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Structure of Bis(2,3-dimercapto-6,7-dihydro-5*H*-1,4-dithiepin)nickel(IV) at 295 and 109 K

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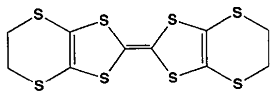
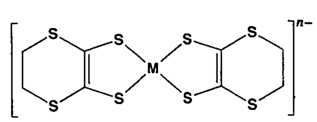
Abstract. $C_{10}H_{12}NiS_8$, $M_r = 447{\cdot}4$, orthorhombic, $Iba2$, $T = 295\ (109)$ K, $a = 13{\cdot}058\ (5)\ [13{\cdot}027\ (3)]$, $b = 16{\cdot}153\ (9)\ [16{\cdot}042\ (6)]$, $c = 7{\cdot}585\ (4)\ [7{\cdot}486\ (2)]$ Å, $V = 1600\ (1)\ [1564{\cdot}5\ (8)]$ Å^3, $Z = 4$, $D_x = 1{\cdot}857$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}20$ mm^{-1}, $F(000) = 912$, final $R = 0{\cdot}036\ (0{\cdot}029)$ for 940 (1355) independent observed reflections with $F_o > 2\sigma(F_o)$. The molecules, which are analogues of the organic donor molecule 3,4;3′,4′-bis(propylenedithio)-2,2′,5,5′-tetrathiafulvalene (BPDT-TTF), contain a markedly nonplanar central NiS_4 entity, as compared with the derivative containing six-membered end-group rings, $Ni(C_4H_4S_4)_2$. The structural changes between the two temperatures are very small.

Introduction. Metal complexes with conjugated dithiolate ligands have been examined extensively in the search for new conducting materials, resulting in the discovery of at least three such superconducting salts: $(TTF)[Ni(dmit)_2]_2$ with transition temperature, $T_c = 1{\cdot}6$ K (under 700 MPa applied pressure; Brossard, Ribault, Bousseau, Valade & Cassoux, 1986); $[(CH_3)_4N][Ni(dmit)_2]_2$ (TTF = tetrathiafulvalenium cation; dmit = 4,5-dimercapto-1,3-dithiole-2-thione), $T_c = 5{\cdot}0$ K at 700 MPa (Kobayashi, Kim, Sasaki, Kato, Kobayashi, Moriyama, Nishio, Kajita & Sasaki, 1987) and the virtually indistinguishable α- and α'-phases of $(TTF)[Pd(dmit)_2]_2$, $T_c = 1{\cdot}2$ K (19×10^8 Pa) and 5·9 K (24×10^8 Pa), respectively (Brossard, Ribault, Valade & Cassoux, 1989). Complexes of the donor molecule 2,3-dimercapto-5,6-dihydro-1,4-dithiin (dddt) have also been studied because of their close structural analogy with the organic donor molecule 3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene (BEDT-TTF, also known as ET), which has yielded most of the organic superconductors known to date (for a review, see Williams, Wang, Emge, Geiser, Beno, Leung, Carlson, Thorn, Schultz & Whangbo, 1987). Apart from some Cu, Co (Welch, Bereman, Singh & Moreland, 1989) and Au complexes (Schultz, Wang, Soderholm, Sifter, Williams, Bechgaard & Whangbo, 1987; Geiser, Schultz, Wang, Beno & Williams, 1988), most dddt-containing compounds have been nickel salts. The neutral complex (Kim, Kobayashi, Sasaki, Kato & Kobayashi, 1988), as well as the tetraethylammonium (Vance, Bereman, Bordner, Hatfield & Helms, 1985), tetrabutylammonium (phase 1: Schultz *et al.*, 1987; phase 2: Welch, Bereman & Singh, 1988), and tetramethylammonium (Welch, Bereman, Singh, Haase, Hatfield & Kirk, 1989) salts of the monovalent anion, containing formally Ni^{3+}, have been characterized. As in the case of BEDT-TTF, we have begun to modify the alkylenedithio end-groups of the ligand in order to increase the ring size, and thus slightly change the packing arrangement of the complex in the solid state. The title compound is the first homologue of $Ni(dddt)_2$ with a 1,3-propylenedithio end-group, thus containing seven-membered outer rings, by analogy to the donor molecule 3,4;3′,4′-bis(propylenedithio)-2,2′,5,5′-tetrathiafulvalene, BPDT-TTF or PT, whose structure we have reported (Porter, Kini & Williams, 1987). The structure of the tetrabutylammonium salt of the monovalent anion is being reported separately (Porter, Wang, Kini, Geiser & Williams, 1991).



BEDT-TTF



$M(dddt)_2^{n-}$

Experimental. Black, rhombic prismatic rod-shaped (forms {110} and {001}) crystals of $Ni(C_5H_6S_4)_2$ were prepared from the reaction of $[N(n\text{-}C_4H_9)_4]$-$Ni(C_5H_6S_4)_2$ (Porter *et al.*, 1991) with a mild oxidant, such as $(TTF)_3(BF_4)_2$ or $[N(n\text{-}C_4H_9)_4]I_3$ in acetonitrile and subsequent recrystallization from 1,1,2-trichloroethane. Crystals can also be grown by the electrochemical oxidation of $[N(n\text{-}C_4H_9)_4]$-

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$Ni(C_5H_6S_4)_2$ in tetrahydrofuran and $[N(n\text{-}C_4H_9)_4]BF_4$ as a supporting electrolyte at a current density of 2·5 μA cm^{-2}. The neutral $Ni(C_5H_6S_4)_2$ is the only product from any of these reactions, indicating great stability of the compound. One crystal (0·07 × 0·08 × 0·44 mm) mounted on Syntex $P2_1$ four-circle diffractometer equipped with nitrogen gas flow cooling system. Lattice parameters from 25 centered reflections, $20 < 2\theta < 30°$. $\theta/2\theta$ scan data, width from 1·0° below 2θ (α_1) to 1·2° above 2θ (α_2), 2–12° min^{-1} for both temperatures. Room-temperature data (in the following, numbers in parentheses refer to the corresponding 109 K values), $2\theta < 55\ (63)°$, $(\sin\theta)/\lambda < 0{\cdot}650\ (0{\cdot}735)$ Å^{-1}, h: 0 to 16 (19), k: −20 (−23) to 20 (23), l: 0 to 9 (11). 2378 (3005) reflections collected (three standards: 002, 112, $\bar{2}\bar{2}2$; less than 5% random intensity variation); all reflections collected (as a check of I-centering; no violations found) with $2\theta < 25°$ (room-temperature data only), but only those with $h + k + l = 2n$ for remainder; 2074 (2915) duplicates averaged, $R_{\rm int}(F) = 0{\cdot}034\ (0{\cdot}023)$; 993 (1407) unique and allowed by space group; 940 (1355) observed with $F_o > 2\sigma(F_o)$; corrected for Lorentz–polarization and absorption [Gaussian integration; min., max. transmission factors 0·808 (0·798)–0·859 (0·859)]. Computer programs supplied by Strouse (1985), scattering factors (including anomalous-dispersion contributions) from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Room-temperature structure solved by direct-methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and completed by Fourier methods. The refined room-temperature structure was the starting point of the refinement of the 109 K data. Full-matrix least-squares refinement of 87 variable parameters, based on $|F_o|$. All non-H atoms refined with anisotropic thermal parameters. H atoms located on difference map and included at calculated positions with $U_{\rm iso} = 0{\cdot}0633\ (0{\cdot}0380)$ Å^2. $(\Delta/\sigma)_{\rm max} = 0{\cdot}02$ in final cycle, with $R = 0{\cdot}036\ (0{\cdot}029)$, $wR = 0{\cdot}033\ (0{\cdot}030)$, $S = 1{\cdot}69\ (1{\cdot}60)$. $w = 1/\sigma^2(F_o)$ and $\sigma(F_o) = [\sigma^2(F_o^2) + (0{\cdot}02F_o^2)^2]^{1/2}/(2F_o)$, with $\sigma(F_o^2)$ based on counting statistics. Largest peaks [+0·5 (0·7) and −0·2 (−0·2) e Å^{-3}] on difference Fourier map in the vicinity of the Ni atom. Small correction for extinction (Larson, 1967): 0·536 (2) × 10^{-6} [0·253 (1) × 10^{-6}]. Final atomic positions and isotropic thermal parameters are given in Table 1.* Relevant geometrical results are listed in Table 2, a drawing of the $Ni(C_5H_6S_4)_2$ molecule is shown in Fig. 1, and a unit-cell packing diagram is depicted in Fig. 2.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^4) *in* $Ni(C_5H_6S_4)_2$ (*first line* 295; *second line* 109 K)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ni	0·0000	0·0000	0·0000	384 (3)
	0·0000	0·0000	0·0000	162 (1)
S1	0·05083 (8)	−0·12482 (7)	0·0053 (3)	430 (4)
	0·05121 (5)	−0·12566 (4)	0·0051 (2)	178 (2)
S2	0·15423 (8)	0·04334 (7)	0·0246 (3)	418 (4)
	0·15455 (5)	0·04403 (5)	0·0249 (2)	178 (2)
S3	0·23412 (9)	−0·22042 (7)	0·0434 (3)	433 (5)
	0·23525 (6)	−0·22181 (5)	0·04578 (15)	173 (2)
S4	0·35677 (10)	−0·02186 (8)	0·0947 (3)	442 (4)
	0·35823 (6)	−0·02140 (5)	0·0968 (2)	182 (2)
C1	0·1798 (3)	−0·1206 (3)	0·0356 (8)	331 (14)
	0·1811 (2)	−0·1216 (2)	0·0358 (5)	149 (8)
C2	0·2274 (3)	−0·0440 (3)	0·0500 (8)	345 (16)
	0·2286 (2)	−0·0436 (2)	0·0514 (5)	155 (8)
C3	0·3652 (4)	−0·2056 (3)	−0·0272 (8)	443 (19)
	0·3666 (3)	−0·2063 (2)	−0·0279 (5)	179 (9)
C4	0·4376 (4)	−0·1830 (3)	0·1233 (9)	443 (19)
	0·4391 (3)	−0·1835 (2)	0·1252 (5)	189 (9)
C5	0·3987 (4)	−0·1089 (3)	0·2290 (8)	386 (17)
	0·4000 (2)	−0·1090 (2)	0·2342 (5)	165 (8)

Table 2. *Interatomic distances* (Å) *and angles* (°) *in* $Ni(C_5H_6S_4)_2$ *at* 295 (*first line*) *and* 109 K (*second line*)

Ni—S1	2·123 (2)	S4—C2	1·759 (5)
	2·1237 (10)		1·759 (3)
Ni—S2	2·140 (1)	S4—C5	1·820 (5)
	2·1418 (8)		1·825 (3)
S1—C1	1·701 (4)	C1—C2	1·389 (6)
	1·709 (3)		1·401 (4)
S2—C2	1·715 (5)	C3—C4	1·526 (8)
	1·717 (3)		1·529 (5)
S3—C1	1·763 (5)	C4—C5	1·528 (7)
	1·756 (3)		1·534 (5)
S3—C3	1·810 (5)		
	1·815 (3)		
S1—Ni—S1$^{\rm i}$	177·84 (13)	C2—C1—S1	119·3 (3)
	177·92 (7)		118·8 (2)
S1—Ni—S2	90·85 (5)	C2—C1—S3	129·2 (3)
	90·93 (3)		129·5 (2)
S1—Ni—S2$^{\rm i}$	88·96 (5)	S1—C1—S3	111·4 (3)
	88·89 (3)		111·6 (2)
S2—Ni—S2$^{\rm i}$	169·98 (13)	C1—C2—S2	118·3 (3)
	170·03 (7)		118·3 (2)
C1—S1—Ni	105·9 (2)	C1—C2—S4	128·7 (3)
	106·12 (11)		128·4 (2)
C2—S2—Ni	105·4 (2)	S2—C2—S4	112·9 (3)
	105·56 (11)		113·3 (2)
C1—S3—C3	104·4 (2)	C4—C3—S3	113·4 (4)
	103·90 (15)		112·8 (2)
C2—S4—C5	103·9 (2)	C3—C4—C5	111·9 (4)
	103·85 (15)		112·4 (3)
		C4—C5—S4	114·3 (4)
			113·5 (2)

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

Discussion. The unit cell contains loosely packed stacks of $Ni(C_5H_6S_4)_2$ molecules along the polar c axis. The non-centrosymmetric packing is due to the non-planarity of the complex molecules which are

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53765 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

located on a twofold rotation axis (parallel to the stacking direction). The seven-membered rings are in an unusual conformation, compared to those found in the organic donor molecule BPDT-TTF in both the neutral (Porter, Kini & Williams, 1987) and charged (Geiser, Wang, Schlueter, Chen, Kini, Kao, Williams, Whangbo & Evain, 1988) state. In BPDT-TTF, the three propylene group C atoms are found in a plane parallel to, but displaced by *ca* 0·8 Å from the plane through the conjugated portion of the molecule ('extended chair' conformation). In the nickel complex, on the other hand, the middle C atom is located approximately in the molecular plane through the ligand atoms, whereas the S-bound C atoms of the propylene group are found on opposite sides of the plane ('twist' conformation, see Fig. 1).

The bond lengths in $Ni(C_5H_6S_4)_2$ are in their expected range. The influence of the charge state of the complex on the Ni—S bond lengths in nickel dithiolate complexes is quite small [2·12–2·13 Å for neutral complexes, 2·13–2·15 Å for monovalent anions, as observed in the above-mentioned $Ni(dddt)_2$ salts; reported e.s.d.'s: 0·002–0·012 Å], in agreement with the suggestion (Schultz *et al.*, 1987) that the extra electron is delocalized primarily over the ligand molecules. In contrast to all the $Ni(dddt)_2$ complexes studied to date, in neutral $Ni(C_5H_6S_4)_2$ the central NiS_4 moiety is noticeably non-planar, with one of the *trans*-S—Ni—S angles being only 170°. The source of this non-planarity is unclear, but it may be related to the unusual conformation of the seven-membered ring.

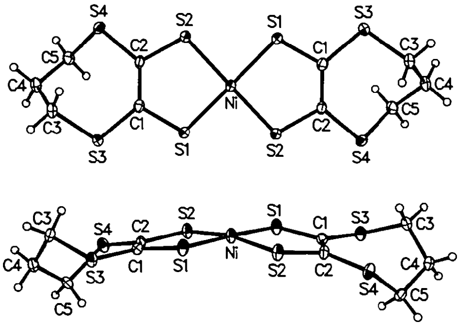

Fig. 1. Top and side views of the $Ni(C_5H_6S_4)_2$ molecule, indicating the atomic numbering scheme used. All atoms (except H) are drawn with 50% probability ellipsoids determined at 109 K.

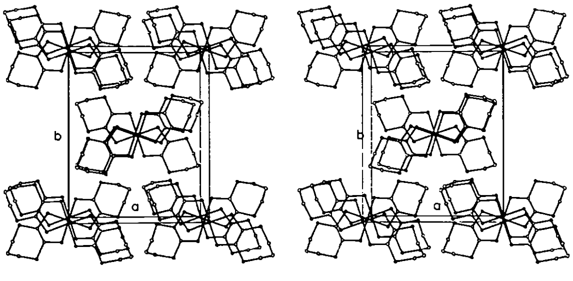

Fig. 2. Unit-cell packing stereo diagram of $Ni(C_5H_6S_4)_2$. H atoms are omitted for clarity.

The changes in the structure, and in particular in the molecular geometry due to cooling, are very small. From the change in unit-cell volume, the thermal expansion coefficient between 109 K and room temperature is estimated to be $\Delta V/(V\Delta T) = 1{\cdot}2 \times 10^{-4}\ K^{-1}$. The intermolecular distances, which are all longer than the sums of the van der Waals radii, are slightly reduced at 109 K. The increase in the data:variables ratio (data collected to higher scattering angle) and the effects of reduced thermal motion at the lower temperature reduce the estimated standard deviations derived from the least-squares refinement.

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Structure of (2,2′-Bipyridine)bis(difluorophosphinato)copper(II), (bpy)Cu(PF_2O_2)$_2$

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Abstract. [Cu($C_{10}H_8N_2$)(PF_2O_2)$_2$], $M_r = 421{\cdot}7$, monoclinic, $C2/c$, $a = 17{\cdot}706\,(4)$, $b = 10{\cdot}465\,(3)$, $c = 7{\cdot}632\,(2)$ Å, $\beta = 90{\cdot}99\,(2)°$, $V = 1414$ Å^3, $Z = 4$, $D_x = 1{\cdot}981$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 18{\cdot}6$ cm^{-1}, $F(000) = 836$, $T = 213$ K, $R = 0{\cdot}030$ for 858 observed data with $I > 3\sigma(I)$. Crystals of (bpy)Cu(PF_2O_2)$_2$ (bpy = 2,2′-bipyridine) form in the decomposition of [Cu_2(bpy)$_2$(phenylacetylene)][PF_6]$_2$ in wet 2-butanone–hexane solution. The arrangement of ligands about the Cu atom is that of a tetragonally distorted octahedron. There are two short Cu—O bonds in the plane of the bipyridine ligand and two long bonds to the Cu atom from O atoms in $PF_2O_2^-$ ligands in planar units above and below the plane containing the first Cu atom.

Introduction. In an attempt to grow crystallographic-quality crystals of the yellow copper(I) alkyne complex [Cu_2(bpy)$_2$(phenylacetylene)][PF_6]$_2$ (Reger & Huff, 1991) (bpy = 2,2′-bipyridine) by the vapor diffusion method, colorless crystals formed that appeared to be different from the starting material. We report here crystallographic characterization of these crystals as (bpy)Cu(PF_2O_2)$_2$, a molecule that has an interesting polymeric structure in the solid state.

Experimental. All operations were carried out under a nitrogen atmosphere either by standard Schlenk techniques or in a Vacuum Atmosphere HE-493 drybox. All solvents were dried, degassed, and distilled prior to use.

Colorless crystals of (bpy)Cu(PF_2O_2)$_2$ are reproducibly obtained as follows. [Cu_2(bpy)$_2$(phenylacetylene)][PF_6]$_2$ (Reger & Huff, 1990) in 2-butanone is placed in one side of a U-tube and hexane in the other. One drop of water from a microsyringe is added to the butanone side and the tube is sealed under vacuum after degassing by three freeze-pump-thaw sequences. After two or three days at 298 K, three types of crystals, colorless, orange and blue, form that can be separated by hand.

A transparent, prismatic crystal with dimensions 0·3 × 0·2 × 0·1 mm was mounted in a thin-walled capillary tube on a CAD-4 diffractometer with a graphite monochromator at 213 K. The unit cell was determined and refined from 25 general reflections ($8 < \theta < 12$) using the ω-scan technique. There were 1142 reflections measured in the 2θ range 4–46° ($0 \leq h \leq 19$, $0 \leq k \leq 11$, $-8 \leq l \leq 8$) with a crystal decay of less than 0·1% for 3 standard reflections. Absorption correction was by the method of Walker & Stuart (1983) with relative transmission factors: max. 1·378, min. 0·696, average 0·983. The structure was solved by the heavy-atom method and refined with use of *SDP-Plus* (Frenz, 1983). H atoms were placed in calculated positions and not refined. Full-matrix least-squares refinements (on F) were carried out with weights $w = [\sigma^2(F) + 0{\cdot}0004F^2]^{-1}$ for reflections with $I > 3\sigma(I)$. At the final stage: 109 variables, $R = 0{\cdot}030$, $wR = 0{\cdot}040$, $S = 1{\cdot}87$, $(\Delta/\sigma)_{\max} = 0{\cdot}04$, max. and min. peak heights in the final difference Fourier synthesis 0·39 and −0·21 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Table 1† shows atomic parameters for (bpy)Cu(PF_2O_2)$_2$.

Discussion. Crystals of (bpy)Cu(PF_2O_2)$_2$ (see below) are obtained from the solution decomposition of [Cu_2bpy$_2$(phenylacetylene)][PF_6]$_2$ in wet butanone.

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53729 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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