major among the type I products.[8] In contrast, **2a**, which generally gives type II products in benzene, gave the type I derived **5** as the major product in M-X zeolite. In both cases, the yield of the rearrangement product **5** was dependent upon the exchangeable cation. It is important to note that the inherent reactivity controlled product distribution has been dramatically altered by the zeolite cavity in both cases.

We believe the preference for **5** among the type I products is a consequence of the restriction experienced by the geminal radical pair (Scheme I).[9] Low yields of coupling products **3** and **4** in the product mixture in the case of **1a** and their absence in **2a** clearly indicate that the translational motion of the radical pair is restricted by the zeolite framework.[10] Even more interesting is the fact that the rotational process required to produce the rearrangement product is greatly dependent upon the cavity free space. It is known that in proceeding from Li-X to Cs-X the degree of "lebensraum" or open void space is significantly reduced.[11] It is of interest to note that the relative yield of **5** decreases in the same order as the increase in the cation size. Such a space dependent rotational restriction is also evident when one compares the product distribution between the dry and the wet zeolites. Water decreases the void space by co-ordinating to the free cations present within the zeolite cavity.[12]

The behavior of benzoin alkyl ethers and alkyl deoxy benzoins when viewed together provides important additional information. The zeolite cavity induces **1a** to yield products derived via the type II pathway, a minor pathway in benzene. On the other hand, zeolites do not cause **2a** to proceed via the type II pathway, which is favored in benzene. We attribute this to the ability of the cation present in the cavity to control the conformation of the included molecules (Figure 1). The presence of an alkoxy chain in **1a** most likely directs the chelation of the cation to a conformer that is favorable for the type II process. Similarly in **2a**, the phenyl ring directs the conformational preference in the cavity.[13] Such a hypothesis is supported by the results on dealuminated zeolite-Y in which the Si to Al ratio is very high (>550).[14] At very low levels of aluminum the cation concentration is also low. Therefore conformational control is expected to be minimal and indeed only the type I products, **3**-**5**, dominated the product mixture. Furthermore, the increase in the yield of benzil from Li-X to Cs-X (Table I) is also a reflection of the decreased interaction between the cation and the benzoyl radical.[15] The increased yield of the type II products in **1a** in zeolite must also be the result of the cage effect as significant C^{13} enrichment (25%) of the oxetanol was observed.[16]

The results presented above illustrate the important role zeolites can play in selective phototransformations. Since zeolites of varied and tailor-made frameworks are readily prepared, the future for zeolites as a reaction medium appears bright.

Acknowledgment. The authors thank A. Pittman and R. Nickle (late) for able technical assistance and Dr. S. J. McLain, Dr. W. E. Farneth, and Prof. N. J. Turro for useful discussion.

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(9) Lehr, G. F.; Turro, N. J. *Tetrahedron* **1981**, *37*, 3411.

(10) By independent experiments it was established that both **3** and **4** can enter and exit the zeolite. Furthermore it was shown that these are stable to acid extraction. Absence of pinacol ethers in zeolites also is a consequence of the fragmentation of the precursor radical to benzaldehyde when translational motion is restricted.

(11) Sefcik, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 2164. Onaka, M.; Isikawa, K.; Izumi, Y. *J. Inclusion Phenomena* **1984**, *2*, 359. Turro, N. J.; Zang, Z. *Tetrahedron Lett.* **1987**, 5637.

(12) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974; pp 412-415. Further experiments are underway to evaluate the effect of water on the product distribution.

(13) Similar chelation of the cation to the guest $Ni(CO)_4$ has been reported recently: Bein, T.; McLain, S. J.; Corbin,D. R.; Farlee, R. F.; Moller, K.; Stucky, G. D.; Woolery, G.; Sayers, D. *J. Am. Chem. Soc.* **1988**, *110*, 1801. Carbonyl stretching frequency of **1a** (1694 cm^{-1}) in THF is also shifted by excess magnesium triflate (1681 cm^{-1}).

(14) Dealuminated zeolite Y was prepared according to the following: Grobet, P.; Jacobs, P. A.; Beyer, H. K. *Zeolites* **1986**, *6*, 47.

(15) Such an increase may not be due to the photolysis of the ketone adsorbed on the surface since the complexes were washed thoroughly with ether before processing for irradiation. No benzil or diphenyl alkanes were detected as products in the case of **2**. We believe that disproportionation occurs between benzoyl and benzyl radical pair to yield benzaldehyde and olefin, a reaction that is not possible in the case of **1**.

(16) Isotope enrichment was estimated by measuring the isotope distribution of the molecular ion peak of the oxetanol product. Oxetanol from benzene irradiation was taken as the standard. The isotope enrichment derives from the enrichment of the starting ketone and not due to the effect on the biradical precursor.

$(\mu\text{-NO})_2[Co(\eta^5\text{-}C_5H_5)]_2$ Is Not Paramagnetic

David J. Berg and Richard A. Andersen*

Chemistry Department, University of California Berkeley, California 94720

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A recent theoretical article, published in this journal, has suggested that the molecule, $Cp_2Co_2(\mu\text{-}NO)_2$, is a ground-state triplet ($S = 1$) and therefore paramagnetic.[1] The only evidence in the literature relative to the magnetic properties of this molecule of idealized D_{2d} symmetry in the solid state[2] is the apparently normal ^1H NMR spectrum (for a diamagnetic molecule) that contains a single resonance at δ 4.77[3] or 4.60,[4] the temperature not being specified. In this brief paper we show that $Cp_2Co_2(\mu\text{-}NO)_2$ is diamagnetic in the solid state (5-280 K) and in solution (C_6H_6, 303-327 K) and conclude that the theoretical calculations of Demuynck, Mougenot, and Benard[1] predict the wrong result.

For a diamagnetic compound the magnetic susceptibility, χ, is negative and on the order of 10^{-6} (emu)(g^{-1}). For a paramagnetic compound χ is positive and on the order of 1-3 times greater than that of a diamagnetic compound. As can be seen from Table I, the only χ value that is negative is the value at 281 K at 5 kG. The other values of χ are positive though very small. The slightly positive values of χ could be due to trace metal or other paramagnetic impurities (cobalt metal is ferromagnetic with a magnetic moment of 1.7 μ_B)[5c] or due to the TIP (temperature independent paramagnetism) term being positive, the TIP term for Co(II) can be as high as 10^{-4} emu mol^{-1}. Further, the molecule is diamagnetic as deduced by the Evans' method. Thus, 19.8 mg ml^{-1} of $Cp_2Co_2(\mu\text{-}NO)_2$ in C_6H_6 does not shift the ^1H NMR absorption of C_6H_6 (internal) relative to C_6H_6 (external) by a detectable amount at 32 °C and 54 °C. The resonance due to the equivalent protons of the C_5H_5 rings occurs at δ 4.54 at 32 °C and 54 °C with a line width at half height of 1.7 Hz.

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(5) (a) Van Vleck, J. H. *The Theory of Electric and Magnetic Susceptibilities*; Clarendon Press: Oxford, 1932. (b) Bondreaux, E. A.; Mulay, L. N. *Theory and Application of Molecular Paramagnetism*; Wiley: New York, 1976. (c) Goodenough, J. B. *Magnetism and the Chemical Bond*; Wiley: New York, 1963.

(6) Magnetic susceptibility measurements were made on a SHE Model 905 superconducting magnetometer (SQUID). Sample containers were made from two tightly fitting KEL-F half-containers. In a typical experiment 78.01 mg of $Cp_2Co_2(\mu\text{-}NO)_2$, which was freshly sublimed and ground to a fine powder before weighing, was placed into a KEL-F container inside of an argon-filled drybox. The two halves of the container were sealed with the aid of a small amount of silicone grease. After removal of the container from the drybox, the container was wired shut with nylon, microfilament thread and suspended in the sample chamber of the magnetometer by cotton thread. Samples were measured automatically at two fields and at temperatures between 5 and 280 K. Measurements were taken at 5 and 40 K with the following temperature intervals: 3 K from 6-21 K; 5 K from 25-50 K; 10 K from 50-100 K; 20 K from 100-280 K. Sample data were corrected for container (including grease) diamagnetism. In this case, a duplicate determination on a different chemical specimen gave the same result. An additional sublimation of the compound gave essentially the same χ_g values as those of the once sublimed compound though the value of χ_g for the crystallized specimen was 2 orders of magnetiude higher than that of the sublimed specimen.

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Table I. Magnetic Susceptibility, χ_M, of $Cp_2Co_2(\mu\text{-}NO)_2$[6]

T (K)	χ_M (emu mol^{-1})	μ_{eff} (in μ_B)[a]	H_0 (kG)
9	12.9×10^{-4}	0.30	5
9	8.45×10^{-4}	0.26	40
281	-2.35×10^{-6}		5
281	3.32×10^{-6}	0.085	40

[a] This value is calculated by using the equation, $\mu_{eff} = 2.823 (\chi_M T)^{1/2}$.

The conclusion is inescapable, $Cp_2Co_2(\mu\text{-}NO)_2$ has a diamagnetic ground state.

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Registry No. $Cp_2Co_2(\mu\text{-}NO)_2$, 51862-20-5.

Mycalamide A, an Antiviral Compound from a New Zealand Sponge of the Genus *Mycale*

Nigel B. Perry, John W. Blunt,* and Murray H. G. Munro*

Department of Chemistry, University of Canterbury Christchurch, New Zealand

Lewis K. Pannell

National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health Bethesda, Maryland 20892

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Many sponge metabolites with in vitro biological activities have been identified,[1] but very few have been reported with in vivo antitumor or antiviral activity.[2,3] We now report the bioactivity-directed isolation and structure determination of mycalamide A (**1**), from a sponge extract with in vivo antiviral properties.

In our screening of New Zealand marine invertebrates, an extract of a sponge of the genus *Mycale*[4] from the Otago Harbour showed promising in vitro antiviral activity.[5] Reverse phase flash chromatography[6] on a larger scale extract (11.0 g from 200 g of sponge) concentrated the bioactivity into a brown oil (307 mg) with significant in vivo antiviral activity.[7] Gel permeation and silica gel chromatography on a subsample of this material (140 mg) gave mycalamide A (**1**, 1.7 mg),[8] a new compound with strong in vitro antiviral activity.[9]

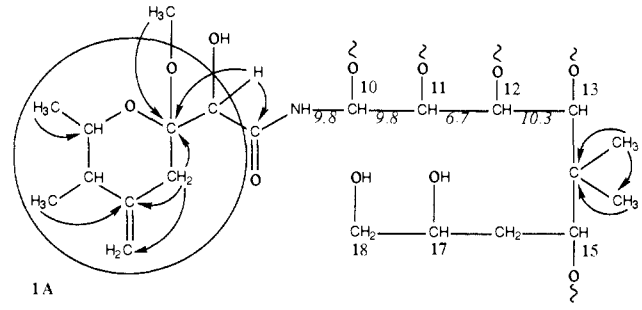


Figure 1. Connectivities from NMR experiments with long-range HETCOR linkages and selected proton–proton coupling constants (in Hz) shown.

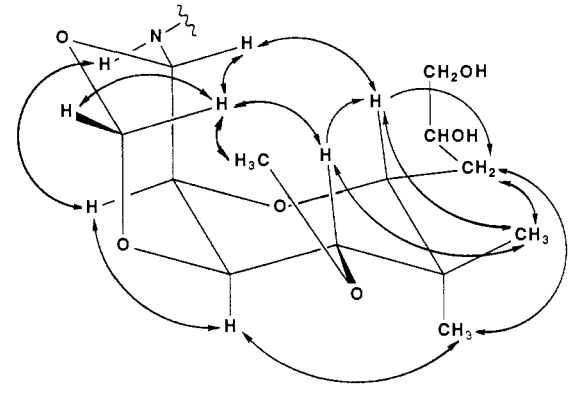
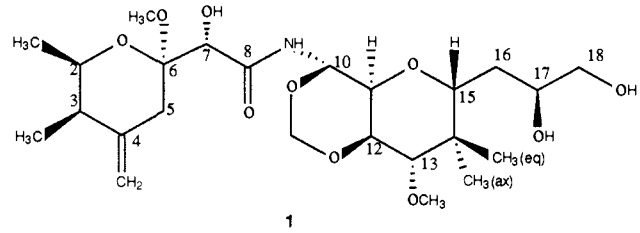
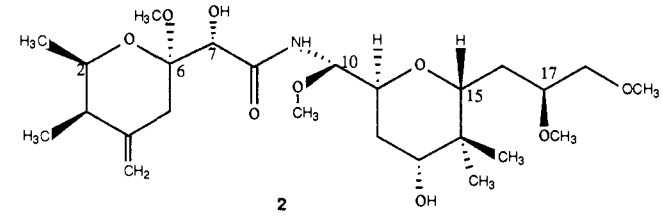


Figure 2. Configuration of the central region of mycalamide A (**1**) showing NOE interactions.





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(4) This *Mycale* sp. (type specimen PML1-9, Chemistry Department, University of Canterbury) family Mycalidae Lundbeck, order Poecilosclerida, is undescribed and is not included in a recent review: Bergquist, P. R.; Fromont, J. *The Marine Fauna of New Zealand: Porifera, Demospongiae: Part 4 (Poecilosclerida)*; D.S.I.R.: Wellington, in press. The sponge is distinctive in that it is nearly always host to tube worm colonies giving the surface a stippled appearance. Individuals are yellow to brown, often with a purple tinge over the surface and may be massive or encrusting. Spiculation distinguishes this species from other Mycalidae as it only has one size class of subtylostyles, and microscleres (two size classes of anisochelae and one of sigmas) are always of a very delicate structure (<0.5 μm thick). Other *Mycale* chemistry: Kato, Y.; Fusetani, N.; Matsunaga, S.; Hashimoto, K. *Tetrahedron Lett.* **1985**, *26*, 3483–3486. Capon, R. J.; MacLeod, J. K. *Tetrahedron* **1985**, *41*, 3391–3404. Capon, R. J.; MacLeod, J. K. *J. Nat. Prod.* **1987**, *50*, 225–229.

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(7) This material, ca. 2% mycalamide A (**1**), was tested in mice infected with A59 coronavirus: four mice dosed with virus, and the extract at 0.1 mg/kg survived 14 days; eight mice dosed with virus only all died within 8 days.

(8) Mycalamide A (**1**), an oil, $[\alpha]_{365}$ +110° (*c* 0.2, $CHCl_3$): IR (film) 3700–3100, 2960, 1740, 1700, 1540, 1470, 1390, 1100, 1080, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.49 (NH9, d, 9.8), 5.87 (H10, t, 9.8), 5.13 (10-O-CH_2, d, 6.9), 4.87 (10-O-CH_2, d, 6.9), 4.84 (4=CH_2, m), 4.73 (4=CH_2, m), 4.30 (H7, s), 4.22 (H12, dd, 6.7, 10.3), 3.98 (H2, dq, 2.7, 6.6), 3.86 (H11, dd, 6.7, 9.8), 3.74 (H17, m), 3.60 (H15, dd, 4.0, 5.5), 3.55 (13-O-CH_3, s), 3.55 (H18, m, hidden), 3.46 (H13, d, 10.3), 3.38 (H18, dd, 6.2, 11.2), 3.29 (6-O-CH_3, s), 2.36 ($H_2$5, m), 2.24 (H3, dq, 2.7, 7.0), 1.54 ($H_2$16, m), 1.19 (2-CH_3, d, 6.6), 0.99 (3-CH_3, d, 7.0), 0.98 (14-CH_3(eq), s), 0.87 (14-CH_3(ax), s) ppm (couplings in Hz); ^{13}C NMR ($CDCl_3$) δ 171.52 (C8), 145.40 (C4), 110.41 (4=CH_2), 99.66 (C6), 86.71 (10-O-CH_2), 79.01 (C13), 78.91 (C15), 74.30 (C12), 73.62 (C10), 72.77 (C7), 71.51 (C17), 71.16 (C11), 69.70 (C2), 66.41 (C18), 61.75 (13-O-CH_3), 48.88 (6-O-CH_3), 41.61 (C14), 41.31 (C3), 33.70 (C5), 31.95 (C16), 23.10 (14-CH_3(eq)), 17.89 (2-CH_3), 13.51 (14-CH_3(ax)), 12.03 (3-CH_3).

(9) The minimum dose of mycalamide A (**1**) that inhibited the cytopathic effect of either test virus[5] over a whole (17 mm) well was 5 ng/disk. No in vivo antiviral results on pure mycalamide A (**1**) have yet been obtained, but in vitro assays showed that it was responsible for the in vitro activity of the crude extract and thus probably the in vivo activity as well.[7]

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