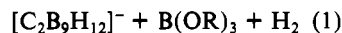
closo-2,4-C₂B₅H₇nido-2,4-C₂B₄H₇⁻**Figure 1.** Conversion of closo-2,4-C₂B₅H₇ to [nido-2,4-C₂B₄H₇]⁻.

¹¹B NMR spectrum after 12 days at room temperature exhibits the resonances of C₂B₅H₇⁶ (19%), [nido-2,4-C₂B₄H₇]⁻ (38%), and compound A (33%) (¹¹B NMR: δ(B(1)) -39.1 (area 1), J(BH) = 152 Hz; δ +7 (d, area 2); δ +21.3 (d, area 1); δ +48.4 (area 1)); the remainder of the boron resonances in the NMR spectrum could not be assigned but were present as small peaks in the regions of δ +27 (broad), +29 (d), and +12. A monitoring of the ¹¹B NMR spectra over the next 3 months revealed a gradual disappearance of both C₂B₅H₇ and compound A coupled with a buildup of [2,4-C₂B₄H₇]⁻.

(c) With Li[N(CH(CH₃)₂)₂]. In a manner similar to that described in section a, Li[N(CH(CH₃)₂)₂] (Aldrich, 0.23 mmol), closo-2,4-C₂B₅H₇ (0.15 mmol), and CH₃CN (1.5 mmol) were mixed. The sample slowly turned to a clear yellow-orange liquid, with no solids present. After the sample was kept at room temperature for 4.5 h, a ¹¹B NMR spectrum indicated the presence of (a) [nido-2,4-C₂B₄H₇]⁻ (40%) (¹¹B NMR: δ(B(1)) -52.5, J(BH) = 157 Hz; δ(B(3)) +20.9, J(BH) = 121 Hz; δ(B(5,6)) +0.8, J(BH) = 125 Hz),^{1,2} (b) starting material, closo-2,4-C₂B₅H₇⁶ (51%), compound A (4%) (¹¹B NMR: δ -39.5 (d), J = 154 Hz; δ +7 (d); δ +21 (d); δ +47 (d, broad)), and an assortment of small resonances (accounting for ca. 4% of total boron) appearing in the regions of δ +27 (broad), +12, -5 to -20, -47, and -54. After 26 h at room temperature the percentages of each compound were as follows: C₂B₅H₇, 37%; [2,4-C₂B₄H₇]⁻, 54%; compound A, 3%; an assortment of small resonances (accounting for ca. 5% of total boron) appearing in the regions of δ +27 (broad), +11, -5 to -20, and -47 (d). After 16 days at room temperature the major change observed in the ¹¹B spectrum was that the ratio [2,4-C₂B₄H₇]⁻:C₂B₅H₇ had increased to 2.3.

Discussion

It is well-known that alkoxide/alcohol mixtures can convert isomers of closo-C₂B₁₀H₁₂ to isomers of the [nido-C₂B₉H₁₂]⁻ ion according to eq 1.⁷⁻¹² Unfortunately, all attempts to use alk-closo-C₂B₁₀H₁₂ + RO⁻ + 2ROH →



oxide/alcohol mixtures for the C₂B₅H₇ → [C₂B₄H₇]⁻ conversion were unsuccessful,¹³ and only cage decomposition products of the type experienced when ROH alone was utilized as the reagent¹⁴ were generally observed (e.g. B(OR)₃, CH₃B(OR)₂, (RO)₂BCH₂B(OR)₂).

The conversion of closo-2,4-C₂B₅H₇ to [nido-2,4-C₂B₄H₇]⁻ (Figure 1) can be accomplished, however, with the use of Li[N(R)₂], R = CH₃, C₂H₅, CH(CH₃)₂, as the reagent and acetonitrile as the solvent. The stoichiometry for the reaction appears to be somewhat greater than 1:1 Li[N(R)₂]:C₂B₅H₇. The conversion of closo-2,4-C₂B₅H₇ to [nido-2,4-C₂B₄H₇]⁻ is nearly quantitative at room temperature, but during the course of the reaction at least two intermediates are seen in the ¹¹B NMR spectrum. Neither of these two intermediates is normally found in high percentage at any time during the reaction. Both of these intermediates

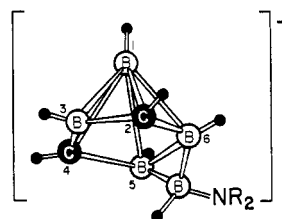
**Figure 2.** Plausible structure for compound A, [(μ^{5,6}-R₂NBH)-nido-2,4-C₂B₄H₆]⁻.

exhibit a high-field doublet in the region of δ -45 to -50, very reminiscent of an apical boron for open-face pyramidal systems.⁶ In one of these intermediates (arbitrarily called compound A in the Experimental Section) two sets of ¹¹B NMR BH doublets in a ratio of 2:1 are seen in the midfield region expected for the basal-situated borons of such a pyramid; a somewhat broadened boron resonance, which sharpens to a measurable extent upon proton decoupling, is observed downfield in a region that is consistent with a "non"-cage boron but one that could well be attached, in a bridging environment,¹⁵ to two atoms of the pentagonal base (e.g. borons 5 and 6). A definitive structure cannot be assigned at this time, but it is highly possible that compound A is [(μ^{5,6}-R₂NBH)-nido-2,4-C₂B₄H₆]⁻, displayed in Figure 2. The structure of the other intermediate, never present in quantities greater than for compound A, is more difficult to assess, but from the appearance of a high-field BH doublet, assignable to a boron in an apical environment of a pyramidal-shaped compound (see above), it could well represent further progress of the reaction to eventually give [nido-2,4-C₂B₄H₇]⁻.

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Registry No. A (R = CH₃), 116303-14-1; A (R = C₂H₅), 116303-15-2; A (R = CH(CH₃)₂), 116303-16-3; closo-2,4-C₂B₅H₇, 20693-69-0; [nido-2,4-C₂B₄H₇]⁻, 39394-97-3; Li[N(CH₃)₂], 3585-33-9; Li[N(C₂H₅)₂], 816-43-3; Li[N(CH(CH₃)₂)₂], 4111-54-0.

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Comments on the Crystal Structure of Tetrabutylammonium Bis(5,6-dihydro-1,4-dithiin-2,3-dithiolato)nickelate(III)

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There has been considerable interest in transition-metal complexes of dithiolenes and dithiolates, which promise to add to our knowledge of low-dimensional highly conducting materials.¹⁻⁸ We, for example, have reported the synthesis of a new 1,2-dithiolene, 5,6-dihydro-1,4-dithiin-2,3-dithiolate, which when reacted with Ni(II) salts yields a complex whose structure is remarkably similar to BEDT-TTF in the rhenate salt.⁹ We had undertaken a study of the effects of cations on the intermolecular contacts

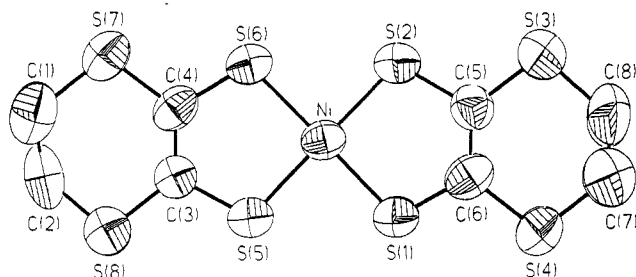
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Table I. X-ray Crystallographic Parameters^a

cell dimens	$a = 15.446 (3) \text{ \AA}$ $b = 12.559 (4) \text{ \AA}$ $c = 17.093 (5) \text{ \AA}$ $\beta = 98.29 (2)^\circ$
vol	$3281 (1) \text{ \AA}^3$
molecules/unit cell	4
2θ range	$3-45^\circ$
scan type	$\theta-2\theta$
no. of unique reflns with $I > 2\sigma(I)$	2089
no. of parameters	320
final R index	$R = 0.067$ $R_w = 0.079$
goodness of fit	1.48

^aThe data fit criteria (based on reflections having $I > 2\sigma(I)$) were $R = \sum ||F_o| - |F_c|| / \sum F_o$, $R_w = [\sum w(\Delta F)^2 / \sum F_o^2]^{0.5}$, and $\text{GOF} = \sum (w - ||F_o| - |F_c||)^2 / N_o - N_r)^{0.5}$.

**Figure 1.** Structure of the monoanion $[\text{Ni}(\text{DDDT})_2]^-$. Thermal ellipsoids are drawn at the 50% probability level.

in the nickel and copper complexes of this ligand¹⁰ and were, therefore, quite interested in the article by Williams et al. reporting the crystal structure of the tetrabutylammonium salt of the $\text{Ni}(\text{DDDT})_2^-$ anion.¹¹ We were also working on this structure, but the report of the triclinic space group $P\bar{1}$ did not agree with our data. We had obtained a monoclinic space group $P2_1/c$ but had not refined our structure to an acceptable level at that time. We assumed these were identical materials and first attempted to transform the $P\bar{1}$ unit cell into the $P2_1/c$, but this proved unsuccessful.¹² We then recrystallized the material from the same solvents and under the same conditions reported by Williams et al. to determine if we could obtain a different crystalline form. This, surprisingly, gave us our original crystalline material in the $P2_1/c$ space group. Since we have been unable to duplicate the reported crystalline material, we are reporting here the brief structural features and magnetic properties of an apparently alternative structure.

Experimental Section

Green needles of $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Ni}(\text{DDDT})_2]$ were synthesized by the same procedure⁹ used to prepare the tetraethylammonium salt with the

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	U^a
Ni	7003 (1)	6187 (1)	1751 (1)	73 (1)
S(1)	7140 (2)	4668 (2)	2318 (2)	101 (1)
S(2)	8368 (2)	6212 (2)	1634 (2)	95 (1)
S(3)	9918 (2)	4923 (3)	2143 (3)	148 (2)
S(4)	8524 (2)	3212 (3)	2950 (3)	137 (2)
S(5)	5660 (2)	6180 (2)	1937 (2)	94 (1)
S(6)	6843 (2)	7714 (2)	1198 (2)	85 (1)
S(7)	5474 (2)	9290 (3)	810 (2)	118 (2)
S(8)	4126 (2)	7539 (3)	1646 (2)	107 (1)
C(1)	4414 (7)	9575 (9)	1141 (7)	123 (6)
C(2)	3810 (7)	8632 (9)	1010 (7)	122 (6)
C(3)	5223 (6)	7360 (7)	1550 (5)	73 (4)
C(4)	5763 (7)	8047 (7)	1226 (5)	80 (4)
C(5)	8796 (6)	5051 (8)	2108 (6)	85 (4)
C(6)	8220 (7)	4382 (8)	2409 (6)	91 (5)
C(7)	9655 (11)	3152 (15)	3018 (13)	210 (12)
C(8)	10121 (11)	3663 (16)	2624 (14)	244 (14)
N	2758 (5)	4115 (7)	1200 (5)	85 (4)
C(9)	2482 (11)	4963 (13)	627 (7)	202 (10)
C(10)	1852 (11)	5633 (12)	477 (8)	177 (9)
C(11)	1649 (10)	6473 (13)	-86 (9)	174 (9)
C(12)	835 (11)	6972 (17)	-197 (11)	245 (12)
C(13)	2552 (15)	4480 (13)	1936 (7)	317 (16)
C(14)	2568 (9)	5203 (10)	2493 (7)	146 (7)
C(15)	2377 (14)	5593 (14)	3143 (8)	246 (13)
C(16)	2421 (13)	6124 (13)	3704 (9)	239 (12)
C(17)	3648 (9)	3911 (12)	1166 (14)	265 (15)
C(18)	4232 (10)	3590 (14)	944 (11)	199 (11)
C(19)	5065 (12)	3336 (19)	957 (15)	236 (15)
C(20)	5699 (14)	3296 (20)	625 (11)	259 (16)
C(21)	2264 (10)	3141 (14)	930 (14)	240 (14)
C(22)	2183 (15)	2168 (13)	992 (13)	247 (15)
C(23)	1667 (15)	1344 (12)	763 (12)	288 (14)
C(24)	1219 (16)	840 (19)	401 (12)	338 (19)

^aEquivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Sulfur-Sulfur Contacts

A	B	dist, \AA	symmetry of B
S(3)	S(4)	4.78	$2 - x, 0.5 + y, 0.5 - z$
S(7)	S(7)	3.43	$1 - x, 2 - y, -z$
S(8)	S(1)	3.88	$1 - x, 0.5 + y, 0.5 - z$
S(8)	S(4)	4.33	$1 - x, 0.5 + y, 0.5 - z$

substitution of tetrabutylammonium iodide for tetraethylammonium bromide. The salt was recrystallized from two different solvent systems, acetonitrile and dichloromethane/ethyl ether, and both yielded identical materials, as determined by crystallography.

A data set was collected on a Nicolet R3m/ μ diffractometer equipped with a graphite monochromator and molybdenum radiation ($\lambda = 0.71069$). Systematic absences indicated the monoclinic space group $P2_1/c$. Pertinent X-ray crystallographic parameters are summarized in Table I. Data were not corrected for absorption due to the low absorption coefficient (11.0 cm^{-1}). The structure was solved by direct methods and refined by the block-diagonal least-squares technique using SHELXTL.¹³ All non-hydrogen atoms were refined with anisotropic temperature factors. A thermal ellipsoid drawing of the anion is shown in Figure 1; atomic coordinates are given in Table II. Bond lengths, bond angles, hydrogen coordinates, anisotropic temperature factors, and calculated and observed structure factors are available as supplementary material.

Magnetic susceptibility data were collected with a Princeton Applied Research Model 155 vibrating-sample magnetometer (VSM) that was operated at 10 kOe by using procedures described previously and was calibrated with $\text{HgCo}(\text{NCS})_4$.^{14,15} Powdered samples of the calibrant and compound, approximately 150 mg of each, were contained in precision-milled Lucite sample holders. Diamagnetic corrections for the

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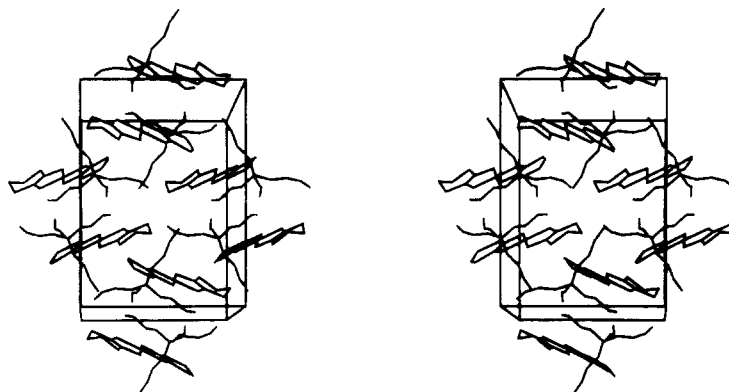


Figure 2. Stereoview of the molecular packing for $[(C_4H_9)_4N][Ni(DDDT)_2]$.

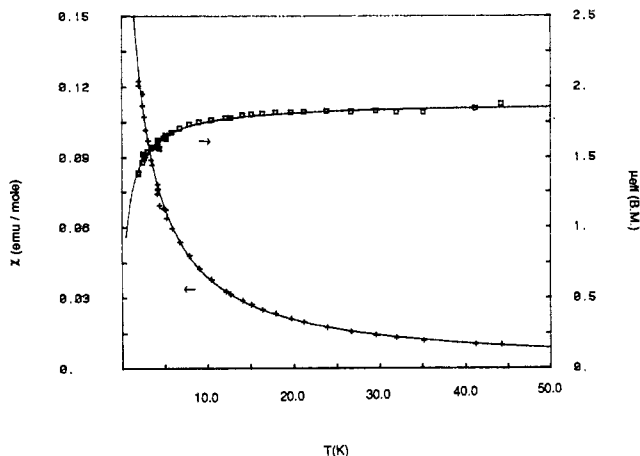


Figure 3. Magnetic susceptibility and magnetic moment of $[(C_4H_9)_4N][Ni(DDDT)_2]$. The solid lines are fit lines to the Curie-Weiss law, $\chi_m = Ng^2\beta^2S(S + 1)/3k(T - \theta)$, with $g = 2.18$ and $\theta = -1.54$ K.

constituent atoms were made by using Pascal's constants, and corrections for temperature-independent paramagnetism were estimated from tabulated data.¹⁶⁻¹⁸

Results and Discussion

The bond lengths and angles of the $Ni(DDDT)_2^-$ anions are essentially the same as those in the two previously published structures.^{9,11} The difference in the two tetrabutylammonium structures is clearly seen by comparing the packing diagrams. The earlier published structure¹¹ indicates two different types of molecules, ones that form stacks aligned along the a axis and ones that lie almost perpendicular to these stacks. The stereoview of the unit cell packing of the monoclinic form (Figure 2) reveals association of the anions into pairs, similar to the structures of $Au(DDDT)_2$ and $BEDT-TTF$.^{11,19}

The major difference between the pairs of $Ni(DDDT)_2^-$ anions and pairs of the two neutral complexes is the separation distance. While S...S contacts within a pair are less than 3.70 Å for $Au(DDDT)_2$ and $BEDT-TTF$, the shortest S...S contact in $Ni(DDDT)_2^-$ pairs is 7.32 Å. The Ni...Ni distance is 8.49 Å. This large separation can be attributed to the presence of the alkyl chains of the tetrabutylammonium cations between anions. Although distances within a pair are quite large, contacts between pairs are comparable to those of the neutral structures. Table III contains the contacts less than 5.00 Å.

Magnetic results are displayed in Figure 3. The magnetic susceptibility as a function of temperature is a smooth curve

indicating simple paramagnetic behavior. However, the room-temperature magnetic moment ($1.9 \mu_B$) decreases slowly with temperature to 10 K and drops significantly to $1.4 \mu_B$ at 1.9 K, indicative of antiferromagnetic interactions. These interactions are weak at best and most likely correspond to interactions between anions in different pairs where the closest contacts exist between sulfur atoms. Although the S...S contacts in this tetrabutylammonium structure are comparable to those of the tetraethylammonium structure, the long-range magnetic ordering observed in the latter solid is probably the result of its layered structure.^{9,20-22} The shortest S...S contacts in our structure are less than those reported for the triclinic structure, and this is reflected in the weak interactions observed in the magnetic moment data.¹¹

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Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates (3 pages); a listing of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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Electron Self-Exchange of Low-Spin Iron Octaethylporphyrin, Chlorin, and Isobacteriochlorin Complexes

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A perennial theme in metalloporphyrin chemistry is the effect of structure on properties and reactivity. The effects of changes in the axial ligands and porphyrin ring substituents and of such structural features as the geometry and coordination number of

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