a significantly nonplanar amido-N ligand (amide O1C1N1: τ = 17.3°, χ_N = 28.6°, χ_C = 2.9°).[12]

The purple complex [Ni(η^4-**1**)]$^-$ has a low affinity for axial ligands in solution at 20 °C. Neat MeCN, pyridine, acetone, 2,5-Me_2THF, THF, CH_2Cl_2, water, and EtOH all give purple solutions.[13] In contrast, addition of cyanide results in an immediate color change from purple to yellow;[14] mole ratio plots indicate a 1:1 adduct ($K_{20°C}$ = 3.2 (9) × 10^3 mol^{-1}). At 77 K, frozen solutions of [Ni(η^4-**1**)]$^-$ in water, MeCN, 2,5-Me_2THF, THF, CH_2Cl_2, or acetone remain purple, as do CH_2Cl_2 solutions containing Cl^-, Br^-, Ph_3P, or Et_3N. In contrast, when purple solutions of [Ni(η^4-**1**)]$^-$ in 2,5-Me_2THF containing any one of the potential ligands ethanol, pyridine, 2,6-lutidine, or Me_3P are cooled to 77 K, pale green (EtOH, pyridine) or yellow (other ligands) glasses are obtained. These observations coupled with the solid-state information suggest that the nickel(III) anion is purple when it is four-coordinate and pale green or yellow when it is higher coordinate.

EPR studies of this system further support this color/coordination number relationship. The 4 K EPR spectrum of [Bu_4N][Ni(η^4-**1**)] with excess CN^- is rhombic in a yellow frozen solution of CH_2Cl_2[15a] or a yellow EtOH glass.[15b] Use of $^{13}CN^-$ confirms that only one CN^- binds at 4 K.[15c] The 5 K spectrum of [Ni(η^4-**1**)]$^-$ in a yellow 2,5-Me_2THF/pyridine (2:1) glass is also rhombic and confirms that one pyridine is coordinated.[15d] While Margerum et al. have found that water coordinates weakly to nickel(III) complexes of tetradentate ligands containing two amido-N donors,[16] in glasses of 2,5-Me_2THF/CH_2Cl_2 or toluene/CH_2Cl_2 at 5 K, [Ni(η^4-**1**)]$^-$ remains purple, suggesting that axial coordination is not occurring.[17] The EPR spectra of these glasses have $g_\perp > g_\parallel$ (e.g., Figure 2). The structuring in $g_\perp$ may indicate slight rhombicity or the presence of frozen-out conformers which might contribute to the structuring in $g_\parallel$. Superhyperfine interactions are also a possible source of some of the structuring in $g_\parallel$. Saturation of the 2,5-Me_2THF/CH_2Cl_2 (1:1) or toluene/CH_2Cl_2 (2:1) aprotic solvent mixtures with $H_2{}^{16}O$ or $H_2{}^{17}O$ (45% enrichment) leads to EPR spectra that are virtually identical with those found in the glasses produced from the dried solvents. This evidence suggests that impurity water or solvent molecules are not axially bound to [Ni(η^4-**1**)]$^-$ in noncoordinating solvent glasses that are purple, i.e., that the EPR spectra of these purple glasses are predominantly of four-coordinate species.[18]

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Supplementary Material Available: Tables of data collection information, atom coordinates, Gaussian amplitudes, and bond lengths and angles, a listing of references to structural studies of four-coordinate nickel(III/II) complexes with noninnocent ligands where an integer oxidation state assignment is impractical, details of ligand synthesis, and EPR spectra (38 pages); listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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(13) Electronic spectra of [Ni(η^4-**1**)]$^-$ (values in parentheses are molar absorptivities in M^{-1} cm^{-1}): CH_2Cl_2, 380 nm (5.48 × 10^3), 532 nm (3.62 × 10^3), 650 nm (2.33 × 10^3), 808 nm (4.18 × 10^3); CH_3CN/CH_2Cl_2 (9:1), 380 nm (5.45 × 10^3), 530 nm (3.59 × 10^3), 650 nm (2.26 × 10^3), 806 nm (3.98 × 10^3); pyridine, 380 nm (4.76 × 10^3), 534 nm (3.10 × 10^3), 647 nm (1.90 × 10^3), 817 nm (3.30 × 10^3); EtOH, 376 nm (4.79 × 10^3), 525 nm (3.00 × 10^3), ≈660 nm (shoulder) (2 × 10^3), 794 nm (3.78 × 10^3); H_2O, 372 nm (2.7 × 10^3), 519 nm (1.7 × 10^3), 767 nm (2.4 × 10^3).

(14) The electronic spectrum of [Ni(η^4-**1**)]$^-$ with excess CN^- in CH_2Cl_2 is a featureless curve, tailing into the visible region from just above the UV cutoff of the solvent, and there is essentially zero absorbance above 450 nm.

(15) EPR spectra of [Ni(η^4-**1**)]$^-$ (4-6 K, 9.46 GHz): (a) excess [Bu_4N][CN] in CH_2Cl_2 (g_1, 2.234; g_2, 2.159; g_3, 2.019); (b) excess KCN in EtOH (g_1, 2.223; g_2, 2.144; g_3, 2.010); (c) excess $K^{13}CN$ in EtOH (g values same as in b; a_1, 89 G; a_2, 83 G; a_3, 100 G); (d) in 2,5-Me_2THF/pyridine (2:1) (g_1, 2.380; g_2, 2.269; g_3, 1.994; superhyperfine on g_3 only, a_3, 25 G).

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(17) All solvents, except 2,5-Me_2THF, Aldrich Sureseal (anhydrous); EPR tubes vacuum dried, charged and sealed under an inert atmosphere.

(18) It is of interest to note that the EPR spectrum of [Ni(η^4-**1**)]$^-$ at 4 K in 2,5-Me_2THF/2,6-lutidine (ca. 2:1) can be interpreted as resulting from a mixture of [Ni(η^4-**1**)]$^-$ and the five-coordinate complex of the sterically hindered 2,6-lutidine ligand (g_1 and g_2 obscured by g_1 and g_2 of [Ni(η^4-**1**)]$^-$; g_3, 1.997; superhyperfine on g_3 only, a_3, 25 G). The spectrum of [Ni(η^4-**1**)]$^-$ in an absolute ethanol glass at 6 K is markedly different from Figure 2, although several features may be interpreted as arising from residual amounts of four-coordinate [Ni(η^4-**1**)]$^-$ (see supplementary material).

Varacin: A Novel Benzopentathiepin from *Lissoclinum vareau* That Is Cytotoxic toward a Human Colon Tumor

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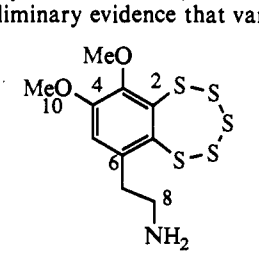
Ascidians of the genus *Lissoclinum* have been an exceptional source of interesting and often biologically active natural products. *Lissoclinum patella* has yielded cytotoxic cyclic peptides,[4] cytotoxic and antiviral polypropionate-derived macrocycles,[5] and a polyketide lactone.[6] *Lissoclinum vareau*, a lavender-colored encrusting species collected in the Fiji Islands, is the source of the recently reported bright red heteroaromatic pigments varamine A and varamine B.[7] We now report the benzopentathiepin varacin (**1**), a novel *L. vareau* metabolite that exhibits potent antifungal activity against *Candida albicans* (14-mm zone of inhibition of 2 μg of varacin/disk) and cytotoxicity toward the human colon cancer HCT 116 with an IC_{90} of 0.05 μg/mL, 100 times the activity of 5-fluorouracil (5-FU) in this assay. Varacin also exhibited a 1.5 differential toxicity toward the CHO cell line EM9 (chlorodeoxyuridine sensitive) versus BR1 (BCNU resistant), providing preliminary evidence that varacin damages DNA.



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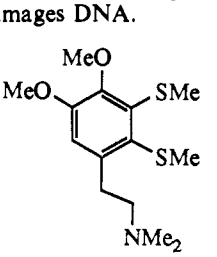

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Table I. ^1H and ^{13}C NMR Data for Varacin (1) and 2

	varacin (1)[a]		2[b]		
C	^{13}C[c]	^1H[d]	^{13}C[c]	^1H[d]	LR ^1H to ^{13}C corr
1	135.94		130.03		
2	141.89		138.21		
3	151.14		150.40		
4	156.54		154.40		
5	117.03	7.07 (s, 1 H)	115.54	7.48 (s, 1 H)	H_3, H_1, H_4 (wk)
6	140.13		137.26		
7	35.10	3.15 (m, 2 H)	29.70	3.57 (m, 2 H)	H_5, H_6
8	41.66	3.25 (m, 2 H)	67.07	3.86 (m, 2 H)	
9	62.15	3.80 (s, 3 H)	60.14	3.78 (s, 3 H)	H_3
10	56.88	3.94 (s, 3 H)	56.88	3.92 (s, 3 H)	H_4
C_1SMe			20.79	2.36 (s, 3 H)	H_1
C_2SMe			19.47	2.47 (s, 3 H)	H_2
NMe			53.50	3.51 (s, 6 H)	H_8

[a] Recorded in $CDCl_3$. [b] Recorded in acetone-d_6. [c] Recorded at 100 MHz. [d] Recorded at 400 MHz.

A MeOH extract of *L. vareau* obtained by soaking 55.7 g of homogenized, freeze-dried tissue was subjected to a solvent partition scheme giving 360 mg of $CHCl_3$-soluble material. Silica gel flash chromatography using a stepwise solvent gradient ($CHCl_3$ to MeOH) followed by reverse-phase HPLC (Rainin Dynamax C18, CH_3CN/0.1% aqueous TFA, 45:55) gave varacin (**1**)[8] as a light brown glass (40 mg, 0.07% yield).

A molecular formula of $C_{10}H_{13}NO_2S_5$ was suggested by the FAB mass spectrum of the *N*-trifluoroacetate (*N*-TFA) derivative, which displayed a prominent ion at m/z 435 (HREIMS 434.9378, Δ 0.5 mmu, calculated for $C_{12}H_{12}NO_3S_5F_3$). The ^{13}C NMR spectrum (Table I) showed 10 signals including six aromatic carbons, two arylmethoxy carbons, and two methylene carbons. The ^1H NMR spectrum (Table I) contained strongly coupled methylene signals centered at δ 3.15 and 3.25 for the methylenes of a phenethylamine side chain and a singlet at δ 7.07 for a lone proton of a pentasubstituted benzene. Difference NOE experiments indicated that the lone aromatic proton exhibited dipolar coupling to the methylene protons H_7 and Me_{10}, and the two O-methyls showed cross relaxation, consistent with structure **1**. To confirm these assignments, varacin was reduced with tri-*tert*-butoxyaluminum hydride in THF at room temperature, followed by a MeI quench to give derivative **2**.[9] Mass spectroscopy established a formula of $C_{12}H_{23}NO_2S_2$, indicating loss of three sulfur atoms and addition of four methyl groups. A dimethylamine terminus on the side chain was confirmed by a 25.41 ppm downfield shift of C_8 in the ^{13}C NMR spectrum, together with the observation of an intense m/z = 58 ion in the EIMS corresponding to $[(CH_3)_2NCH_2]^+$. The ^1H NMR spectrum also contained singlets at δ 2.36 and 2.47 for a pair of aryl SCH_3 groups.[10] A long-range HETCOR experiment (J = 8 Hz, Table I) allowed assignment of the four XCH_3 groups to their respective aromatic carbons by three-bond correlations from each methyl group to a single quaternary carbon. Additionally, aromatic proton H_5 exhibited three-bond coupling to C_1 and C_3, while methylene protons H_7 correlated to C_5 and C_6. Furthermore, irradiation of H_7 in a selective INAPT experiment resulted in signal enhancement for C_1, C_5, and C_6. These data combined with difference NOE results that indicated cross relaxation of H_5 to a single methyl group, Me_{10}, are fully consistent with structure **2** for the reduction product.

Additional evidence for a pentathiepin ring fused to a substituted benzene system was provided by tandem mass spectral studies performed in the negative-ion FAB mode on the *N*-TFA derivative of varacin. Selection of the $[M - H]^-$ ion at 434 generated a daughter spectrum with ions at m/z 370 and 338 for loss of S_2 and S_3, respectively, from the molecular ion. Benzopentathiepins with ortho substituents have been reported to equilibrate with their corresponding trithiole in protic solvents,[10] which presents the possibility that varacin is a mixture of S_3 and S_5 compounds; however, the tandem mass spectral studies seem to argue against this. Therefore varacin must have structure **1**.

Although ascidians have been the source of a large number of modified amino acid derived metabolites[11] and marine algae have yielded simple cyclic polysulfides,[12] this is the first report of a naturally occurring polysulfide modified amino acid. It is also the first report of a naturally occurring benzopentathiepin. Varacin bears an obvious structural and biosynthetic relationship to dopamine; thus it is perhaps not surprising that it exhibits potent biological activity.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of varacin in CD_3OD, ^1H NMR spectrum of **2** in acetone-d_6, and daughter ion spectrum of the molecular ion of varacin *N*-trifluoroacetate in the negative FAB mode (4 pages). Ordering information is given on any current masthead page.

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(8) **1**: IR (film) ν 3354, 3282, 2923, 2851, 1574, 1460, 1410, 1241, 1062 cm^{-1}; UV (MeOH) λ_{max} 214, 244 nm; EIMS of *N*-TFA derivative m/z (relative intensity) 435 (M^+, 25), 403 ($M^+ - S$, 5), 371 ($M^+ - S_2$, 100), 339 ($M^+ - S_3$), 245 (80). The TFA amide derivative of **1** was obtained by heating a dichloromethane solution of **1** and an excess of trifluoroacetic anhydride for 5 min at 150 °C in a sealed Pyrex tube. The excess TFA was removed under a stream of nitrogen and the sample used for mass spectral studies without further purification.
(9) **2**: IR (film) ν 3420, 2921, 2851, 1684, 1463, 1418, 1202, 1071 cm^{-1}; GC EIMS m/z (rel int) 300 ($M^+ - 1$, 0.5), 299 (2), 254 (16), 242 (10), 58 (100); CIMS (NH_3) m/z (rel int) 302 ($M^+ + 1$, 24), 257 (16), 243 (100); HRCIMS (NH_3) calcd for $C_{14}H_{24}NO_2S_2$ 302.1248, found 302.1247.
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Isolation of a New Series of Seven-Coordinate Hydride Compounds of Tantalum(V) and Their Involvement in the Catalytic Hydrogenation of Arene Rings

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There is currently intense research interest into the synthesis, structure, bonding, and reactivity of transition-metal hydride compounds.[1-4] A significant amount of this interest has been stimulated by the recognition that nonclassical structures may exist for di- or polyhydride compounds.[5-7] We wish to report here the isolation of a new series of seven-coordinate hydride compounds of tantalum that contain aryloxide ligation. Besides possessing interesting structure and spectroscopic characteristics, these

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