$\omega/2\theta$ scans
Absorption correction:
empirical *via* ψ scans
(Fair, 1990)
$T_{\rm min} = 0.671$, $T_{\rm max} = 0.832$
5092 measured reflections
4836 independent reflections

$R_{\rm int} = 0.016$
$\theta_{\rm max} = 25.46°$
$h = -13 \rightarrow 0$
$k = -18 \rightarrow 0$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.033$
$wR = 0.040$
$S = 0.93$
3312 reflections
322 parameters
H atoms riding (see below)
$w = 1/[\sigma(F^2) + (0.02F)^2 + 0.5]$; $w = 0$ if $F^2 < 3\sigma(F^2)$

$(\Delta/\sigma)_{\rm max} = 0.00014$
$\Delta\rho_{\rm max} = 0.510$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.121$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Cu—Ni	2.9967 (4)	Ni—O5	2.152 (2)
Cu—O1	2.048 (2)	Ni—N1	2.019 (3)
Cu—O2	2.063 (2)	Ni—N2	2.014 (3)
Cu—O3	2.103 (2)	Ni—N3	2.131 (3)
Ni—O1	2.016 (2)	O3—N3	1.319 (4)
Ni—O2	2.003 (2)	O4—N3	1.183 (4)
O1—Cu—O2	78.70 (8)	O5—Ni—N1	87.3 (1)
O1—Cu—O3	85.16 (9)	O5—Ni—N2	89.0 (1)
O2—Cu—O3	85.86 (9)	O5—Ni—N3	171.0 (1)
O1—Ni—O2	80.88 (8)	N1—Ni—N2	98.5 (1)
O1—Ni—O5	88.83 (9)	N1—Ni—N3	97.3 (1)
O1—Ni—N1	89.4 (1)	N2—Ni—N3	97.9 (1)
O1—Ni—N2	171.7 (1)	Cu—O1—Ni	95.02 (8)
O1—Ni—N3	83.4 (1)	Cu—O2—Ni	94.94 (8)
O2—Ni—O5	90.87 (9)	Cu—O3—N3	110.4 (2)
O2—Ni—N1	170.2 (1)	Ni—N3—O3	116.3 (2)
O2—Ni—N2	91.1 (1)	Ni—N3—O4	129.8 (3)
O2—Ni—N3	83.3 (1)	O3—N3—O4	114.0 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
C19—H191···O6$^{\rm i}$	1.01	2.41	3.332 (6)	152
C21—H21···O4	0.98	2.47	3.387 (5)	154

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$.

All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed geometrically, 0.95 Å from their parent C atoms, except for the H atoms of the dmf and propanediamine ligands, which were refined for a few cycles. A riding model was subsequently used for all H atoms, with $U_{\rm eq}({\rm H}) = 1.3U_{\rm eq}({\rm C})$.

Data collection and cell refinement were performed using *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). *MolEN* (Fair, 1990) was used for data reduction, structure solution and refinement, molecular graphics and the preparation of material for publication. Other programs used include *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1190). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 470–473

Bis(tetra-*n*-butylammonium) Bis[(4-cyanophenyl)dithiocarbimato(2–)-*S*,*S*′]nickel(II)†

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Abstract

The title compound, $[N(C_4H_9)_4]^+_2.[Ni(C_8H_4N_2S_2)_2]^{2-}$, crystallizes with the Ni atom on a crystallographic inversion center. The phenyl rings of the ligands make an angle of 50.50 (5)° with the plane spanned by the central nickel–sulfur fragment. The bond lengths do not indicate that the formal negative charge on the dithiocarbimato moiety is delocalized into the phenyl ring.

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† Alternative name: bis(tetra-*n*-butylammonium) bis[(4-cyanophenylimino)dithiocarboxylato(2−)-*S*,*S*′]nickel(II).

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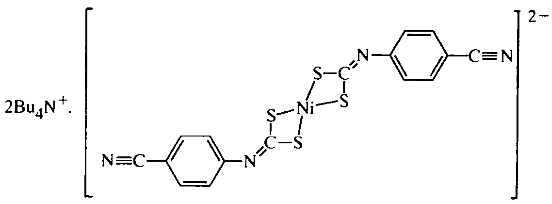
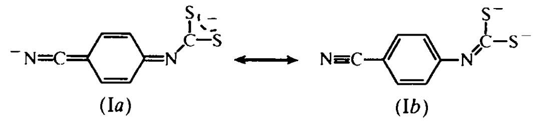
Comment

para-Substituted bis(phenyldithiocarbamato)nickel(II) complexes are promising candidates for third-order non-linear optics because of the possibility for efficient charge-transfer transitions displacing charge from the central Ni–S moiety to the periphery of the molecule (Schougaard, 1995; Schougaard *et al.*, 1997; Bjørnholm, 1997). We have prepared a series of *para*-substituted bis(phenyldithiocarbamato)nickel(II) complexes and have isolated their corresponding bases as bis(tetrabutylammonium) salts. The third-order non-linear optical response, as measured by third-harmonic generation, was found to be highly dependent on the electron-withdrawing ability of the substituent in the *para* position of the phenyl ring, as well as on the overall charge of the complexes (*i.e.* neutral or dianionic) (Schougaard, 1995; Schougaard *et al.*, 1997). The structure determination of the title compound, (I), was undertaken in order to investigate the degree of conjugation between the formal negative charge on the N1 atom and the phenyl moiety, and also to obtain a reliable geometry of the complex for quantum-chemical calculations of the non-linear optical response.



(I)

To gain insight into the relative weight of the quinoid charge-separated resonance structure (I*a*) and the aromatic resonance structure (I*b*) in the ground state of the title compound, the structure is subdivided into fragments, the geometries of which are compared with those of similar fragments of previously studied compounds. Within experimental error, the geometry of the central Ni(S$_2$CN)$_2$ fragment agrees well with an earlier study of bis(tetraphenylarsonium) bis(*N*-cyanodithiocarbimato)nickel(II) (Cotton & Harris, 1968). We find that the C1—N1 bond length of 1.2926 (14) Å reported here corresponds to a double bond and consequently the lone pair on the N1 atom can be expected to be in the sp^2 orbital of N1.



(I*a*) (I*b*)

The effect of conjugation between the N1 sp^2 and p_z orbitals and the phenyl ring can be estimated by comparing the N1—C2 distance of the title compound with the same distance in bis(*N*-methyl-*N*-phenyldithiocarbamato)nickel(II) (Martin *et al.*, 1972). In the latter structure, there is no negative charge on N1 and conjugation is not favored due to the 82° angle between the phenyl ring and the S1–S2–N1 plane. In this structure, the N1—C2 distance is 1.44 (1) Å, which corresponds to a single bond. This distance is significantly longer than the equivalent N1—C2 bond length [1.4010 (14) Å] of the title compound, indicating that the quinoid resonance structure (I*a*) contributes to the electronic structure of the ground state. The contribution is limited since the structural evidence for bond-length alternation in the phenyl ring is very small [C2—C3 1.402 (2) and C4—C5 1.397 (2) Å

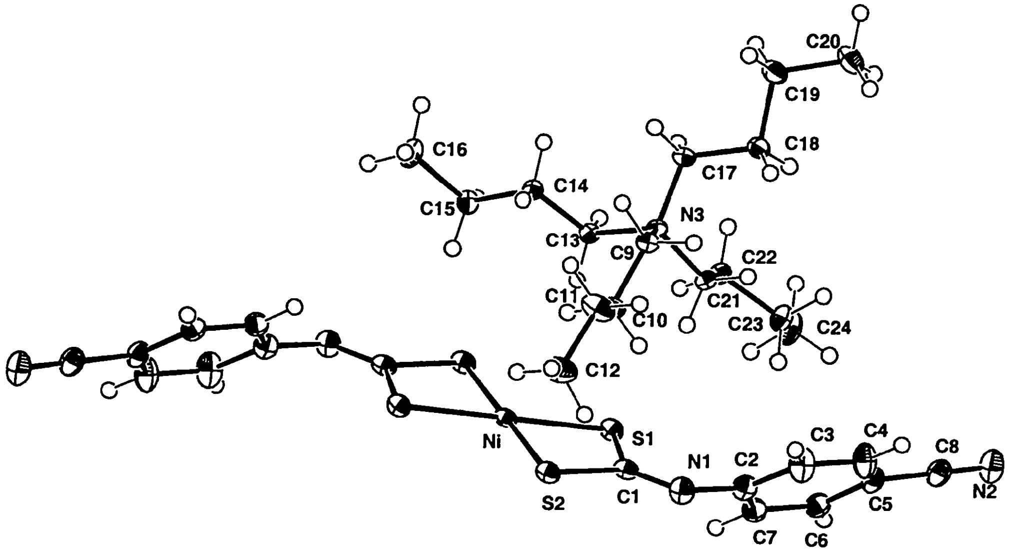


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound. Displacement ellipsoids are drawn at 50% probability.

compared with C3—C4 1.377 (2) Å]. Furthermore, the bond lengths of the cyano group [C5—C8 1.441 (2) and C8—N2 1.1448 (15) Å] do not show the expected effects of conjugation, *i.e.* shortening of the C5—C8 bond and lengthening of the C8—N1 bond compared with the structure of benzonitrile [C5—C8 1.401 (14) and C8—N2 1.137 (14) Å; Fauvet *et al.*, 1978]. Hence, the ground state of the title compound is probably dominated by the aromatic resonance structure (I*b*).

The stereo-pair drawing (Fig. 2) shows that the arrangement of the anions does not provide any evidence for aromatic π–π stacking, nor Ni d_{z^2}–d_{z^2} overlap. It is also evident that the well ordered tetrabutylammonium cation does separate the anions so well that they can be considered as isolated entities surrounded by a dielectric medium.

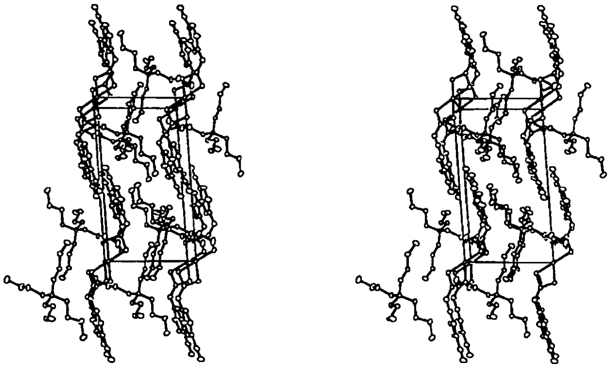


Fig. 2. *ORTEP*II (Johnson, 1976) packing drawing of the unit cell viewed along the *b* axis.

Experimental

Synthesis was carried out according to the literature methods of Schougaard (1995) and Coucouvanis & Fackler (1967). Crystals were obtained by cooling a saturated solution of the salt in acetone.

Crystal data

$(C_{16}H_{36}N)_2[Ni(C_8H_4N_2S_2)_2]$
$M_r = 928.13$
Triclinic
$P\bar{1}$
$a = 8.540 (3)$ Å
$b = 9.536 (2)$ Å
$c = 15.819 (6)$ Å
$\alpha = 93.31 (2)°$
$\beta = 94.12 (3)°$
$\gamma = 90.67 (2)°$
$V = 1282.6 (7)$ Å^3
$Z = 1$
$D_x = 1.202$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 19.45$–$22.75°$
$\mu = 0.578$ mm^{-1}
$T = 122.0 (5)$ K
Needle
0.44 × 0.40 × 0.18 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
12 294 measured reflections
11 260 independent reflections
9544 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.019$
$\theta_{\rm max} = 34.96°$
$h = -13 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = 0 \rightarrow 25$
5 standard reflections
frequency: 166.7 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.062$
$S = 2.474$
11 248 reflections
428 parameters
H atoms refined with individual isotropic displacement parameters

$w = 1/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\rm max} = 0.007$
$\Delta\rho_{\rm max} = 0.508$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.480$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ni—S1	2.1988 (8)	C2—C3	1.402 (2)
Ni—S2	2.2009 (7)	C3—C4	1.377 (2)
S1—C1	1.7633 (11)	C4—C5	1.397 (2)
S2—C1	1.7461 (12)	C5—C6	1.395 (2)
C1—N1	1.2926 (14)	C5—C8	1.441 (2)
C2—N1	1.4010 (14)	C6—C7	1.385 (2)
C2—C7	1.4030 (15)	C8—N2	1.1448 (15)
S1—Ni—S2'	100.62 (3)	C4—C3—C2	121.16 (11)
S1—Ni—S2	79.37 (3)	C3—C4—C5	120.17 (11)
C1—S1—Ni	86.92 (4)	C6—C5—C4	119.46 (10)
C1—S2—Ni	87.27 (4)	C6—C5—C8	121.18 (10)
N1—C1—S2	122.78 (8)	C4—C5—C8	119.34 (10)
N1—C1—S1	130.75 (8)	C7—C6—C5	120.14 (10)
S2—C1--S1	106.37 (6)	C6---C7 C2	120.85 (10)
N1—C2—C7	124.27 (10)	N2—C8—C5	178.20 (12)
N1—C2—C3	117.53 (10)	C1—N1—C2	121.49 (9)
C7—C2—C3	118.14 (10)		
S2—Ni—S1—C1	1.73 (3)	S1—C1—N1—C2	4.2 (2)
Ni—S2—C1—N1	−174.57 (9)	C7—C2—N1—C1	47.4 (2)
S2—C1—N1—C2	−179.88 (8)	C3—C2—N1—C1	−135.64 (11)

Symmetry code: (i) $-x, -y, -z$.

The effects of absorption were considered of minor significance, so the data reduction did not include this correction. Only reflections which had $F^2 > -3\sigma(F^2)$ were used in the refinement. Weights calculated from counting statistics were employed as it was found that they provided a reliable estimate of the experimental error. The resulting averaged values of $w\Delta F^2$ as a function of sinθ and F^2 did not show any significant variations. The refinement included the positional parameters and isotropic displacement parameters for the H atoms.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *DREADD* (Blessing, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1504). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 473–475

A *cis*-Dioxomolybdenum(VI) Complex, [Mo{$N_2C_3H_3C(Me)_2O$}$_2$(O)$_2$]

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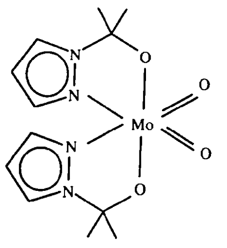
Abstract

In the *cis*-dioxomolybdenum(VI) complex bis[1-methyl-1-(1-pyrazolyl)ethanolato-N^2,O]dioxomolybdenum(VI), [Mo(O)$_2$($C_6H_9N_2O$)$_2$] or $C_{12}H_{18}MoN_4O_4$, the Mo atom has distorted octahedral coordination to two (*cis*) oxo ligands, and two N and two O atoms of the two substituted pyrazole ligands. Mo—O$_{oxo}$ bond distances [mean 1.698 (6) Å] correspond to double bonds, Mo—O$_{oxy}$ [mean 1.951 (2) Å] to single bonds, and Mo—N bonds [mean 2.326 (3) Å] are lengthened as a result of the effect of the oxo ligands, which are *trans* to the N atoms.

Comment

The interest in mononuclear high-valent oxomolybdenum complexes as structural and reactivity models of the molybdenum site in oxo-type molybdoenzymes is well documented (Garner & Bristow, 1985). In addition, O-atom-transfer reactions of dioxomolybdenum(VI) complexes have been discussed (Holm, 1987; Roberts *et al.*, 1988, 1990).



(I)

The present account details two synthetic routes to a novel *cis*-dioxomolybdenum(VI) complex, [Mo{$N_2C_3H_3C(Me)_2O$}$_2$(O)$_2$], (I), and describes its crystal and molecular structure. The first synthetic route, a serendipitous discovery, arose from an attempt to prepare acetone solutions of the all-Mo^{VI} octamolybdenum cluster species, $Mo_8(pz)_6O_{21}(pzH)_6.3pzH.0.5H_2O$, where pzH is pyrazole (Ehlert *et al.*, 1993). Instead of acting as a solvent, the acetone caused a breakdown of the cage structure, became part of a new chelating ligand, *i.e.* $N_2C_3H_3C(Me)_2O$, and was thereby incorporated into the new mononuclear *cis*-dioxomolybdenum complex (Fig. 1). The literature does contain a precedent for this type of reaction. Calhorda & Dias (1980) describe the reaction of Cp_2MoBr_2 with excess pyrazole and acetone in the presence of $TlPF_6$. One of the products from the reaction was formulated as [Cp_2Mo{$N_2C_3H_3C(Me)_2O$}]$^+$.PF_6^- (where Cp is cyclopentadienyl) on the basis of elemental analyses and ^1H NMR data.

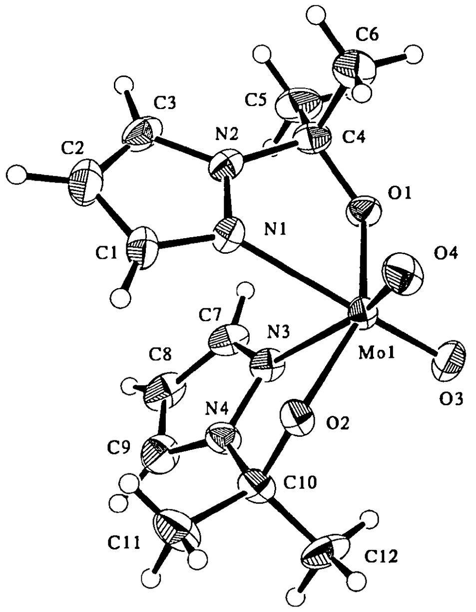


Fig. 1. View of the title molecule (30% probability displacement ellipsoids).