4)	3727 (3)	−390 (3)	70 (3)
C(32)	−1413	3974	−467	100 (5)
C(33)	−1680	4755	−251	108 (5)
C(34)	−1009	5290	43	84 (4)
C(35)	−70	5044	120	62 (3)
C(36)	197	4263	−96	47 (3)
C(41)	3796 (3)	4216 (3)	2481 (3)	52 (3)
C(42)	4433	4368	3069	61 (3)
C(43)	5393	4209	2967	73 (4)
C(44)	5716	3897	2277	72 (4)
C(45)	5079	3745	1688	63 (3)
C(46)	4118	3905	1790	49 (3)
N(1)	9542 (4)	1676 (3)	1531 (3)	38 (2)
C(51)	8746 (5)	2194 (4)	1828 (4)	51 (3)
C(52)	8134 (6)	2596 (5)	1219 (5)	72 (3)
C(53)	9188 (6)	1041 (4)	989 (4)	61 (3)
C(54)	8360 (6)	535 (5)	1261 (5)	80 (4)
C(55)	9976 (5)	1226 (4)	2205 (4)	48 (3)
C(56)	10377 (6)	1748 (5)	2824 (4)	65 (3)
C(57)	10254 (5)	2219 (4)	1155 (5)	57 (3)
C(58)	11126 (6)	1782 (6)	837 (6)	97 (4)
N(2)	5311 (4)	6582 (4)	1548 (4)	56 (2)
C(61)	5848 (8)	5983 (6)	1039 (6)	101 (5)
C(62)	5218 (7)	5502 (6)	485 (5)	101 (5)
C(63)	4720 (7)	7147 (6)	1029 (6)	101 (5)
C(64)	5236 (6)	7602 (6)	429 (5)	86 (4)
C(65)	4674 (8)	6108 (7)	2024 (7)	112 (5)
C(66)	4131 (7)	6637 (6)	2634 (5)	88 (4)
C(67)	6007 (7)	7095 (6)	1943 (5)	96 (4)
C(68)	6687 (7)	6616 (7)	2477 (6)	111 (5)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

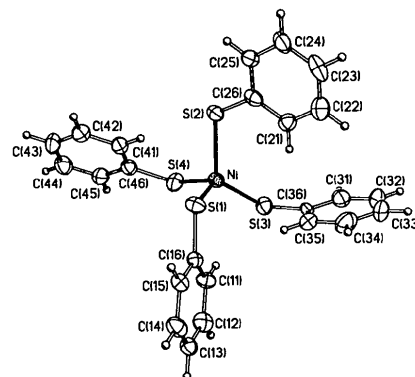| Ni—S(1)	2.258 (2)	Ni—S(3)	2.293 (2)
Ni—S(2)	2.331 (2)	Ni—S(4)	2.302 (2)
S(1)—Ni—S(2)	97.7 (1)	S(2)—Ni—S(3)	122.1 (1)
S(2)—Ni—S(4)	102.5 (1)	S(1)—Ni—S(3)	123.2 (1)
S(3)—Ni—S(4)	92.5 (1)	S(1)—Ni—S(4)	118.3 (1)

Fig. 1. Structure of the anion in the title compound drawn with 35% thermal ellipsoids.
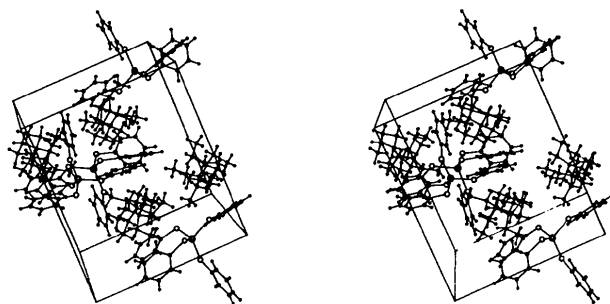

Fig. 2. Unit-cell packing diagram.

Related literature. Yamamura, Miyamae, Katayama & Sasaki (1985) report the structure of a monoclinic (*M*) polymorph of the orthorhombic (*O*) title compound. The average Ni—S bond distances are not statistically different from *M* [Ni—S = 2.292 (1) Å], and for *O* [Ni—S = 2.296 (3) Å] forms. In *M* the Ni—S distances vary from 2.279 (3) to 2.306 (3) Å, while a wider range is found in *O*, from 2.258 (2) to 2.331 (2) Å. The same anion is also found in the tetraphenylphosphonium salt with a similar average Ni—S distance of 2.288 (1) Å (Swenson, Baenziger & Coucouvanis, 1978). In all cases, the angular distortions from a regular tetrahedral coordination are large; the range of S—Ni—S angles in *O* is 92.5 (1) to 123.2 (1)° and in *M* 97.2 (1) to 123.7 (1)°, and largest of all in the PPh₄⁺ salt: 92.0 (2) to 124.9 (2)°. The distortions may be resolved into compressions along one of the twofold axes.

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