

of these atoms from their mean plane are -0.015 (3), -0.04 (3), 0.0005 (2), -0.021 (2) and -0.008 (2) Å, respectively.

The angle Cu—O(4)—Cu' [106.3 (1)°], which is in agreement with pseudotetrahedral geometry for the O(4) atom, is strictly related to the Cu...Cu' separation of 3.418 (1) Å, which is close to the values found for other dinuclear Cu^{II} complexes (De Munno, Denti & Dapporto, 1983; Dapporto, De Munno, Segá & Mealli, 1984). The bond distances and angles within the 2,2'-bipyrimidine ligand, which is strictly planar [torsion angle N(2)—C(2')—C(2)—N(1) 0.6 (5)°], are in accordance with those previously reported (Fernholt, Rømming & Samdal, 1981), the greatest difference being found in the C(2)—C(2') distance [1.432 (8) Å], which is shorter than the corresponding distance in non-coordinated 2,2'-bipyrimidine [1.511 (2) Å in the gaseous state and 1.497 (4) Å in the solid state], and is also shorter than that found in the coordinated 2,2'-bipyridyl (Procter & Stephens, 1969), which is 1.501 (17) or 1.502 (16) Å in the nitrito-bis(2,2'-bipyridyl)copper(II) nitrate complex. This shortening indicates a greater conjugation which is probably due to the double chelation of the ligand, which with the two Cu^{II} atoms forms a particular conjugate system. The two Cu atoms are in the same plane as the two pyrimidine rings; in fact, the torsion angle C(3)—

N(2)—Cu—O(1) is 0.1 (4)° and the dihedral angle between the Cu—N(1)—N(2) and N(1)—N(2)—C(2)—C(2') planes is 176.0 (1)°.

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Structure of Bis(tetraethylammonium) Bis[dimercaptomaleodinitrilato(2—)-S,S']-nickelate(II), [N(C₂H₅)₄]₂[Ni(C₄N₂S₂)₂]

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(Received 6 April 1984; accepted 27 July 1984)

Abstract. $M_r = 599.57$, triclinic, $P\bar{1}$, $a = 7.5608$ (7), $b = 8.7017$ (9), $c = 12.626$ (3) Å, $\alpha = 93.73$ (1), $\beta = 104.27$ (1), $\gamma = 75.257$ (9)°, $V = 779$ Å³, $Z = 1$, $D_m = 1.286$, $D_x = 1.279$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 8.54$ cm⁻¹, $F(000) = 318$, $T = 293$ K. Final $R = 0.058$ for 1550 unique observed diffractometer data. The metal atom of the anion has an approximately square-planar configuration and the amino atoms of the cations an approximately tetrahedral configuration. The Ni—S distances are 2.171 (2) and 2.177 (2) Å and the bite angle is 92.3 (1)°. The anion is essentially planar with the Ni atom deviating most by 0.047 (1) Å.

Introduction. The present work forms a part of our research program of structural studies of 1,2-dithiolato complexes of transition metals.

Experimental. Crystals obtained by the procedure of Billig, Williams, Bernal, Waters & Gray (1964). Approximate density measured by flotation in CCl₄/benzene showed $Z = 1$.

Unit-cell parameters obtained by least-squares refinement of θ values of 25 high-angle reflections. Crystal $0.1 \times 0.3 \times 0.25$ mm, three-dimensional intensity data collected on an Enraf-Nonius CAD-4 diffractometer

with graphite-monochromated Mo $K\alpha$ radiation; $\omega/2\theta$ scan mode; standard reflections ($3\bar{1}\bar{1}$ and $2\bar{3}\bar{5}$) showed no significant change. All reflections (h : -8 to 8, k : -9 to 9, l : 0 to 14) in range $2 < 2\theta < 48^\circ$ measured; max. counting time for each reflection 60 s; 2694 reflections measured, 1550 unique reflections with $I > 3\sigma(I)$ considered observed; R_{int} from merging 113 equivalent reflections 0.049; intensities not corrected for absorption.

The space group was tentatively fixed as $P\bar{1}$ which proved later to be correct. Since there is only one molecule in the unit cell, the Ni atom was assigned the special position (0,0,0). Successive difference Fourier maps revealed the positions of all other non-H atoms. Structure refined by full-matrix least squares minimizing $\sum w|\Delta F|^2$ with *SHELX76* (Sheldrick, 1976), initially with isotropic and then anisotropic thermal parameters for non-H atoms. Refinement of 160 positional and thermal parameters including the scale factor converged to $R = 0.058$. Max. and average shift/e.s.d. 0.961 and 0.150. Final difference Fourier maps revealed the positions of 11 of the 20 H atoms. Ten of these were refined once and the eleventh was fixed during the refinement since it did not converge to a reasonable position. Max. and min. heights in final difference Fourier map 0.75 and -0.3 e \AA^{-3} . $R_w = 0.086$, $w = 1.00/[\sigma^2(F_o) + 0.1818|F_o|^2]$. Atomic scattering factors for non-H atoms from Cromer & Mann (1968), anomalous-dispersion correction factors from Cromer & Liberman (1970); H-atom scattering factors from Stewart, Davidson & Simpson (1965).

Discussion. Atomic coordinates with equivalent isotropic thermal parameters are listed in Table 1.* Table 2 contains the interatomic distances and angles. Figs. 1

* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters and atom to plane distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39667 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

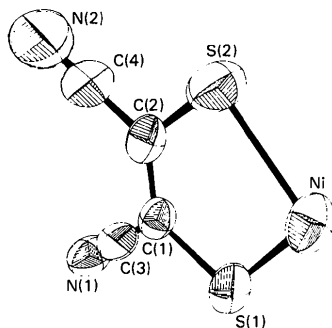


Fig. 1. Perspective view of the asymmetric unit of the anion.

and 2 show respectively the *ORTEP* plots (Johnson, 1965) of the asymmetric unit of the anion and the cation with numbering scheme.

Table 1. Final fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^4$ for Ni and S, $\times 10^3$ for others) with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Ni	0	0	10000	534 (4)
S(1)	508 (2)	1640 (2)	8944 (1)	503 (6)
S(2)	-2829 (2)	152 (2)	9011 (1)	584 (7)
C(1)	-1540 (8)	2015 (7)	7908 (5)	41 (2)
C(2)	-2988 (9)	1379 (7)	7932 (5)	43 (2)
C(3)	-1646 (9)	3019 (8)	7050 (5)	52 (2)
C(4)	-4665 (10)	1644 (8)	7112 (6)	57 (3)
N(1)	-1735 (9)	3852 (8)	6342 (5)	68 (2)
N(2)	-6071 (10)	1868 (9)	6425 (5)	79 (3)
N(3)	-2636 (6)	3052 (6)	2671 (4)	44 (1)
C(5)	-3699 (10)	3695 (9)	3552 (6)	67 (3)
C(6)	-4514 (12)	2470 (11)	3943 (6)	92 (4)
C(7)	-1007 (10)	1621 (8)	3079 (6)	56 (2)
C(8)	444 (11)	1934 (12)	4083 (7)	83 (4)
C(9)	-1924 (10)	4430 (9)	2379 (6)	65 (3)
C(10)	-841 (12)	4018 (10)	1475 (7)	85 (3)
C(11)	-3877 (10)	2435 (9)	1677 (6)	60 (3)
C(12)	-5637 (11)	3694 (11)	1130 (7)	78 (3)

Table 2. Bond distances (\AA) and bond angles ($^\circ$)

Ni-S(1)	2.177 (2)	Ni-S(2)	2.171 (2)
S(1)-C(1)	1.737 (5)	S(2)-C(2)	1.747 (5)
C(1)-C(2)	1.35 (1)	C(1)-C(3)	1.41 (1)
C(2)-C(4)	1.403 (8)	C(3)-N(1)	1.17 (1)
C(4)-N(2)	1.176 (9)	N(3)-C(5)	1.527 (9)
C(5)-C(6)	1.52 (1)	N(3)-C(7)	1.524 (7)
C(7)-C(8)	1.52 (1)	N(3)-C(9)	1.53 (1)
C(9)-C(10)	1.54 (1)	N(3)-C(11)	1.527 (8)
C(11)-C(12)	1.53 (1)		
S(1)-Ni-S(2)	92.3 (1)	Ni-S(1)-C(1)	103.0 (2)
Ni-S(2)-C(2)	103.1 (3)	S(1)-C(1)-C(2)	121.0 (5)
S(2)-C(2)-C(1)	120.5 (4)	S(1)-C(1)-C(3)	117.6 (5)
S(2)-C(2)-C(4)	116.5 (5)	C(2)-C(1)-C(3)	121.4 (5)
C(1)-C(2)-C(4)	123.0 (6)	C(1)-C(3)-N(1)	179.9 (2)
C(2)-C(4)-N(2)	179.9 (1)	C(5)-N(3)-C(7)	111.3 (5)
C(5)-N(3)-C(9)	105.7 (5)	C(5)-N(3)-C(11)	112.0 (5)
C(7)-N(3)-C(9)	111.1 (5)	C(7)-N(3)-C(11)	104.7 (5)
C(9)-N(3)-C(11)	112.1 (5)	N(3)-C(5)-C(6)	112.9 (6)
N(3)-C(7)-C(8)	114.8 (6)	N(3)-C(9)-C(10)	113.5 (6)
N(3)-C(11)-C(12)	113.7 (6)		

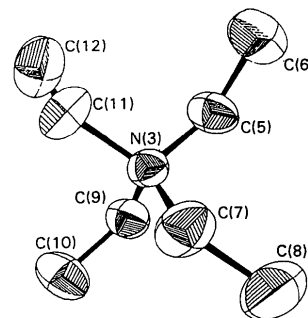


Fig. 2. Perspective view of the cation.

Unlike the Ni atom in [Ni(mnt)₂]⁻ compounds, Ni in [Ni(mnt)₂]²⁻ compounds [mnt = dimercaptomaleodinitrilato(2-)] always occupies an inversion center to make the [NiS₄] chromophore strictly planar. In the present structure also, the Ni atom occupies the inversion center at (0,0,0). This occurs because the spread of electron density which favors the square-planar configuration is more likely to occur for the *d*⁸ electron configuration in which a non-bonding electron pair is located in the *d*_{z²} orbital.

The Ni atom has an approximately square-planar configuration with all the Ni—S distances equal within experimental error. The bite angle is 92.3 (1)°. The intra- and interligand S—S distances are 3.135 (3) and 3.013 (3) Å respectively. These distances compare well with those of similar compounds having square-planar geometry. The whole anion is essentially planar, the r.m.s. deviation being 0.023 Å, with the Ni atom deviating most [0.047 (1) Å].

McCleverty (1968) considered all types of ligands which form [Ni—S_z]^z (where *z* = 0, -1 and -2) complexes and compared the variation of Ni—S, S—C and C=C bond lengths with respect to variation of overall charge *z*. According to McCleverty (1968), increase in overall charge is accompanied by a small decrease in C=C lengths and a small increase in Ni—S and S—C distances. Since we felt it is better to deal with the same ligand we consider only the mnt ligand in the following discussion.

To study the significance of the overall charge (or the oxidation state of the Ni atom) of the anion, we calculated the average values of the reported Ni—S, S—C, C=C, C—C and C≡N bond distances separately for [Ni(mnt)₂]⁻ and [Ni(mnt)₂]²⁻ anions and then studied the variation of each type of bond by means of a significance test. The results are given in Table 3. The [Ni(mnt)₂]⁻ structures included in the calculation are [PMePh₃][Ni(mnt)₂] (Fritchie, 1966), [NEt₄][Ni(mnt)₂] (Kobayashi & Sasaki, 1977), [C₇H₇][Ni(mnt)₂] (Manoharan, Noordik, de Boer & Keijzers, 1981), [TMPD][Ni(mnt)₂] (TMPD = tetramethylphenylenediamine) (Ramakrishna & Manoharan, 1983), [TMP][Ni(mnt)₂] (TMP = trimethylphenyleneamine) (Mahadevan, Seshasayee, Murthy, Kuppusamy & Manoharan, 1983) and [NMP][Ni(mnt)₂] (NMP = *N*-methylphenazinium) (Kuppusamy, Mahadevan, Seshasayee & Manoharan, 1984). The [Ni(mnt)₂]²⁻ structures included in the calculation are [NMe₄]₂[Ni(mnt)₂] (Eisenberg & Ibers, 1965), [TMPD]₂[Ni(mnt)₂] (Hove, Hoffman & Ibers, 1972), [N(*n*-Bu)₄]₂[Ni(mnt)₂] (Kobayashi & Sasaki, 1977), [NMP]₂[Ni(mnt)₂] (Endres, Keller, Moroni & Nöthe, 1979) and the present structure. Only the variations of the Ni—S and S—C bond distances between [Ni(mnt)₂]⁻ and [Ni(mnt)₂]²⁻ are highly significant. From this, it

Table 3. Average values of the bond distances in [Ni(mnt)₂]ⁿ⁻ complexes

Type of bond	For <i>n</i> = 1 (Å)	For <i>n</i> = 2 (Å)	Significance of the variation
Ni—S	2.145 (2)	2.170 (3)	Highly significant
S—C	1.715 (2)	1.736 (2)	Highly significant
C=C	1.352 (8)	1.356 (8)	Insignificant
C—C	1.434 (2)	1.421 (5)	Marginally significant
C≡N	1.137 (5)	1.145 (7)	Insignificant

can be concluded that the overall charge (or the oxidation state of the Ni atom) of the anion plays an important role only in the case of the Ni—S and S—C bonds.

The average Ni—S and S—C bond distances and the C=C distance [2.174 (3), 1.742 (5) and 1.35 (1) Å respectively] of the present structure compare well with the average values calculated for the [Ni(mnt)₂]²⁻ structures (the deviations are insignificant); the average C—C and C≡N bond distances [1.407 (4) and 1.173 (3) Å] are respectively smaller and larger (see Table 3). The deviations are marginally and highly significant for C—C and C≡N bonds respectively.

The atoms of the cation have approximately tetrahedral geometry with all N—C and C—C distances quite normal. The terminal C atoms show high thermal parameters due to their free rotation. There are no unusually short intra- or intermolecular contacts.

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