HREIMS on mycalamide A (**1**) showed a weak molecular ion at 503.27220 daltons corresponding to a molecular formula of $C_{24}H_{41}NO_{10}$ (calculated 503.27305, −1.7 ppm), consistent with the ^1H and ^{13}C NMR data.[8] A DEPT NMR experiment showed 37 protons attached to carbon atoms, while CIMS using ND_3 as the reagent gas[10] confirmed the presence of four exchangeable protons. A one-proton doublet at δ_H 7.49 ppm, which exchanged slowly with D_2O, together with an IR absorption at 1700 cm^{-1} and a quaternary carbon at δ_c 171.52 ppm, indicated a secondary amide. The other three exchangeable protons were therefore present in hydroxyl groups. The NMR spectra showed only one other double bond, a 1,1'-disubstituted carbon–carbon double bond (δ_c 110.41, 145.40 ppm). The remaining unsaturation required by the molecular formula had to be satisfied by three rings.

A recollection of this active *Mycale* species allowed the isolation of enough mycalamide A (**1**, 10 mg) to solve its structure by a combination of HETCOR, COSY, long-range HETCOR (Figure 1) and difference NOE experiments.[11] These results, and consideration of chemical shifts,[8] led to the connectivities shown in Figure 1, with only a methoxyl group and a dioxymethylene group remaining unconnected. A search[12] on the substructure 1A (Figure 1) retrieved pederin (**2**)[13] and related compounds. The ^1H NMR shifts of the region of pederin (**2**) from C2 to C7[14] matched closely those for the corresponding protons in mycalamide A (**1**),[8] thus establishing the structure and relative stereochemistry of this region.[15] Comparison of the rest of the substructure in Figure 1 with pederin (**2**) showed that the same length carbon chain was present but with a different substitution pattern. The different vicinal substituents at C17 and C18 (methoxyl groups in pederin (**2**), hydroxyl groups in mycalamide A (**1**)) were shown by the sharpening of the H17 and H18 NMR signals on D_2O-exchange and confirmed by the chemical shifts of C17 and C18.[16]

The central section of mycalamide A (**1**) had to contain two rings, a methoxyl, a dioxymethylene group in a six-membered or larger ring,[17] and no hydroxyls. These constraints allowed a number of trial structures, but only that shown in Figure 2 satisfied the geometric requirements of the coupling constants (Figure 1) and the NOE results. This structure contained C11 to C15 in a tetrahydropyran ring as in pederin (**2**), with the dioxymethylene group attached to C12 and C10 forming an unusual 2,4,7-trioxadecalin.[18] Further work is under way to establish the absolute stereochemistries of C2 to C7, C10 to C15, and C17 (drawn as for pederin (**2**)[13] for convenience).

It is quite remarkable that pederin (**2**) and related compounds, isolated from the terrestrial beetle *Paederus fuscipes*,[13,19] are the only previously known compounds with structures similar to mycalamide A (**1**), isolated from a marine sponge. However, within weeks of the structural assignment described here, the closely related structure of a Japanese sponge component onnamide A was established independently.[20] It is not yet known whether mycalamide A (**1**) is a sponge metabolite, produced by a symbiotic organism or accumulated from a dietary source.[21] Experiments to explore this point are under way.

Acknowledgment. Research support from the Harbor Branch Oceanographic Institution, Inc. (HBOI) and SeaPharm, Inc. is gratefully acknowledged. We thank Professor J. Jillett and his staff at the Portobello Marine Laboratory, University of Otago, for assistance with collections; Professor P. R. Bergquist, University of Auckland, and Dr. C. N. Battershill for sponge identifications; V. L. Calder, G. Barns, Dr. M. Lui (HBOI), and Dr. S. Cross (HBOI) for bioassays; Dr. S. Bloor, D.S.I.R., Wellington, for rotation measurements; and the Canterbury Medical Research Foundation and the New Zealand University Grants Committee for equipment.

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(16) Butane-1,2-diol: C1, 66.3 ppm; C2, 73.8 ppm. 1-Methoxybutan-2-ol: C1, 77.3 ppm; C2, 71.5 ppm. 2-Methoxybutan-1-ol: C1, 63.5 ppm; C2, 83.4 ppm. From Bremser, W.; Ernst, L.; Franke, B.; Gerhards, R.; Hardt, A. *Carbon-13 NMR Spectral Data (Microfiche collection)*; Verlag Chemie: Basel, 1981. See also the vicinal diol side chain in halichondrin B.[3]
(17) Geminal coupling 6.9 Hz, see: Burden, I. J.; Stoddart, J. F. *J. Chem. Soc. Perkin Trans. 1* **1975**, 666–674.
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Isolation and Structure Elucidation of Onnamide A, a New Bioactive Metabolite of a Marine Sponge, *Theonella* sp.

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Marine sponges of the genus *Theonella* have been shown to elaborate diverse chemical structures with interesting biological activities.[1] We have recently described the isolation of misakinolide A, a dimeric 40-membered lactone having antitumor activity from a species of *Theonella*.[1a] In our screening for bioactivity in marine organisms occurring in Okinawan waters, another species of *Theonella* gave an extract showing antiviral activity. Bioassay-guided separation led to the isolation of an active constituent, onnamide A (**1**)[2] which belonged to a class of metabolites new to *Theonella* species. We herein report the isolation and structure elucidation of onnamide A (**1**).

A sample (7.5 kg) of *Theonella* sp.[3] was extracted by steeping in methanol. Evaporation gave an aqueous suspension which was

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(2) Potent antiviral activity (in vitro) was observed against herpes simplex virus type-1, vesicular stomatitis virus, and coronavirus A-59.
(3) Collected at a coral reef of Kerama, Okinawa in May 1986. A small collection was initially made at the coast of Onna from which the name of the compound was derived. Taxonomic identification of the sponge was carried out by Dr. Takaharu Hoshino of Hiroshima University.

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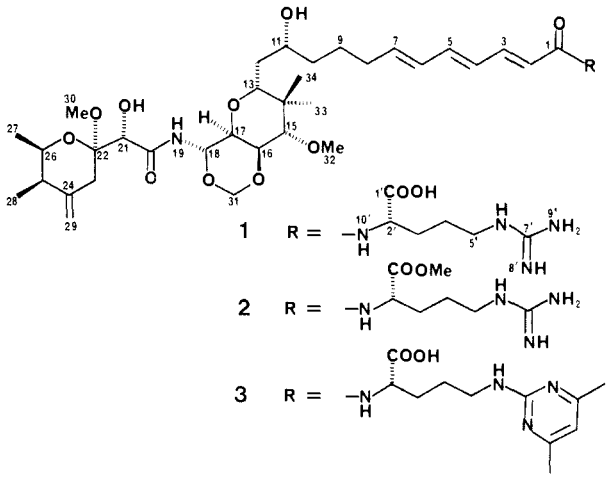

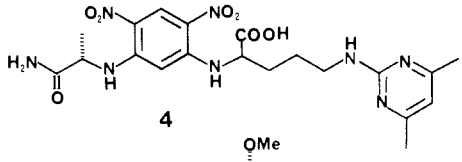

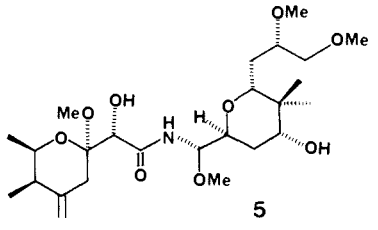

extracted with ethyl acetate. The residue of the aqueous layer on evaporation was extracted with methanol to give 114 g of brown solid. The solid (100 g) was successively chromatographed on NS gel[4] ($MeOH/H_2O$) and silica gel ($CHCl_3$/MeOH). Fractions showing antiviral activity were finally purified by centrifugal counter current chromatography ($ClCH_2CH_2Cl/CHCl_3$/MeOH/H_2O, 2:3:10:6; mobile phase: top layer) to give 470 mg of onnamide A (**1**)[5] as a light yellow, amorphous solid, $[\alpha]_D^{20}$ +99.1° (*c* 5.5, MeOH).

The molecular formula of **1** was deduced as $C_{39}H_{63}N_5O_{12}$ from high resolution FABMS (M + H: *m/z* 794.4557, Δ +0.6 mmu). The ^{13}C NMR spectrum[5] revealed signals for all 39 carbons. Since the 12 sp^2-carbon signals [3 C=O (δ 179.0, 174.3, 168.3), 1 N=C(N) (δ 158.7), 4 C=C] account for eight of the 11 unsaturations required by the formula, **1** must contain three rings. The presence of a carboxyl (δ 179.0) and guanidyl (δ 158.7) group was shown by the formation of a methyl ester (**2**)[6] and a pyrimidine derivative (**3**).[7] These two functional groups were part of an arginine residue as shown by 2D NMR study and by acid hydrolysis[8] of **3**. The hydrolysate contained a pyrimidine identical in TLC comparison with the pyrimidines formed from both authentic D- and L-arginine. Further reaction of each pyrimidine with Marfey's reagent[9] gave a diastereomeric product **4**. TLC comparison clearly demonstrated that the arginine derivative from **3** was the L-isomer.[10]

Strong UV absorption at λ_{max}^{MeOH} 299 nm (ε 38800) was attributed to the conjugation of a carbonyl group (δ 168.3, C_1) to a triene (C_2-C_7). This conjugation was also shown by COSY and HETCOSY. Long range C-H couplings between C_1 and the protons on $C_{2'}$, $N_{10'}$, C_2, and C_3 enabled us to link C_1 to the α-amino group of the arginine moiety. The connectivity for the remaining portion of the molecule was obtained by application of 2D NMR techniques (COSY, long range COSY, HETCOSY) on compounds **1**–**3** in CD_3OD and in DMSO-d_6/C_5D_5N (1:1). The spectra recorded in the latter showed signals for hydroxyl [δ 4.59 (br s, C_{11}-OH), 6.59 (br s, C_{21}-OH)] and imino protons [δ 8.69 (br s, N_{19}-H), 8.43 (br s, $N_{10'}$-H)] that were useful in the connectivity study. COSY and long range COSY established the connectivities for the segments of C_7-C_8-C_9-C_{10}-C_{11}(OH)-C_{12}-C_{13}(O), C_{15}(O)-C_{16}(O)-C_{17}(O)-C_{18}-N_{19}, C_{16}-O-C_{31}-O-C_{18}, C_{23}-(C_{24})-C_{29}, C_{29}-(C_{24})-C_{25}(Me)-C_{26}(O)-C_{27}, and C_{21}-OH. HETCOSY revealed the following linkages: C_{12}-C_{13}(O)-C_{14}(Me, Me)-C_{15}-OMe, C_{16}-O-C_{31}-O-C_{18}-(N_{19})-C_{20}(=O)-C_{21}(OH)-C_{22}(O,O)-C_{23}, C_{13}-O-C_{17}-C_{18}, C_{22}-OMe, and C_{23}-C_{24}(=CH_2)-C_{25}(Me)-C_{26}. No long range C-H coupling was detected between C_{22} and H_{26}, but an NOE observed between H_{26} and H_{30} enabled us to connect C_{22} to C_{26} through an oxygen to form a tetrahydropyran ring. Thus, the gross structure of **1** was defined, and all the ^1H and ^{13}C NMR signals were unambiguously assigned.[5]

The geometries of the triene were assigned as all trans by the H-H coupling constants (J = 14.7–15.2 Hz) of the olefinic protons. The relative configurations for the ring portions were established by NOE difference spectroscopy. At this point it was brought to our attention that the heterocyclic portion of **1** had a striking resemblance to pederin (**5**), an insect toxin known to have some significant biological activities,[11] and most remarkably to mycalamide A, an antiviral compound isolated recently from a New Zealand collection of a *Mycale* sp. of sponge.[12] Since the relative configurations for the ring portions of onnamide A (**1**) are fully identical with those of pederin (**5**) and mycalamide A, the configurations at C_{11} and C_{21} of **1** are tentatively assigned by analogy to these compounds. We are currently working on defining the absolute stereochemistry of onnamide A (**1**).

Acknowledgment. This is Harbor Branch Oceanographic Institution Contribution No. 647. We thank Dr. Sue Cross for

(4) A gel made of styrene–divinylbenzene copolymer, distributed from Nihon Seimitsu Kagaku, Tokyo.

(5) UV (MeOH) λ_{max} 202 (ε 7500), 299 nm (ε 38 800); IR (KBr) 3360 br, 2965, 2935, 1650 br, 1590 br, 1512 br, 1450 br, 1391, 1320 br, 1265, 1226, 1170, 1092, 1071, 1030, 1008, 910, 880, and 788 cm^{-1}; ^1H NMR (CD_3OD) δ 7.13 (1 H, dd, J = 15.0, 11.2 Hz, H-3), 6.50 (1 H, dd, J = 14.8, 10.7 Hz, H-5), 6.23 (1 H, dd, J = 14.7, 11.3 Hz, H-4), 6.19 (1 H, dd, J = 15.3, 10.7 Hz, H-6), 6.07 (1 H, d, J = 15.0 Hz, H-2), 5.93 (1 H, dt, J = 15.2, 6.9 Hz, H-7), 5.79 (1 H, d, J = 9.3 Hz, H-18), 5.48 (1 H, d, J = 6.9 Hz, H-31), 4.80 (1 H, d, J = 6.9 Hz, H-31), 4.79 (1 H, br s, H-29), 4.63 (1 H, br s, H-29), 4.36 (1 H, dd, J = 7.9, 5.3 Hz, H-2'), 4.23 (1 H, s, H-21), 4.16 (1 H, dd, J = 9.7, 6.5 Hz, H-16), 3.98 (1 H, dd, J = 9.3, 6.5 Hz, H-17), 3.87 (1 H, qd, J = 6.5, 2.4 Hz, H-26), 3.64 (1 H, m, H-11), 3.62 (1 H, d, J = 9.6 Hz, H-15), 3.55 (3 H, s, H-32), 3.47 (1 H, dd, J = 8.1, 3.6 Hz, H-13), 3.22 (3 H, s, H-30), 3.19 (2 H, m, H-5'), 2.40 (1 H, br d, J = 14.4 Hz, H-23), 2.32 (1 H, br d, J = 14.4 Hz, H-23), 2.21 (1 H, m, H-8), 2.18 (1 H, m, H-25), 2.13 (1 H, m, H-8), 1.89 (1 H, m, H-3'), 1.75 (1 H, m, H-3'), 1.63 (2 H, m, H-4'), 1.59 (1 H, m, H-9), 1.53 (2 H, m, H-12), 1.49 (1 H, m, H-10), 1.40 (1 H, m, H-9), 1.28 (1 H, m, H-10), 1.17 (3 H, d, J = 6.5 Hz, H-27), 1.00 (3 H, s, H-34), 0.96 (3 H, d, J = 6.9 Hz, H-28), and 0.85 (3 H, s, H-33); ^{13}C NMR (CD_3OD) δ 179.0 (s, C-1'), 174.3 (s, C-20), 168.3 (s, C-1), 158.7 (s, C-7'), 148.1 (s, C-24), 141.9 (d, C-3), 141.2 (d, C-5), 140.4 (d, C-7), 131.5 (d, C-6), 129.5 (d, C-4), 124.4 (d, C-2), 110.1 (t, C-29), 101.3 (s, C-22), 87.6 (t, C-31), 80.6 (d, C-15), 78.7 (d, C-13), 75.5 (d, C-16), 74.9 (d, C-18), 74.0 (d, C-21), 71.0 (d, C-11), 70.8 (2 d, C-17, 26), 61.9 (q, C-32), 55.6 (d, C-2'), 48.8 (q, C-30), 43.0 (d, C-25), 42.2 (s, C-14), 42.0 (t, C-5'), 37.3 (t, C-12), 36.8 (t, C-10), 34.8 (t, C-23), 33.9 (t, C-8), 31.2 (t, C-3'), 26.3 (t, C-4'), 26.1 (t, C-9), 23.7 (q, C-34), 18.2 (q, C-27), 14.5 (q, C-33), and 12.4 (q, C-28).

(6) Since diazomethane did not react with **1**, the methylation was carried out by heating **1** with iodomethane and potassium carbonate in acetone. **2**: δ_H (CD_3OD) 3.73 (3 H, s, COOMe), δ_C (CD_3OD) 173.7 (s, C-1'), 52.8 (q, OMe).

(7) Pyrimidine **3** was obtained by condensation of **1** with pentane-2,4-dione. For the condensation of guanidines, see: Carter, G. T.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 4302–4304. **3**: λ_{max}^{MeOH} 239 (ε 19 100), 299 nm (ε 41 200); additional NMR signals in CD_3OD: δ_H 6.39 (1 H, s), 2.26 (6 H, s); δ_C 169.0 (2 s), 110.2 (d).

(8) Compound **3** was treated with 2 N HCl (aqueous) in DMSO at 100 °C for 6 h.

(9) Marfey, P. *Carlsberg Res. Commun.* **1984**, *49*, 591–596.

(10) Compounds **4** from D- and L-arginine showed R_f 0.23 and 0.31 in 3:1 $CHCl_3$/MeOH and 0.25 and 0.41 in 10:1 EtOAc/MeOH, respectively, on silica gel TLC plates.

(11) Cardani, C.; Ghiringhelli, D.; Mondelli, R.; Quilico, A. *Tetrahedron Lett.* **1965**, 2537–2545. Furusaki, A.; Watanabe, T.; Matsumoto, T.; Yanagiya, M. *Tetrahedron Lett.* **1968**, 6301–6304. Brega, A.; Falaschi, A.; De Carli, L.; Pavan, M. *J. Cell Biol.* **1968**, *36*, 485–496. Matsuda, F.; Tomiyoshi, N.; Yanagiya, M.; Matsumoto, T. *Tetrahedron Lett.* **1983**, *24*, 1277–1280. Nakata, T.; Nagao, S.; Oishi, T. *Tetrahedron Lett.* **1985**, *26*, 6465–6468. Willson, T.; Kocienski, P.; Faller, A.; Campbell, S. *J. Chem. Soc., Chem. Commun.* **1987**, 106–108.

(12) Perry, N. B.; Blunt, J. W.; Munro, M. H. G.; Pannell, L. K. *J. Am. Chem. Soc.* **1988**, preceding paper in this issue.

biological tests and Drs. Murray Munro and John Blunt for providing data on mycalamide A prior to publication and helpful comments on the manuscript.

Supplementary Material Available: Relative configuration of onnamide A (**1**) (1 page). Ordering information is given on any current masthead page.

Synthesis and Physical Properties of a Dinuclear Tantalum-Cobalt Radical with Spin Localized at One Metal Center

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We wish to report the synthesis, physical characterization, and redox properties of $Cp_2Ta(\mu\text{-}CH_2)_2CoCp$, a heterodinuclear organometallic radical species in which the unpaired electron is localized at one metal center.

Expecting to generate a diamagnetic $M(\mu\text{-}CH_2)M'$ adduct analogous to those that have been obtained previously,[1,2] we allowed the methylidene complex $Cp_2Ta(CH_2)CH_3$ (**1**)[3] to react with $CpCo(C_2H_4)_2$[4] (**2**) in C_6D_6 at 25 °C. However, when the reaction was monitored by ^1H NMR spectrometry, the reactants were seen to disappear over the course of 2.5 h, and resonances at δ 5.25 and 4.48, assignable to C_2H_4 and H_2, grew in along with a single broad resonance at δ 3.1. Orange X-ray quality crystals of an analytically pure product were isolated directly from the reaction solution in 64% yield. Elemental and mass spectrometric analyses were consistent with the formula $C_{17}H_{19}CoTa$ for this material and led to the suggestion that it has structure **3** shown in Scheme I.[5]

In order to confirm this supposition, a single-crystal X-ray diffraction study was undertaken; an ORTEP diagram of the structure of the complex is shown in Scheme I.[6] Crystals of **3** exist in space group $P2_12_12_1$. Both metal centers and the μ-methylene carbons lie in a plane which reflects the two equivalent tantalum cyclopentadienyl rings. This plane and the plane containing the metal centers and the centroids of all three cyclopentadienyl rings are almost exactly perpendicular (dihedral angle = 89.9°). The Ta-Co distance is 2.708 Å. The two $\mu\text{-}CH_2\text{-}Ta$ distances of 2.11 and 2.13 Å are slightly shorter but consistent with those observed in other heteronuclear μ-methylene structures of tantalum (2.14-2.16 Å).[3] These distances fall roughly midway between those characteristic of a tantalum-carbon single bond (ca. 2.25 Å) and a tantalum-carbon double bond (ca. 2.03 Å).[7] The $\mu\text{-}CH_2\text{-}Co$ distances of 1.98 and 1.97 Å are longer than those observed in homonuclear examples of μ-methylene cobalt complexes (1.91-1.92 Å).[8]

The ill-defined ^1H NMR spectrum of **3** and electron-counting formalisms (33 valence electrons) suggest that the molecule is paramagnetic. Magnetic susceptibility studies of **3** were carried out with a SHE Squid magnetometer, at 40 kG, over the temperature range 5-262 K. Curie-Wiess behavior was observed, and an effective magnetic moment of 1.91 μ_B was calculated from the data, indicating the presence of one unpaired electron.[9]

Electrochemical analysis indicates that **3** can be both oxidized and reduced reversibly in THF, with corresponding potentials of -0.38 and -2.44 V (relative to NHE).[10] The complete reversibility of the voltammogram and the relatively large difference in oxidation and reduction potentials of 2 V are indicative of the robust nature of **3** and suggest that the corresponding anion and cation salts might be stable. We have not yet been able to prepare the anion, but cationic salts can be readily generated. Thus, reaction of orange **3** with $Cp_2Fe^+BF_4^-$ in acetonitrile proceeded cleanly at 20 °C to give ferrocene and the purple diamagnetic complex $[Cp_2Ta(\mu\text{-}CH_2)_2Co(CH_3CN)Cp]^+BF_4^-\cdot CH_3CN$ (**4**) in 94% yield. Variable temperature NMR data indicate that the molecule is fluxional and are consistent with a process involving rapid dissociation and recoordination of the acetonitrile ligand above and below the plane of the $M\text{-}(CH_2)_2\text{-}M$ bridge. This process renders equivalent the two tantalum cyclopentadienyl signals, the two $\mu\text{-}CH_2$ hydrogens in each methylene unit, and the two CH_3CN ligands. Consistent with this mechanism, reaction of **4** with dative ligands PMe_3 and CO converts it rapidly to complexes **5a** and **5b**, respectively.

An important question concerning the electronic structure of **3** is the distribution of unpaired spin density about the two metal centers. The Ta/Co complex is an interesting heterodinuclear analogue of the dimeric cyclopentadienylcobalt "mixed valent"[11] radical anion $[CpCo(CO)]_2^-$, salts of which were prepared and studied several years ago.[12] The EPR spectrum of the dicobalt complex shows equivalent hyperfine coupling to the two cobalt atoms (^{59}Co, 100% abundant, $I = 7/2$), leading to a 15-line spectrum. Thus the unpaired electron is delocalized and is shared equally by the two metal centers. The EPR spectrum of **3** (note: ^{181}Ta, 99.99% abundant, $I = 7/2$) is quite different. At room temperature, the spectrum shows a single line with $g = 2.15$, having a line width of 143 G and no resolved hyperfine coupling. At low temperature the spectrum (obtained in a toluene glass at 8 K) shows an anisotropic signal with only an eight-line hyperfine coupling pattern (Figure 1). A simulated spectrum of an orthorhombic system with $I = 7/2$ allows assignment of the anisotropic g tensors and hyperfine coupling constants as indicated in the figure caption.[13]

The eight-line spectrum is thus consistent with isolation of the unpaired spin on one of the identical $I = 7/2$ metal centers, at least at low temperature. It is possible to write valence-bond structures (e.g., **3a** and **3b**; cf. Scheme I) that place the unpaired spin on either cobalt (a Co(II)/Ta(V) resonance form) or tantalum (a Co(III)/Ta(IV) form). Literature values for mononuclear

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(5) Anal. Calcd for $C_{17}H_{19}CoTa$: C, 44.08; H, 4.13. Found: C, 44.41; H, 4.26. HRMS(EI) 463.0298. Calcd for $C_{17}H_{19}CoTa$: 463.0298.

(6) The structure was determined by Dr. F. J. Hollander of the UC Berkeley College of Chemistry X-Ray Diffraction Facility (CHEXRAY). Crystal data: 1003 reflections; $R = 2.65\%$; space group $P2_12_12_1$; $a = 9.7333$ (9) Å, $b = 10.5263$ (13) Å, $c = 14.1131$ (17) Å; $\alpha = \beta = \gamma = 90.0°$; $Z = 4$, $d_{calcd} = 2.13$ g/cm^3. Other details of the structure determination are provided as Supplementary Material.

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