

N(1)—Cr—N(2)	79.3 (2)	N(1)—Cr—N(4)	89.7 (2)
N(2)—Cr—N(4)	98.8 (2)	N(1)—Cr—N(5)	94.6 (2)
N(2)—Cr—N(5)	173.6 (2)	N(4)—Cr—N(5)	79.2 (2)
N(1)—Cr—N(6)	171.3 (2)	N(2)—Cr—N(6)	97.2 (2)
N(4)—Cr—N(6)	98.7 (2)	N(5)—Cr—N(6)	89.1 (2)
N(1)—Cr—N(7)	93.0 (2)	N(2)—Cr—N(7)	87.2 (2)
N(4)—Cr—N(7)	173.8 (2)	N(5)—Cr—N(7)	95.0 (2)
N(6)—Cr—N(7)	78.8 (2)	Cr—N(1)—C(1)	128.6 (5)
Cr—N(1)—C(5)	113.0 (3)	C(1)—N(1)—C(5)	118.4 (5)
Cr—N(2)—C(6)	114.7 (4)	Cr—N(2)—C(7)	125.9 (4)
C(6)—N(2)—C(7)	119.4 (6)	C(8)—N(3)—C(9)	116.3 (6)
C(8)—N(3)—C(17)	117.2 (5)	C(9)—N(3)—C(17)	118.6 (6)
Cr—N(4)—C(10)	125.7 (4)	Cr—N(4)—C(11)	114.0 (4)
C(10)—N(4)—C(11)	120.2 (5)	N(1)—C(1)—C(2)	121.5 (7)
N(1)—C(5)—C(4)	122.5 (5)	N(1)—C(5)—C(6)	114.2 (5)
N(2)—C(7)—C(8)	109.4 (5)	N(2)—C(6)—C(5)	118.7 (6)
N(3)—C(9)—C(10)	111.4 (5)	N(3)—C(8)—C(7)	111.0 (6)
N(4)—C(11)—C(12)	119.2 (6)	N(4)—C(10)—C(9)	109.9 (5)

Intensity data were corrected for Lorentz–polarization effects. A face-indexed numerical absorption correction was applied (Sheldrick, 1991) on seven crystal faces. The atomic scattering factors for neutral atoms were corrected for anomalous dispersion using the values of Sheldrick (1991). Four reflections (200, 011, 220, $\bar{1}11$) were omitted from the final calculations due to extinction effects. Final refinement was by full-matrix least-squares employing anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for H atoms fixed at 0.08 Å² (positioned in geometrically idealized positions, C—H = 0.96 Å). The high displacement parameters (supplementary material) for the perchlorate anions are typical for this group for a refinement on room temperature data (see McLachlan, Fallon, Martin & Spiccia, 1995) and may be indicative of slight disorder. All calculations were performed on a MicroVAX 2000 computer.

Data collection: *Siemens P3/IV Data Collection System* (Siemens, 1989). Cell refinement: *Siemens P3/IV Data Collection System*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 2:1 Mixture of Tetrabutylammonium Bis(4,5-dimercapto-1,3-dithiole-2-thionato)-nickelate(II) and its 2-Selenone Analogue

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Abstract

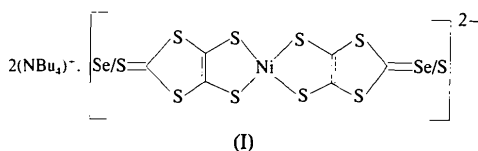
The X-ray analysis of the title compound, (C₁₆H₃₆N)₂–[Ni(C₃S_{4.67}Se_{0.33})₂], reveals that the anion contains 4,5-dimercapto-1,3-dithiole-2-thionato and 4,5-dimercapto-1,3-dithiole-2-selenato ligands in the ratio 2:1. The anion as a whole is planar and the central Ni atom has a square-planar coordination environment. The disorder in the tetrabutylammonium cation has been modelled to give acceptable geometric parameters.

Comment

There has been particular interest in complexes of the DMIT ligand C₃S₅²⁻ (4,5-dimercapto-1,3-dithiole-2-thionato) since the discovery of superconductivity in salts of nickel and palladium DMIT complexes (Bousseau, Valade, Legros, Garbaskas & Interrante, 1986). Intermolecular interaction through S···S contacts is the basic requirement for high conductivity in this

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kind of material. It is believed that the substitution of sulfur by selenium has a pronounced effect on the electrochemical behaviour and the crystal structure (Cornelissen *et al.*, 1992). These conducting compounds were also found to exist as salts in mixed valence states (Valade, Bousseau, Gleizes & Cassoux, 1983). Dealing with the more relevant cases only, the crystal structures of nickel complexes with pure $C_3S_5^{2-}$, a mixture of $C_3S_5^{2-}$ and $C_3Se_5^{2-}$ and pure $C_2S_3Se_3^{2-}$ as ligands have been reported (Lindquist, Sjolín, Sieler, Steimecke & Hoyer, 1979; Matsubayashi, Tanaka & Yokozawa, 1992; Olk *et al.*, 1992); all these compounds crystallize in the same space group ($P2_1/c$) and with almost the same cell parameters. We have attempted to substitute completely the terminal S atom with Se to obtain the ligand $C_3S_4Se^{2+}$ but the X-ray analysis shows only partial substitution (33% selenium). In our structure, (I), as in those previously mentioned, tetrabutylammonium is the counteranion.



The anion is completely planar with a maximum deviation of 0.079 (5) Å for S4. The central Ni atom has square-planar coordination and the Ni—S4 and Ni—S5 distances are 2.1967 (5) and 2.1932 (6) Å, respectively. The Se1/S1=C1 distance of 1.735 (2) Å is longer than the pure S=C distance of 1.680 (Lindqvist *et al.*, 1979) and shorter than the pure Se=C distance of 1.810 Å (Olk *et al.*, 1992); the Se/S=C length is 1.771 Å in a 61% Se and 39% S complex of the same type (Yao *et al.*, 1995). The Se/S=C bond length is found to vary linearly with the stoichiometric ratio of Se/S; a plot of bond length *versus* Se percentage is shown in Fig. 2. Disorder in the NBu_4^+ cation has been observed in all the previous structure determinations but was not

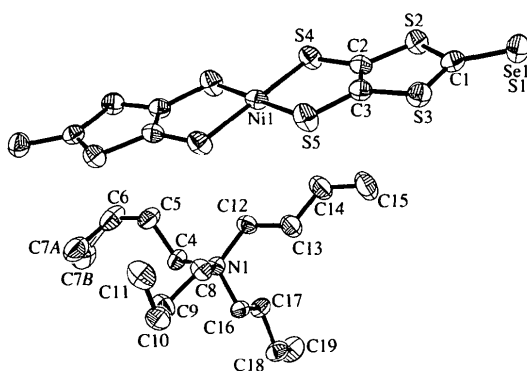


Fig. 1. Structure showing 50% probability displacement ellipsoids with numbering scheme.

modelled satisfactorily. The butyl chains are found to be disordered with rather large thermal motions; in our case one of the terminal methyl C atoms of a butyl chain (C7) was split into two positions, each of occupancy 0.5, and the disorder was resolved. The bond lengths and angles observed in the cation are now normal. There are no S...S or Se...S distances shorter than 3.7 Å in this complex and this may lead to poor conductive properties. The crystal structure is stabilized by van der Waals interactions.

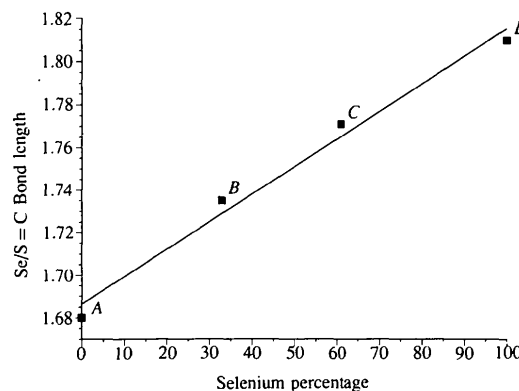


Fig. 2. Plot of Se/S=C bond length *versus* Se percentage. (A) Lindqvist *et al.* (1979); (B) present study; (C) Yao *et al.* (1995); (D) Olk *et al.* (1992).

Experimental

The complex was synthesized by a similar procedure to that given by Yao *et al.* (1995). Single crystals were obtained from acetone solution by slow evaporation at room temperature.

Crystal data

$(C_{16}H_{36}N)_2-$
 $[Ni(C_3S_{4.67}Se_{0.33})_2]$
 $M_r = 967.264$
 Monoclinic
 $P2_1/c$
 $a = 8.420$ (2) Å
 $b = 14.796$ (2) Å
 $c = 19.5040$ (1) Å
 $\beta = 96.22$ (1)°
 $V = 2415.5$ (7) Å³
 $Z = 2$
 $D_x = 1.330$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 40 reflections
 $\theta = 10-25^\circ$
 $\mu = 1.331$ mm⁻¹
 $T = 293$ (2) K
 Prism
 $0.76 \times 0.50 \times 0.40$ mm
 Blue

Data collection

Siemens P4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 ψ scans (Siemens, 1994)
 $T_{min} = 0.818$, $T_{max} = 0.950$
 7096 measured reflections
 5500 independent reflections
 4366 observed reflections
 $[I > 2\sigma(I)]$

$R_{int} = 0.0254$
 $\theta_{max} = 27.5^\circ$
 $h = -1 \rightarrow 10$
 $k = -1 \rightarrow 19$
 $l = -25 \rightarrow 25$
 3 standard reflections monitored every 100 reflections
 intensity decay: <3%

Refinement

Refinement on F^2

$$R[F^2 > 2\sigma(F^2)] = 0.0335$$

$$wR(F^2) = 0.0969$$

$$S = 1.070$$

5499 reflections

277 parameters

Only H-atom U 's refined

$$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 0.1746P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

$$0.0107(8)$$

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

C3—C2—S4	121.5 (2)	C8—C9—C10	110.8 (2)
C3—C2—S2	115.11 (15)	C11—C10—C9	115.0 (2)
S4—C2—S2	123.39 (11)	C13—C12—N1	115.4 (2)
C2—C3—S5	122.0 (2)	C12—C13—C14	110.1 (2)
C2—C3—S3	115.6 (2)	C15—C14—C13	111.8 (2)
S5—C3—S3	122.39 (11)	C17—C16—N1	115.32 (15)
C8—N1—C4	111.71 (14)	C16—C17—C18	110.9 (2)
C8—N1—C12	108.64 (14)	C19—C18—C17	111.8 (2)
C4—N1—C12	108.82 (15)		

The structure was solved by direct methods and refined by full-matrix least-squares techniques. The disorder at the terminal Se/S position was noticed in the initial stages of refinement and later the refinement was continued with the same positional and displacement parameters for Se1 and S1. Their relative occupancy was refined until convergence [Se occupancy 0.325 (2)] which gave the effective stoichiometric ratio of Se1/S1 as 1:2. H atoms were geometrically fixed and allowed to ride on the atoms to which they are bonded, except the H atoms attached to C7A and C7B.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC (Sheldrick, 1990). Software used to prepare material for publication: SHELXL93. Geometry calculations: PARST (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1199). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Ni1	0	0	0	0.04210 (11)
Se1/S1	0.31366 (5)	-0.04232 (3)	0.35967 (2)	0.0618 (2)
S2	0.09963 (6)	-0.10536 (4)	0.23264 (3)	0.05141 (14)
S3	0.29421 (7)	0.04977 (4)	0.21990 (3)	0.05343 (15)
S4	-0.03446 (6)	-0.10020 (3)	0.08018 (3)	0.05167 (14)
S5	0.17888 (7)	0.07491 (4)	0.06771 (3)	0.0605 (2)
C1	0.2374 (2)	-0.03277 (14)	0.27368 (10)	0.0473 (4)
C2	0.0860 (2)	-0.05724 (13)	0.15039 (10)	0.0432 (4)
C3	0.1780 (2)	0.01673 (13)	0.14465 (10)	0.0451 (4)
N1	-0.4651 (2)	0.25167 (10)	-0.06281 (8)	0.0391 (3)
C4	-0.5763 (2)	0.22381 (14)	-0.12602 (10)	0.0465 (4)
C5	-0.5151 (3)	0.1484 (2)	-0.16940 (12)	0.0610 (6)
C6	-0.6300 (3)	0.1302 (2)	-0.23255 (14)	0.0777 (8)
C7A†	-0.5874 (9)	0.2060 (5)	-0.2853 (4)	0.099 (3)
C7B†	-0.6889 (11)	0.2014 (6)	-0.2800 (4)	0.112 (3)
C8	-0.3059 (2)	0.28533 (14)	-0.08220 (10)	0.0458 (4)
C9	-0.3138 (3)	0.3577 (2)	-0.13783 (12)	0.0575 (5)
C10	-0.1520 (3)	0.40340 (15)	-0.13911 (13)	0.0604 (6)
C11	-0.0217 (3)	0.3433 (2)	-0.15855 (14)	0.0669 (6)
C12	-0.4353 (2)	0.17012 (13)	-0.01548 (10)	0.0450 (4)
C13	-0.3347 (3)	0.1881 (2)	0.05215 (11)	0.0567 (5)
C14	-0.3343 (3)	0.1058 (2)	0.09840 (13)	0.0684 (7)
C15	-0.2307 (4)	0.1195 (2)	0.16524 (14)	0.0923 (10)
C16	-0.5457 (2)	0.32814 (12)	-0.02702 (9)	0.0412 (4)
C17	-0.6959 (2)	0.30189 (14)	0.00457 (11)	0.0492 (5)
C18	-0.7752 (3)	0.3843 (2)	0.03215 (13)	0.0592 (6)
C19	-0.9330 (3)	0.3609 (2)	0.0579 (2)	0.0770 (8)

† Occupancy = 0.5.

Table 2. Selected geometric parameters (\AA , $^\circ$)

Ni1—S5	2.1932 (6)	C4—C5	1.523 (3)
Ni1—S4	2.1967 (5)	C5—C6	1.506 (3)
Se1—C1	1.735 (2)	C6—C7A	1.454 (8)
S2—C1	1.714 (2)	C6—C7A	1.588 (8)
S2—C2	1.747 (2)	C8—C9	1.520 (3)
S3—C1	1.711 (2)	C9—C10	1.524 (3)
S3—C3	1.743 (2)	C10—C11	1.493 (3)
S4—C2	1.734 (2)	C12—C13	1.512 (3)
S5—C3	1.731 (2)	C13—C14	1.516 (3)
C2—C3	1.353 (3)	C14—C15	1.502 (4)
N1—C8	1.516 (2)	C16—C17	1.516 (3)
N1—C4	1.522 (2)	C17—C18	1.517 (3)
N1—C12	1.524 (2)	C18—C19	1.512 (3)
N1—C16	1.527 (2)		
S5—Ni1—S4	92.72 (2)	C8—N1—C16	108.64 (14)
C1—S2—C2	98.47 (10)	C4—N1—C16	107.82 (13)
C1—S3—C3	98.47 (10)	C12—N1—C16	111.23 (14)
C2—S4—Ni1	101.76 (7)	N1—C4—C5	115.6 (2)
C3—S5—Ni1	101.74 (7)	C6—C5—C4	111.1 (2)
S3—C1—S2	112.38 (12)	C7B—C6—C5	122.4 (4)
S3—C1—Se1	123.49 (12)	C5—C6—C7A	103.5 (4)
S2—C1—Se1	124.12 (12)	N1—C8—C9	116.0 (2)

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Bis(dimethylglyoximato-*N,N'*)(isopropyl)-(triphenylphosphine)rhodium(III)

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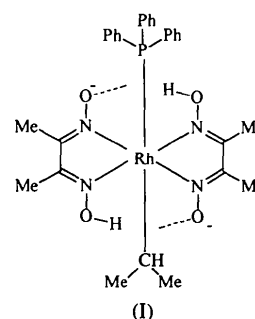
Abstract

The structure of the title compound, $[\text{Rh}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\{\text{CH}(\text{CH}_3)_2\}(\text{P}(\text{C}_6\text{H}_5)_3)]$, consists of discrete complexes in which the Rh atom has distorted octahedral coordination. The two dimethylglyoximato ligands lie in the equatorial plane and the isopropyl and triphenylphosphine species occupy the axial positions. The Rh atom is displaced by 0.096(1) Å from the mean plane through the four oxime N donor atoms towards the P atom. The average Rh—N distance is 1.975(10) Å, while the axial Rh—P and Rh—C distances are 2.489(2) and 2.146(6) Å, respectively. Comparison of the results with those obtained previously for other compounds of this type indicates that the *trans* influence of *R* in the axial fragment $\text{Ph}_3\text{P—Rh—R}$ is determined by its σ -donor power.

Comment

This work is a continuation of a project aimed at the elucidation of the mutual influence of ligands in organometallic compounds (Steinborn, 1992). The *trans* influence of σ -organo ligands is of particular interest. We have demonstrated (Steinborn & Ludwig, 1993a; Ludwig & Steinborn, 1996) that in complexes $[\text{Rh}(\text{dmgH})_2(\text{PPh}_3)\text{R}]$ (dmgH = monoanion of dimethylglyoxime, PPh_3 = triphenylphosphine, *R* = organo group) the *trans* influence of *R*, as measured by $^1J(^{103}\text{Rh—}^{31}\text{P})$ coupling constants, is in the unusual order $^i\text{Bu} \gg \text{cyclohexyl} > ^i\text{Pr} > \text{CPr}=\text{CH}_2 > \text{CH}_2\text{OMe} > \text{CH}=\text{CHPr} = ^i\text{Bu} = ^n\text{Pr} = \text{Ph} = \text{Et} = ^n\text{Bu} = \text{CH}=\text{CHPh} > \text{CH}=\text{CH}_2 > \text{CH}_2\text{SiMe}_3 = \text{Me} > \text{CH}_2\text{Cl} = \text{CH}_2\text{SPh} = \text{Bz} = \text{CH}_2\text{Br} \gg \text{C}\equiv\text{CPh}$. To investigate the dependence of the *trans* influence mea-

sured by NMR spectroscopy on the structure of the complexes, we decided to study the structures of the complexes by systematically changing the type of hybridization of the donor orbital ($R = \text{Et}$, $\text{CH}=\text{CH}_2$ and $\text{C}\equiv\text{CPh}$) as well as the branching within the alkyl ligands ($R = \text{Me}$, Et, ⁱPr and ^tBu) ($\text{C}\equiv\text{CPh}$: Dunaj-Jurčo, Kettmann, Steinborn & Ludwig, 1995; $\text{CH}=\text{CH}_2$: Dunaj-Jurčo, Kettmann, Steinborn & Ludwig, 1994; Et: Kettmann, Dunaj-Jurčo, Steinborn & Ludwig, 1994; ^tBu: Kettmann, Dunaj-Jurčo, Steinborn & Ludwig, 1996; Me: Potočnák, Dunaj-Jurčo, Ludwig & Steinborn, 1996). Here we report the structure of the isopropyl complex, (I).



The $[\text{Rh}(\text{dmgH})_2(\text{PPh}_3)^i\text{Pr}]$ complex crystallizes with discrete molecules, in which the Rh atom exhibits distorted octahedral coordination, with four oxime N donors in the equatorial positions. The two dimethylglyoximate ligands are stabilized by two intramolecular hydrogen bonds, acting between O1 and O4 [$\text{O}\cdots\text{O} = 2.686(7) \text{ \AA}$] and between O2 and O3 [$\text{O}\cdots\text{O} = 2.692(7) \text{ \AA}$]. On the basis of the refined H-atom positions, both hydrogen bridges in the $\text{Rh}(\text{dmgH})_2$ unit are asymmetric [$\text{O1}\cdots\text{H4} = 1.93(7)$, $\text{O4—H4} = 0.78(7)$, $\text{O3}\cdots\text{H2} = 2.01(7)$, $\text{O2—H2} = 0.69(7) \text{ \AA}$].

The four Rh—N bond distances range from 1.963(5) to 1.990(5) Å, with a mean value of 1.975(10) Å. This value is larger than those of the vinyl and the *tert*-butyl derivatives [1.957(2) and 1.955(3) Å, respectively (Dunaj-Jurčo *et al.*, 1994b; Kettmann *et al.*, 1996)] but is similar to those of the phenylacetyl-ide and methyl complexes [1.971(2) and 1.976(9) Å, respectively (Dunaj-Jurčo *et al.*, 1994a; Potočnák *et al.*, 1996)]. As found in other derivatives of the series, the two dmgH^- ligands are tilted away from the triphenylphosphine ligand so that their normal vectors make an angle of $9.74(7)^\circ$ with each other. As a result, though the four oxime N donors are coplanar to within $\pm 0.002 \text{ \AA}$, the Rh atom is displaced by 0.0961(10) Å from their mean plane toward the P atom. The dmgH^- ligands themselves are also not strictly planar; the lack of planarity originates from twisting of the two halves of the ligand about the central C—C bond, the dihedral angle formed by the planes O1—N1—C1—C3 and O2—N2—C2—C4 being $2.9(3)^\circ$ and that formed by