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change. Transannular interactions do not occur and the positions of the hydrogen atoms in **4** do not differ significantly from their positions in **3.**

From the activation enthalpies for the valence tautomerization of cyclooctatetraene (28.1 kcal/mol),[12] phenylcyclooctatetraene (25.1 kcal/mol),[12] and COT bromide (23.1 kcal/mol),[6] the half-life of COT bromide was calculated to be 31 days at room temperature.[13] It is then reasonable to assume that the value for the valence tautomerization of COT triflate (**3**) also lies in the same range. Therefore the slow reaction path **3 → 5 → 6** plays no role in the fast solvolysis reaction of COT triflate since only eight-ring products were obtained from the solvolysis.[14]

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Unusual Coordination of the α-Dioxime Ligand in Bis(camphorquinone dioximato)nickel(II)

Sir:

Metal complexes[1] of the dimethylglyoximate ligand (HDMG⁻) have served as models for vitamin B_{12},[2] have been shown to have some one-dimensional metallic properties,[3] and have long been of importance in analytical chemistry.[4] In all of the known structures, the HDMG⁻ ligand behaves as a bidentate ligand coordinating to the metal through both nitrogen atoms.

Our interest in these compounds evolved from previous studies of optically active ligands[5] and a desire to prepare complexes with optically active α-dioxime ligands. We expected these complexes to have catalytic properties similar to those known for Co(HDMG)₂.[6] The chosen ligand, γ-camphorquinone dioxime (H₂CQD), was prepared from *d*-camphor according to the procedures of Forster.[7] ¹H NMR studies[8] and an X-ray structural study[9] indicate that this γ isomer
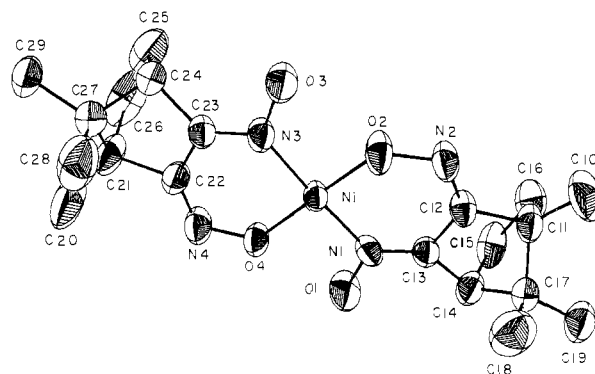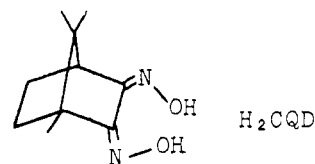

Figure 1. Computer-generated perspective drawing of Ni(HCQD)₂.

has a syn structure with the OH group orientations as shown at the N atoms. Recently, complexes of the α, β, and δ isomers of camphorquinone dioxime were reported to catalyze the

cyclopropanation of olefins, and it was suggested that these complexes had structures involving N–O as well as N–N ligand bonding.[10]

The nickel(II) complex was prepared by mildly refluxing a MeOH solution of 0.64 mmol of Ni(NO₃)₂·6H₂O and 1.28 mmol of H₂CQD for 10 min. After adding 1.28 mmol of NaOMe in MeOH, the solution was refluxed for an additional 2 h. Following filtration while warm, the solution was evaporated under vacuum to a green solid, which was dissolved in a minimum volume (~10 mL) of CH₃CN. The solution was filtered immediately and allowed to stand overnight whereupon reddish brown tetrahedral crystals of Ni(HCQD)₂ formed in 20% yield. Anal. (C₂₀H₃₀N₄O₄Ni) C, H, N.

A single tetrahedral crystal of Ni(HCQD)₂ ~0.4 mm on an edge was chosen for the X-ray diffraction study. The observed Laué symmetry and extinctions correspond to the orthorhombic space group $P2_12_12_1$ with $a = 13.175$ (1), $b = 13.652$ (2), $c = 12.031$ (3) Å; $Z = 4$; and $\rho_{calcd} = 1.378$ g/mL. Four octants of data were collected on a four-circle diffractometer designed and built in the Ames Laboratory[11] using graphite monochromated Mo Kα X-rays (λ = 0.70954 Å) up to a 2θ limit of 60°. Of the 11 562 measured intensities 7923 were judged observed ($I > 3.0\sigma I$). Correction for Lorentz and polarization effects and averaging of equivalent data yielded 2253 independent reflections. No correction was applied for absorption and an extinction correction was made with $g = 4.5 \times 10^{-7}$. The heavy atom was readily located on a Patterson map.[12] Full-matrix least-squares refinement[13] of the structure with anisotropic thermal parameters and fixed hydrogen positions yielded a conventional residual $R = 0.066$ and a weighted residual $R = 0.085$. A computer-generated perspective view of the essential configuration of the ligand and the coordination sphere around the nickel atom is shown in Figure 1.

The six-membered rings give the Ni atom an almost square-planar configuration. The distances from Ni to O-2, O-4, N-1, and N-3 are 1.820 (4), 1.840 (3), 1.859 (4), and 1.851 (4) Å, respectively. The HCQD⁻ ligand coordinates to the Ni via N and O donor atoms rather than the common N–N coordination characteristic of other α-dioxime ligands. We believe the reason for this coordination is the bicyclic nature of the ligand which causes the C–C–C angles at C-12, C-13,

C-22, and C-23 to be 106.6 (4), 105.1 (4), 104.9 (4), and 107.4 (4)°, respectively, which are substantially smaller than found (121 and 124°) for the corresponding angles of Ni-(HDMG)$_2$.[14]

The small magnitude of these angles presumably increases the C-C-N angles in the chelate ring to the point where formation of a larger ring by N-O coordination becomes more favorable. However, even in the six-membered ring there appears to be some strain due to the sharp angle (94.2 (2) and 93.9 (2)°) at the Ni in the chelate ring. Thus all the following angles in the ring are larger than corresponding angles in Ni(HDMG)$_2$ (the given angle is listed first followed by the corresponding angle in the other ring): N-3-C-23-C-22, 122.1 (5), 122.9 (5)°; N-4-C-22-C-23, 132.0 (5), 129.6 (4)°; Ni-N-3-C-23, 124.8 (4), 126.3 (3)°. These unusually large angles suggest that the six-membered chelate rings may also be strained. The delicate balance between N-O and N-N coordination in HCQD$^-$ complexes is supported by the fact that we find the ligand to be N-N coordinated in Cu(HCQD)$_2$. The now known existence of these two modes of bonding suggests that N-O-bonded forms may be present as intermediates in reactions of complexes of other α-dioxime ligands.

Although the O-1-O-4 and O-2-O-3 distances (2.49 and 2.50 Å) are not so short as those (2.40 Å)[14] in Ni(HDMG)$_2$, it appears that some hydrogen bonding does occur. There are no short distances which permit intermolecular hydrogen bonding. The molecules pack in the unit cell such that the closest distance between Ni atoms in parallel complexes is one unit cell length (12.031 Å) along the *c* axis. Thus there is no Ni-Ni interaction such as occurs in Ni(HDMG)$_2$.[14]

The infrared spectrum of Ni(HCQD)$_2$ taken in a KBr pellet shows a medium-intensity absorption at 1690 cm^{-1}, an unusually high frequency uncharacteristic of N-bonded α-dioxime ligands.[15] Deuteration studies indicate that the band is not associated with the OH group but presumably arises from a vibration which has considerable C=N stretching character. This absorption may allow easy identification of other complexes which contain α-dioxime ligands coordinated via their N and O atoms.

Supplementary Material Available. Fractional coordinates and thermal parameters (Table I), bond distances (Table II), important bond angles (Table III), and structure factors (14 pages). Ordering information is given on any current masthead page.

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Preparation of Macrolides via the Wittig Reaction. A Total Synthesis of (−)-Vermiculine

Sir:

The antibiotic (−)-vermiculine (**1**) was isolated in 1972 from the fermentation broth of *penicillium vermiculatum* Dangeard.[1] The originally proposed structure of a nine-membered lactone[2] was revised to that of the 16-membered dilide system **1** on the basis of an X-ray analysis.[3] Subsequently, two nonstereospecific syntheses of (±)-vermiculine were published.[4] More recently, a stereospecific synthesis via an optically active synthon of known chirality produced the unnatural enantiomer of vermiculine, allowing the 8S,16S configuration to be assigned to the natural product.[5] A feature common to all of the above syntheses is the formation of the macrolide ring by lactonization.

We would like to record the total synthesis of natural (−)-vermiculine (**1**). In our scheme (Scheme I), the Wadsworth–Emmons modification of the Wittig reaction serves to achieve the critical closure of the macrolide ring. Although this principle has been used for the construction of smaller rings,[6] we are aware of only one application to macrolide synthesis.[7]

The dithiane olefin **2**[8] was transformed into the aldehyde **3** (bp 100-104 °C (0.5 mm)) via its lithium salt in standard fashion[9] (Scheme I). In a 1,3-dipolar cycloaddition, acetonitrile oxide was added regiospecifically[10] to the terminal double bond to yield the isoxazoline **4** (mp 72-73 °C). Simultaneous aldehyde reduction and cleavage of the isoxazoline ring occurred upon treatment with diisobutylaluminum hydride, producing stereospecifically the aminodiol **5a**. Its relative configuration is the result of hydride addition to the imino double bond from the less hindered side of the isoxazoline ring in **4**, apparently prior to the cleavage of the N-O bond.[11]

Scheme I[a]
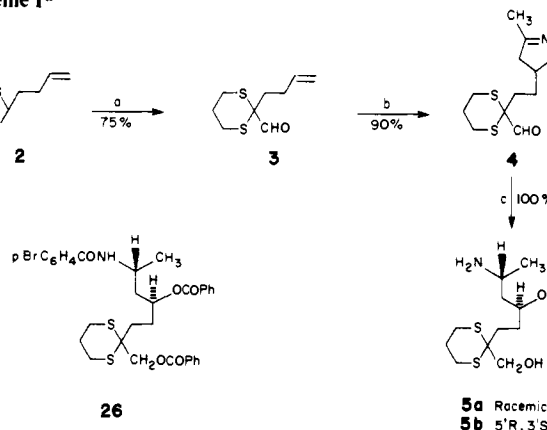
[a] (a) BuLi, then DMF, THF, −30 °C → room temperature. (b) PhNCO, EtNO$_2$, NEt$_3$ catalyst, PhH. (c) *i*-Bu$_2$AlH, THF, 55 °C.