

to the chloride site maintains charge balance in the crystal and is supported by crystallographic data in refinement, chemical analyses and density measurements. The chloride ion participates in four hydrogen bonds contributed by two molecules of glucose and the water molecule (Table 5). However, when water is present instead of Cl⁻, the atom H(O4) occupies an alternative site H'(O4), permitting O(4) to serve as an acceptor in a donor-acceptor link with O(w). Two hydrogen bonds between the glucose molecules and three hydrogen bonds between the glucose and water molecules also participate in stabilizing the crystal (Table 5). The Cremer & Pople (1975) ring-puckering parameters for the pyranose ring of glucose are $q_2 = 0.052 \text{ \AA}$, $q_3 = 0.570 \text{ \AA}$, $Q = 0.573 \text{ \AA}$, $\theta = 5.23^\circ$ and $\varphi_2 = -31.3^\circ$. The torsion angle O(6)—C(6)—C(5)—O(5) is $-68.5 (6)^\circ$.

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Structure of the Square-Planar Complex Bis(dimethyl tetrathiomalonato)nickel(II)

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Abstract. [Ni(C₅H₇S₄)₂], $M_r = 449.43$, triclinic, $P\bar{1}$, $a = 4.0633 (5)$, $b = 9.091 (1)$, $c = 11.532 (1) \text{ \AA}$, $\alpha = 80.632 (4)$, $\beta = 84.083 (3)$, $\gamma = 86.290 (4)^\circ$, $V = 417.6 \text{ \AA}^3$, $Z = 1$, $D_m = 1.76$, $D_x = 1.79 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu(\text{Mo } K\alpha) = 21.12 \text{ cm}^{-1}$, $F(000) = 230$, $T = 296 \text{ K}$, $R = 0.041$ for 1582 observed reflections. The structure consists of discrete molecular units of composition Ni(ligand)₂. The molecules stack along the a direction with a short Ni—Ni distance of $4.0633 (5) \text{ \AA}$. The coordination around Ni^{II} is distorted square-planar with an S—Ni—S angle of $98.47 (3)^\circ$, and Ni—S distances of $2.1749 (9)$ – $2.1764 (9) \text{ \AA}$.

Introduction. Square-planar transition metal complexes have been considered as possible components of molecular metals (Wudl, 1975; Miller, 1982) and, more recently, superconductors (Brossard, Ribault,

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Bousseau, Valade & Cassoux, 1986; Kobayashi, *et al.* 1987). While metal dithiolene complexes (McCleverty, 1968; Schrauzer & Maymeg 1965), where the metal is part of a five-membered chelate ring, have been extensively studied, the corresponding dithioacetylacetonate complexes, where the metal is part of a six-membered ring, have received little attention. This may be due to the fact that they are not as easily prepared in high yield as their five-ring counterparts. A number of complexes of the ligand dithioacetylacetone (sacsac, pentane-2,4-dithione) with both divalent and trivalent transition metals have been reported (Bowden, Holloway & Geiger, 1978; Bowmaker, Boyd, Zvagulis, Cavell & Masters, 1985; Boyd, Hope & Martin, 1986; Heath & Leslie, 1983; Herman, Kirchner, Loew, Mueller-Westerhoff, Nazzal & Zerner, 1982; Lockyer & Martin, 1980). The syntheses of these complexes were carried out

using the method of Martin *et al.* (Barraclough, Martin & Stewart, 1969) by reaction of the metal ion, the oxo ligand and HCl in ethanol with H₂S at 273 K. Some complexes have also been prepared by the reduction of 1,2-dithiolium salts (Hendrickson, 1972) to the corresponding dithioacetylacetonate anion.

In this paper we report the crystal structure of the nickel bis(3,5-methylthio-2,6-dithioacetylacetonate) complex whose preparation and preliminary structural characterization are the subject of a separate publication (Singh, Jacobson, Hinkelmann, Srdanov & Wudl, 1989). The salient feature of this crystal structure is that substitution of two methyl groups of saccac by thiomethyl groups causes the molecular units to form *uniform stacks* with a relatively short Ni—Ni distance of 4.0633 (5) Å. This is the shortest distance observed to date in organosulfur-ligated nickel complexes such as those of dithiolene, dithiolate and saccac.

Experimental. The crystals were prepared by the method described by Singh *et al.* (1989). Purple-red needles were recrystallized from toluene to give a single crystal suitable for the X-ray measurements. D_m was measured by the flotation method using saturated CsCl solution in water. A prismatic crystal of dimensions 0.705 × 0.193 × 0.065 mm was mounted on a Huber four-circle automated diffractometer equipped with a graphite monochromator. The unit-cell dimensions were obtained from a least-squares fit for 25 strong reflections with $6 < 2\theta < 12^\circ$. $\theta/2\theta$ scans were applied for half of the reflection sphere ($0 \leq h \leq 5$, $-11 \leq k \leq 11$, $-14 \leq l \leq 14$) with a scan speed of 6° min^{-1} up to $2\theta \leq 55^\circ$ [$(\sin\theta)/\lambda = 0.650 \text{ \AA}^{-1}$]. Three standard reflections (11 $\bar{4}$, 012, 11 $\bar{3}$) were monitored every 97 reflections and showed a maximum decrease in intensity of 1.2%. A total of 2192 reflections were collected, (0*kl*) data averaged, 1582 unique observed [$I \geq 3\sigma(I)$] were used for refinement. The data were corrected for Lorentz and polarization effects, as well as for absorption (max. and min. transmission factors 0.886 and 0.627). Neutral-atom scattering factors and anomalous-dispersion corrections for Ni and S were from *International Tables for X-ray Crystallography* (1974). The structure was solved by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) which provided positions for the Ni and coordinated S atoms. Two subsequent Fourier maps indicated positions of all non-H atoms, which were refined with anisotropic temperature factors. In the final refinement, the contributions of hydrogens in calculated positions with estimated isotropic temperature factors were included. Full-matrix least-squares refinement gave residual $R(F) = 0.041$ and $wR(F) = 0.059$. $w =$

$1/\sigma^2(F)$, with $\sigma(F)$ based on counting statistics. $S = 2.02$, $(\Delta/\sigma)_{\text{max}} = 0.032$, $(\Delta/\sigma)_{\text{av}} = 0.009$, $(\Delta\rho)_{\text{max}} = 0.79 \text{ e \AA}^{-3}$ near the Ni atom. All the computations were performed on a MicroVAXII computer using the *UCLA Crystallographic Program Package* (Strouse, 1985).

Discussion. Positional and equivalent isotropic thermal parameters are listed in Table 1.* Interatomic distances and angles are summarized in Table 2. The atomic numbering scheme and molecular geometry of the complex are shown in Fig. 1. The structure is composed of approximately planar molecules placed on a crystallographic inversion center (Fig. 2). The Ni^{II} atom is displaced by 0.008 Å from the best least-squares plane through one ligand. The planes of the molecule are tilted by an angle of 156° relative to the *bc* crystallographic plane. The angle between the NiS₄ plane and the best least-squares fit through one ligand is 0.4° which is much smaller than the one found previously in Ni(saccac)₂ (Beckett & Hoskins, 1974). The coordination around Ni^{II} is distorted square planar with a $98.47(3)^\circ$ angle formed by the coordinated sulfurs, which is slightly (1.25°) higher than the one found in Ni(saccac)₂. The consequence of the larger S—Ni—S angle is that the transannular S(1)—S(2) distance [2.841(1) Å] decreases by 0.012 Å relative to Ni(saccac)₂. Since this value is 0.76 Å shorter than the sum of the van der Waals radii for sulfur (3.60 Å), one can assume the existence of some interaction between those two atoms. Such an interaction is reflected in the oxidation product [2,4-bis(methylthio)-1,2-dithiolium cation] of the complex (Singh *et al.*, 1989). The Ni—S bond distances [2.1747–2.1764(9) Å] are slightly longer than previously reported values for square planar Ni^{II} complexes containing Ni—S bonds (Brown, Weiss & Wu, 1969–1971) but they are still much shorter than for octahedral Ni^{II} complexes (Lopez-Castro & Truter, 1963). More recently, Ni—S values of 2.179–2.204 Å were reported (Steimecke, Sieler, Kirmse & Hoyer, 1979; Steimecke, Sieler, Kirmse, Dietzsch & Hoyer, 1982) for the *dianionic* forms of Ni square-planar complexes with chelating five-membered rings. C—S bond distances in the six-membered ring [1.682–1.686(3) Å] are shorter than normally expected values for *sp*² hybridized C and S atoms, while the C—C distances [1.377–1.382(4) Å] are very close to the distances found in aromatic systems. Those values are indicative of delocalization

* Tables of anisotropic thermal parameters, H-atom parameters, distances and angles involving H atoms, and observed and calculated structure amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52387 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and thermal parameters ($\text{\AA}^2 \times 10^4$)

	x	y	z	U_{eq}^*
C(1)	-0.1833 (8)	-0.0500 (4)	0.2881 (3)	344 (20)
C(2)	-0.0780 (10)	0.0870 (4)	0.3010 (3)	416 (23)
C(3)	0.0570 (8)	0.1950 (4)	0.2140 (3)	342 (20)
C(4)	0.3307 (11)	0.4790 (4)	0.1466 (3)	495 (27)
C(5)	-0.4808 (12)	-0.3218 (4)	0.3915 (4)	555 (29)
Ni	0.0000	0.0000	0.0000	324 (4)
S(1)	-0.1864 (3)	-0.1302 (1)	0.1663 (1)	440 (6)
S(2)	0.1329 (3)	0.1959 (1)	0.0677 (1)	444 (6)
S(3)	-0.3328 (3)	-0.1517 (1)	0.4250 (1)	469 (7)
S(4)	0.1573 (3)	0.3539 (1)	0.2717 (1)	448 (6)

$$*U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

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

C(1)—C(2)	1.377 (5)	C(3)—S(4)	1.772 (3)
C(1)—S(1)	1.686 (3)	C(4)—S(4)	1.798 (4)
C(1)—S(3)	1.765 (3)	C(5)—S(3)	1.807 (4)
C(2)—C(3)	1.381 (5)	Ni—S(1)	2.1749 (9)
C(3)—S(2)	1.682 (3)	Ni—S(2)	2.1764 (9)
C(2)—C(1)—S(1)	130.5 (3)	S(2)—C(3)—S(4)	118.0 (2)
C(2)—C(1)—S(3)	111.5 (2)	S(1)—Ni—S(2)	98.47 (3)
S(1)—C(1)—S(3)	118.0 (2)	C(1)—S(1)—Ni	116.5 (1)
C(1)—C(2)—C(3)	127.7 (3)	C(3)—S(2)—Ni	116.9 (1)
C(2)—C(3)—S(2)	129.9 (3)	C(1)—S(3)—C(5)	105.8 (2)
C(2)—C(3)—S(4)	112.0 (3)	C(3)—S(4)—C(4)	105.2 (2)

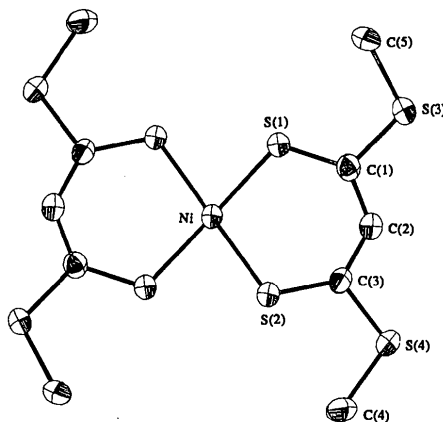
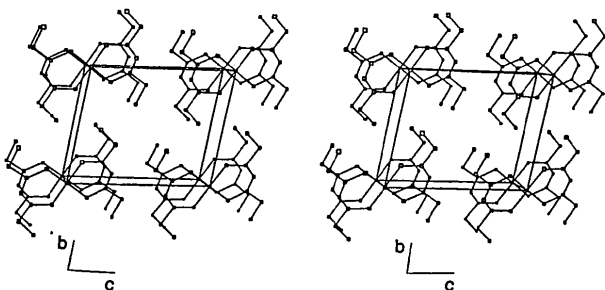


Fig. 1. ORTEP (Johnson, 1965) drawing of the molecule (two asymmetric units) with labeled atoms to conform to Table 2.

Fig. 2. Stereoview of the crystal packing in $\text{Ni}[\text{S}_2\text{C}_3\text{H}(\text{SCH}_3)_2]_2$.

in the six-membered ring. The bond lengths for the thiomethyl groups are within the normally expected ranges. The position of the methyl groups (pointing 'out' from the central C atom in the six-membered ring) is probably caused by steric repulsion between the methyl hydrogens and the methine hydrogen [at C(2)].

The crystal packing is rather unusual for this type of complex. The Ni atoms occupying the inversion centers are separated by a lattice repeat of only 4.0633 (5) \AA , which is the shortest reported Ni—Ni contact for this kind of compound. A similar way of 'stacking' of the planar molecules with much longer lattice repeat of 8.04 \AA was found in $[(\text{CH}_3)_4\text{N}]_2[\text{Ni}(\text{MNT})_2]$ (Eissenberg & Ibers, 1965).

The structure does not have any remarkably short intermolecular contacts. The shortest intermolecular distance is between two centrosymmetrically related thiomethyl sulfurs (3.6 \AA), which is exactly the sum of the van der Waals radii for sulfur; contrary to the trimeric $\text{Ni}(\text{acac})_2$ (Bullen, Mason & Pauling, 1965) and as previously found in $\text{Ni}(\text{sacsac})_2$ (Beckett & Hoskins, 1974), this structure is composed of the monomeric molecules.

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Structure of Sodium 4-Carbamoyl-5,5-dimethyl-5H-1,2-oxaphosphole 2,2-Dioxide Tetrahydrate

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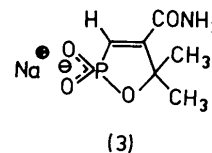
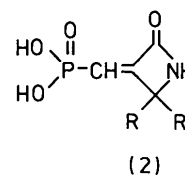
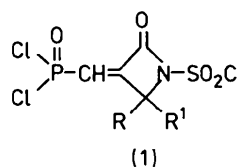
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Abstract. $\text{Na}^+ \cdot \text{C}_6\text{H}_9\text{NO}_4\text{P}^- \cdot 4\text{H}_2\text{O}$, $M_r = 285.17$, triclinic, $P\bar{1}$, $a = 6.019$ (1), $b = 6.676$ (1), $c = 16.650$ (2) Å, $\alpha = 83.88$ (1), $\beta = 86.55$ (1), $\gamma = 74.80$ (1)°, $V = 641.6$ (2) Å³, $Z = 2$, $D_x = 1.476$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.710793$ Å, $\mu = 2.66$ cm⁻¹, $F(000) = 300$, $T = 293$ K, $R = 0.028$ for 2490 observed reflections with $I > 3\sigma(I)$. The oxaphosphole anions are linked *via* hydrogen bonds to positively charged zigzag chains of edge-shared $\text{Na}(\text{H}_2\text{O})_6$ octahedra extending along the a axis. The distorted tetrahedral PO_3C group has essentially equal *exo* P—O bond lengths [1.497 (1) and 1.498 (1) Å], the *endo* P—O and P—C being 1.607 (1) and 1.773 (1) Å respectively. The carboxamide fragment is tilted from the plane of the five-membered oxaphosphole ring by 34.7°.

Introduction. The synthesis of 4,4-dialkyl-1-chlorosulfonyl-3-dichlorophosphonylmethylene-2-azetidinones (1), which appear to be stable only in inert organic solvents, has recently been reported (Mondeshka, Parashikov & Angelov, 1987). On treating (1) with $\text{NaOH}/\text{H}_2\text{O}$ by known methods (Graf, 1963; Durst & O'Sullivan, 1970), aiming to obtain the more stable 4,4-dialkyl-3-dihydroxyphosphonylmethylene-2-azetidinones (2), crystalline substances were formed for which structures could not be unambiguously established by the known spectral methods: IR, MS and ¹H, ¹³C and ³¹P NMR. In the present paper we report the structure of the title

compound (3) which was unexpectedly obtained instead of the corresponding derivative of (2). The details of the synthesis of (3) together with spectral and analytical data will be published elsewhere (Mondeshka, Parashikov & Angelov, 1990).



Experimental. A transparent well formed crystal obtained from methanol with approximate dimensions 0.1 × 0.02 × 0.02 mm was investigated. D_m not determined. Enraf–Nonius CAD-4 diffractometer (graphite monochromator, Mo $K\alpha$ radiation); ω - 2θ scan; speed 2 to 10° min⁻¹, width = [1.2 + 0.40 tan(θ)]°. Cell constants by least squares for 25 reflections with $20.0 < \theta < 22.0^\circ$. 6165 reflections measured with $(\sin \theta)/\lambda < 0.660$ Å⁻¹ ($h: -7$ to $7, k: -8$ to $8, l: -21$ to 21). Three standard reflections monitored every 4.0 h, intensity variation < 0.1%. No