is observed between the amido NH bonds of **2** and C_6D_6 after days at 100 °C in a sealed tube. Both five-coordinate arylimido compounds do not react with 3-hexyne.[6]

Acknowledgment. We thank the National Science Foundation (Grant CHE-8915573) for support of this research.

Supplementary Material Available: Description of the experimental procedure for the X-ray structural determination and tables of crystallographic data, positional parameters and isotropic thermal parameters, anisotropic thermal parameters, complete bond distances, and complete bond angles for **2** and **4** (57 pages); tables of structure factors for **2** and **4** (40 pages). Ordering information is given on any current masthead page.

Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Robert D. Profilet
Cesar H. Zambrano
Phillip E. Fanwick
John J. Nash
Ian P. Rothwell*

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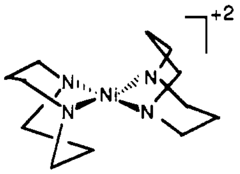
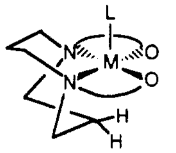
Sterically Protected Nickel(II) in a N_2S_2 Donor Environment: 1,5-Bis(mercaptoethyl)-1,5-diazacyclooctane and Its Methylated Derivative

The macrocyclic diazacyclooctane ligand, DACO,[1] offers several attractive features as a framework for ligand development: an exceptionally strong ligand field, unique conformational requirements (aptly demonstrated in the $(DACO)_2Ni^{II}$ complex ion),[2a,b] and the potential for further functionalization. Such functionalization led to the synthesis of 1,5-diazacyclooctane-1,5-diacetato, DACODA, derivatives of Co and Ni for which the chair/boat configurations of the $Ni-N(CH_2CH_2CH_2)N$ rings resulted in the first recognized examples of agostic C–H interactions in classical coordination complexes.[3,4] In the case of M = Co, a unique heterolytic C–H bond cleavage followed the oxidation of Co(II) to Co(III).[4]



$(DACO)_2$ Ni(II) [2a,b]

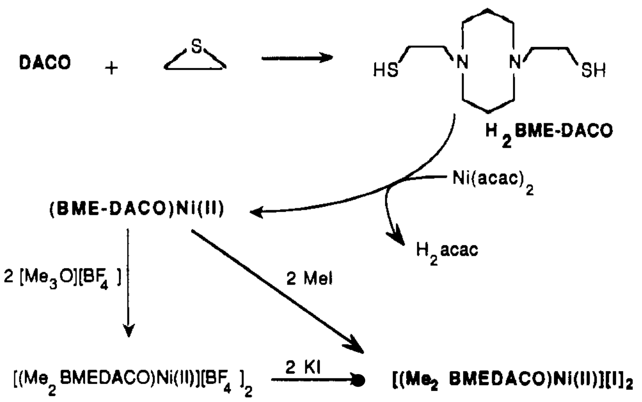


(DACODA)M(II) [3,4]

N⌒O is NCH_2CO_2

This interesting chemistry prompted our investigation of DACO modified with sulfur ligation sites for the following purposes: such donor environments for Ni^{2+} are expected to be important as prototypes for the active site in nickel-containing hydrogenases,[5] the ligand field and presumably the redox properties of Ni may be systematically tuned by variation of additional axial ligand(s), and, on the basis of precedents from organometallic chemistry[6] and recent similar bioinorganic model chemistry,[7] we reason that the flap-over ring could provide a sterically protected metal coordination site capable of supporting interactions of small molecules, such as H_2 or CO_2, or a highly reactive metal hydride functionality. (Although there are no known biomolecules containing metal hydrides, there are growing allegations of their feasibility as intermediates in reaction pathways,[7-10] and examples of well-characterized "organometallic" nickel hydrides are legend.)[11] The synthesis of 1,5-bis(mercaptoethyl)-1,5-diazacyclooctane, BME-DACO, and the complexes (BME-DACO)Ni^{II} and $[Me_2BME\text{-}DACONi][I]_2$ is reported herein. The latter is the first reported structure of the well-studied sulfur alkylation of Busch-type N_2S_2 complexes[12] and answers an old question of whether the thioether produced is Ni-coordinated.

Scheme I



The BME-DACO ligand is obtained as its thiol (Scheme I), via reaction of diazacyclooctane[13] with ethylene sulfide,[14] and used in situ. Addition of 1:1 equiv of the thiol to nickel acetylacetonate yields a yellow-brown toluene solution from which a purple powder (40–60% yield based on DACO) precipitates on standing overnight. The complex is readily soluble in water, acetonitrile, and methanol and less so in THF and acetone, in all yielding purple, air-stable solutions. Crystalline material, formulated as $Ni(C_{10}H_{20}N_2S_2)$ according to elemental analysis,[15a] is produced on layering pentane over an acetone solution of (BME-DACO)Ni^{II}. Diamagnetism is inferred from sharp resonances in the complex ^1H NMR spectrum, which differ substantially from that of the free ligand.[16] Broad bands of λ_{max} = 602, 500, and 346 nm (sh

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(1) Musker, W. K.; Hussain, M. S. *Inorg. Chem.* **1966**, *5*, 1416.

(2) (a) Royer, D. J.; Schievelbein, V. H.; Kalyanaraman, A. R.; Bertrand, J. A. *Inorg. Chim. Acta* **1972**, *6*, 307. (b) Boeyens, J. C. A.; Fox, C. C.; Hancock, R. D. *Inorg. Chim. Acta* **1984**, *87*, 1. (c) Yamaki, S.; Fukuda, Y.; Sone, K. *Chem. Lett.* **1982**, 269. (d) Fecher, B.; Elias, H. *Inorg. Chim. Acta* **1990**, *168*, 179. (e) Billo, E. J. *Inorg. Chem.* **1973**, *12*, 2783. (f) Hay, R. W.; Pujari, M. P.; Bembi, R. *Inorg. Chim. Acta* **1984**, *85*, 191. (g) Musker, W. K.; Hussain, M. S. *Inorg. Chem.* **1969**, *8*, 528.

(3) (a) Legg, J. I.; Neilson, D. O.; Smith, D. L.; Larsen, M. L. *J. Am. Chem. Soc.* **1968**, *90*, 5030. (b) Nielson, D. O.; Larson, M. L.; Willet, R. D.; Legg, J. I. *J. Am. Chem. Soc.* **1971**, *93*, 5079.

(4) Broderick, W. E.; Jordan, R. F.; Kanamori, K.; Legg, J. I.; Willet, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 7122.

(5) (a) *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Ed.; VCH Publishers, Inc.: New York, 1988. (b) Krüger, H.-J.; Holm, R. H. *Inorg. Chem.* **1987**, *26*, 3645; **1989**, *28*, 1148. (c) Kumar, M.; Day, R. O.; Colpas, G. J.; Maroney, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5974. (d) Kumar, M.; Colpas, G. J.; Day, R. O.; Maroney, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 8323 and references therein.

(6) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

(7) Stavropoulos, P.; Carrie, M.; Muetterties, M. C.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 5385.

(8) (a) Kojima, N.; Fox, J. A.; Hausinger, R. P.; Daniels, L.; Orme-Johnson, W. H.; Walsh, C. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 378. (b) Van der Zwaan, J. W.; Albracht, S. P. J.; Fontijn, R. D.; Slater, E. C. *FEBS Lett.* **1985**, *179*, 271.

(9) Teixeira, M.; Moura, I.; Xavier, A. V.; DerVartanian, D. V.; Legall, J.; Peck, H. D., Jr.; Huynh, B. H.; Moura, J. J. G. *Eur. J. Biochem.* **1983**, *130*, 481.

(10) Orme-Johnson, W. H.; Averill, B. A. *J. Am. Chem. Soc.* **1978**, *100*, 5234.

(11) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. Darensbourg, M. Y.; Riordan, C. G.; Ludvig, M. *Inorg. Chem.* **1989**, *28*, 1630.

(12) Busch, D. H.; Jicha, D. C.; Thompson, M. C.; Wrathall, J. W.; Blinn, E. *J. Am. Chem. Soc.* **1964**, *86*, 3642.

(13) Buhle, E. L.; Moore, A. M.; Wiselogle, F. Y. *J. Am. Chem. Soc.* **1943**, *65*, 29.

(14) Wineman, R. J.; Gollis, M. H.; James, J. C.; Pomponi, A. M. *J. Org. Chem.* **1962**, *27*, 4222.

(15) Elemental analysis (Galbraith Laboratories): (a) Calcd for $NiN_2S_2C_{10}H_{20}$ (found): C, 41.3 (40.8); H, 6.92 (6.90); N, 9.62 (9.42). (b) Calcd for $NiN_2S_2C_{12}H_{26}I_2$ (found): C, 25.1 (24.9); H, 4.56 (4.66); N, 4.87 (4.90). (c) Calcd for $NiN_2S_2C_{12}H_{26}Br_2$ (found): C, 31.7 (31.7); H, 5.32 (5.56); N, 5.68 (5.67).

(16) ^1H NMR (CD_3OD), δ (ppm): 3.23, m (4 H); 3.13, m (2 H); 2.62, t (3 H); 2.51, m (4 H); 2.08, m (2 H); 1.82, m (4 H).

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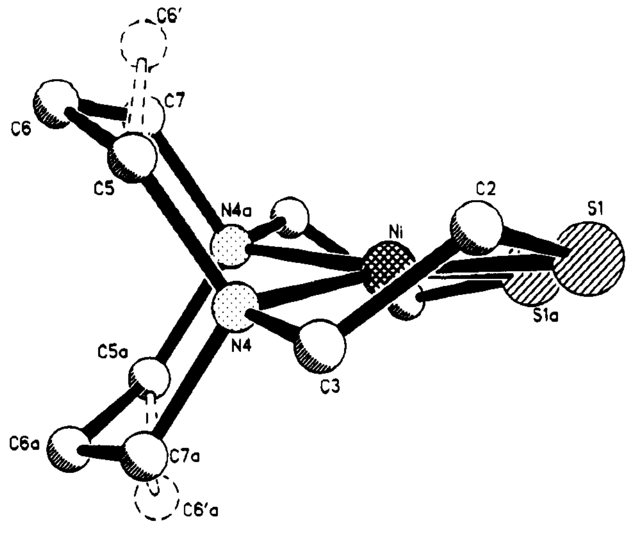

Figure 1. Molecular structure of (BME-DACO)Ni^{II}. The atoms labeled a are related by a crystallographic center of symmetry. Bond lengths (Å): Ni–S(1), 2.159 (2); Ni–N(4), 1.985 (6); S(1)–C(2), 1.824 (9); C(3)–N(4), 1.506 (10); C(6)–C(7), 1.407 (13); C(2)–C(3), 1.496 (13); N(4)–C(5), 1.505 (10); C(5)–C(6), 1.419 (15); C(7)–N(4a), 1.479 (10). Selected bond angles (deg): S(1)–Ni–S(1a), 89.5 (1); N(4)–Ni–N(4a), 89.8 (3); N(4)–Ni–S(1a), 170.6 (2); N(4a)–Ni–S(1), 170.6 (2).

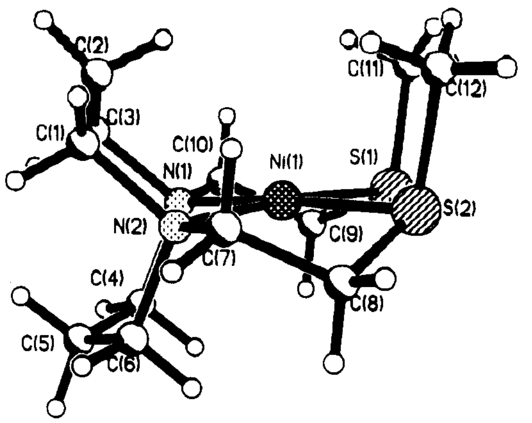

Figure 2. One of the two independent cations in the unit cell of [(Me$_2$BME-DACO)Ni][I]$_2$. Selected bond lengths (Å): Ni(1)–S(1), 2.211 (3); Ni(1)–S(2), 2.104 (3); Ni(1)–N(1), 1.974 (7); Ni(1)–N(2), 1.972 (7); S(1)–C(11), 1.804 (11); S(2)–C(12), 1.826 (10); S(2)–C(8), 1.797 (9). Selected bond angles (deg): S(1)–Ni(1)–S(2), 88.3 (1); N(1)–Ni(1)–N(2) 91.1 (3); N(1)–Ni(1)–S(1), 90.3 (2); N(2)–Ni(1)–S(2), 90.0 (2); Ni(1)–S(1)–C(11), 108.0 (4); Ni(1)–S(2)–C(12), 108.0 (4); Ni(1)–S(2)–C(8), 96.3 (3); N(2)–Ni–S(1), 174.3 (2).

on intense charge-transfer band) are observed in the vis–UV spectrum in CH_3CN solution. The cyclic voltammogram, measured in CH_3CN with 0.1 M $[Et_4N][PF_6]$ as supporting electrolyte, shows two features: an irreversible anodic wave at +0.40 V (vs Ag/AgCl) is assigned to a metal-based (presumably $Ni^{2+} \rightarrow Ni^{3+}$) oxidation, and a quasi-reversible cathodic wave at −0.5 V results from a low-concentration, unidentified species produced only after the oxidation.

Addition of excess MeI (3 equiv) to (BME-DACO)Ni^{II} (0.2 g in 10 mL of CH_3CN) affords dark crystals of the dimethylated derivative on standing for 72 h. When the solid is redissolved in CH_3CN, a green solution is obtained from which a red-brown powder is regained on evaporation of solvent. The coral-colored BF_4^- salt produced by methylation with Meerwein's reagent can be converted into the green derivative upon addition of I^- (Scheme I). The I^- salt dissolves readily in water to give a coral-colored solution; it is bright yellow in CH_2Cl_2. The cyclic voltammogram shows a reversible wave at −0.40 V in CH_3CN, assigned to the Ni^{2+}/Ni^+ couple. This assignment is supported by the observation of an EPR-active species of $S = {}^1/_2$ after bulk chemical reduction with Zn^0. Magnetic susceptibility studies found [(Me$_2$BME-DACO)Ni][I]$_2$ to be diamagnetic in the solid state, and frozen solutions (in a mixture of CH_2Cl_2 and CH_3CN at 77 and 4 K) were EPR silent. At similar concentrations (0.01 M in CD_3CN) ^1H NMR spectra were observed; however 0.005 M solutions of analytically pure[15b] [(Me$_2$BME-DACO)Ni][I]$_2$ were paramagnetic (Evans' method $\mu_{eff} = 2.71\ \mu_B$[17] at 22 °C). Hence, solutions display the complicated magnetic (and spectral) behavior of the "poised system" equilibria,[18] well-documented for Ni(II) systems,[19] i.e., showing a coordination sphere and spin state interdependence on concentration, counterion, solvent, solvent activity, and temperature.[20]

As demonstrated in Figures 1 and 2, the molecular structures of the new complexes contain nickel in a nearly square-planar N_2S_2 environment.[21] A slight tetrahedral twist is seen for the neutral (BME-DACO)Ni^{II} complex for which the angle of intersection of the normals of the S(1)–Ni–S(1A) and N(4)–Ni–N(4A) planes is 13.3°. Methylation of the sulfurs results in significant increases of the Ni–S distances by 0.05 Å whereas the Ni–N distances contract significantly by 0.01 Å in the dication as compared to the neutral derivative. The ethylene linkages between N and S eclipse each other across the NiN_2S_2 square plane for the cation whereas they are staggered in the neutral complex.

The (BME-DACO)Ni^{II} structure can be refined in either the space group *Cc* or *C*2/*c*. The latter was preferred and found the central carbon of the six-membered $NiNCH_2CH_2CH_2N$ rings to be disordered between two positions (C(6), C(6′)). The site occupation factor for C(6) was refined to 75%, and for C(6′), to 25%. That is, the DACO conformer preferred on the basis of analysis of the free ligand[1] is in a smaller amount in the complexed structure. The packing diagram (supplementary material) suggests that intermolecular steric interactions may disfavor the chair/boat form of the six-membered metalla rings. The six-membered rings in [(Me$_2$BME-DACO)Ni][I]$_2$ clearly adopt chair/boat configurations with the boat form placing the C–H of the central CH_2 group within 2.91 and 2.64 Å, respectively, of Ni. Both methyl groups are on the same side of the NiN_2S_2 square plane, with Ni–C$_{Me}$ distances >3.0 Å, presumably in order to minimize cross-plane interactions with the DACO ring hydrogens. Thus the nickel is well shielded from axial interactions on the side of the two methyl groups and the boat portion of the Ni–DACO cycle but is open on the other. In fact, the packing diagram (supplementary material) shows one iodide counterion approaching that open side with the other dispersed in the lattice. Interestingly, the closer iodide is almost equidistant from Ni, 3.60 Å, and from each of the sulfurs, 3.65 and 3.75 Å. The observed equivalent conductance in CH_3CN of 166 Ω cm^2 mol^{-1} is appropriate for a 1:1 electrolyte, i.e., [(Me$_2$BME-DACO)NiI]$^+$[I]$^-$ and the green complex observed in CH_3CN is tentatively formulated as this 5-coordinate species. That a metal sequestered in the BME-DACO^{2-} ligand can be 5-coordinate has been demonstrated in the molecular structure of [(BME-DACO)Fe]$_2$, in which square-pyramidal Fe binds a sulfur from an adjacent (BME-DACO)Fe in an axial position, producing a 2Fe–2S core.[22,23] In

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(17) Gerger, W.; Mayer, U.; Gutmann, V. *Monatsh. Chem.* **1977**, *108*, 417.

(18) Busch, D. H. *Adv. Chem. Ser.* **1966**, *40*, 616.

(19) Di Casa, M.; Fabbrizzi, L.; Mariani, M.; Seghi, B. *J. Chem. Soc., Dalton Trans.* **1990**, 55. Fabbrizzi, L. *Inorg. Chem.* **1977**, *16*, 2667. Sabatini, L.; Fabbrizzi, L. *Inorg. Chem.* **1978**, *18*, 438.

(20) The bromide salt of the bicyclic complex, formed by reaction of $Br(CH_2)_3Br$ with (BME-DACO)Ni^{II}, i.e., [((CH$_2$)$_3$BME-DACO)Ni][Br]$_2$,[15c] has a visible spectrum highly similar to that of the BF_4^- salt of (Me$_2$BME-DACO)Ni^{2+} in CH_3CN, suggesting that in this case the increased coverage of the Ni(II) center prevents coordination by bromide or solvent. A full report of this and the structures reported above is in preparation for submission to *J. Am. Chem. Soc.*

(21) X-ray diffraction data were collected at 23 °C on a Nicolet R3m/V diffractometer. Structures were solved by standard procedures; empirical absorption corrections were applied. (BME-DACO)Ni: a = 16.184 (5), b = 7.791 (3), c = 10.671 (3) Å; β = 113.30 (2)°; space group *C*2/*c*; $Z = 4$; 2θ range = 4.0°/50.0°; no. of unique observed reflns = 831 ($I > 3\sigma(I)$); R (R_w) = 6.33 (7.48). [(Me$_2$BME-DACO)Ni][I]$_2$: a = 13.001 (4), b = 17.594 (8), c = 17.603 (7) Å; β = 92.26 (3)°; space group $P2_1/n$; $Z = 8$; 2θ range = 4.0°/50.0°; no. of unique observed reflns = 5531 ($I > 2\sigma(I)$; R (R_w) = 5.35 (7.22).

view of the recent demonstrations of the importance of a sulfur-rich environment about Ni in order to observe both the redox properties[24] and the functionalities[7] appropriate to biological nickel, the ability of our new complexes to bind a fifth anion is important and studies of exchange of I^- for RS^- (and H^-) are in progress.

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Supplementary Material Available: Tables of atom positional parameters for (BME-DACO)Ni^{II} [(Me_2BME-DACO)Ni][I]$_2$ and a crystal packing diagram for [(Me_2BME-DACO)Ni][I]$_2$ (3 pages). Ordering information is given on any current masthead page.

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[22] Mills, D. K.; Farmer, P. J.; Reibenspies, J. H.; Darensbourg, M. Y. To be submitted for publication.

[23] Karlin, K. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 6951. A similar tetradentate N_2S_2 donor ligand, *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine, produced a dimeric iron complex analogous to [(BME-DACO)Fe]$_2$.

[24] Fox, S.; Wang, Y.; Silver, A.; Millar, M. *J. Am. Chem. Soc.* **1990**, *112*, 3218.

Department of Chemistry
Texas A&M University
College Station, Texas 77843

Daniel K. Mills
Joseph H. Reibenspies
Marcetta Y. Darensbourg*

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Synthesis and Crystal Structure of a Nine-Coordinate Gadolinium(III) Complex of 1,7,13-Triaza-4,10,16-trioxacyclooctadecane-*N,N',N''*-triacetic Acid

The synthesis of the [18]-N_3O_3 triacetic acid and the crystal structure of its gadolinium(III) complex are described, providing the first 9-coordinate Gd(III) complex in which all donor atoms are derived from the same ligand. There is great interest in the design and synthesis of new ligands for the complexation of Gd(III) as NMR imaging agents.[1-3] Several reports on the parent [18]-N_3O_3 macrocycle (7 in Scheme I) and two derivatives containing noncoordinating pendant substituents on the amino groups have been published.[4,5] However, there is little information about the synthetic routes employed for their preparation. Reported here is the synthesis and study of a new macrocyclic ligand, [18]-N_3O_3 triacetic acid, which forms a 9-coordinate neutral Gd(III) complex.

The synthetic route is shown in Scheme I. Compounds **1-5** were prepared with published procedures[6] or published methods for intermediates employed in the synthesis of macrocyclic and macrobicyclic ligands.[7] In all reaction steps the yields were higher than 80%. [18]-N_3O_3·3HBr (**7**) was obtained by the condensation

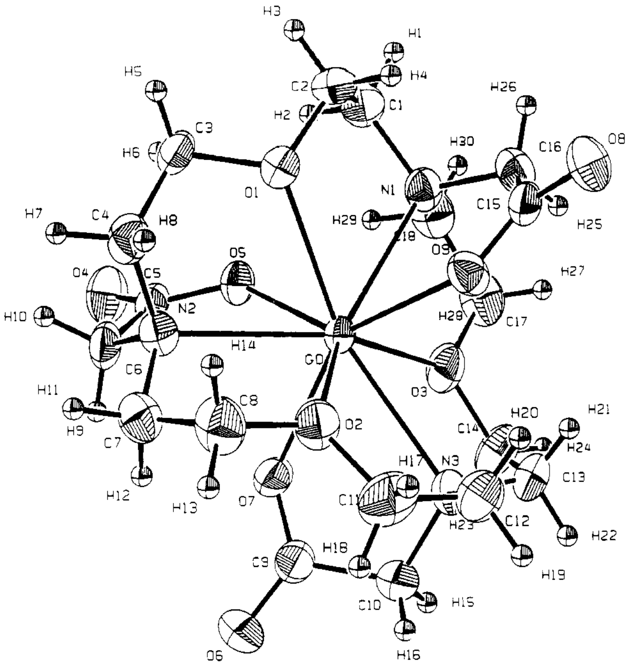

Figure 1. ORTEP diagram of the X-ray crystal structure of $GdC_{18}H_{30}N_3O_9$. Thermal ellipsoids are shown at the 50% probability level.

Table I. Selected Bond Lengths (Å) and Angles (deg) for $GdC_{18}H_{30}N_3O_9$

Gd-O(5)	2.310 (4)	Gd-O(1)	2.609 (3)
Gd-O(9)	2.328 (4)	Gd-N(1)	2.641 (4)
Gd-O(7)	2.341 (3)	Gd-N(2)	2.642 (5)
Gd-O(2)	2.467 (3)	Gd-N(3)	2.686 (4)
Gd-O(3)	2.508 (3)		
N(1)-Gd-N(2)	124.3 (1)	O(7)-Gd-N(3)	64.8 (1)
N(1)-Gd-N(3)	115.7 (1)	O(9)-Gd-N(2)	121.2 (1)
N(2)-Gd-N(3)	119.7 (1)	O(5)-Gd-N(2)	67.6 (1)
O(1)-Gd-N(2)	64.8 (1)	O(2)-Gd-O(3)	130.0 (1)
O(3)-Gd-N(1)	64.0 (1)	O(7)-Gd-O(2)	77.6 (1)
O(2)-Gd-N(2)	66.0 (1)	O(5)-Gd-O(3)	86.7 (1)

Table II. Atomic Coordinates

atom	*x*	*y*	*z*	*B*(eq), Å^2
Gd	0.10900 (2)	0.35741 (2)	0.13772 (1)	2.04 (1)
O(1)	0.1728 (4)	0.5876 (3)	0.1123 (1)	2.9 (1)
O(2)	0.0471 (4)	0.2940 (4)	0.0369 (1)	3.4 (2)
O(3)	0.0189 (4)	0.2709 (4)	0.2244 (1)	3.5 (2)
O(4)	0.5777 (4)	0.3616 (4)	0.2160 (2)	4.4 (2)
O(5)	0.3335 (3)	0.3944 (3)	0.1959 (1)	2.8 (1)
O(6)	0.2333 (4)	−0.0277 (4)	0.0961 (2)	4.5 (2)
O(7)	0.2203 (4)	0.1589 (3)	0.1377 (2)	3.1 (1)
O(8)	−0.2946 (4)	0.6009 (4)	0.1157 (2)	4.4 (2)
O(9)	−0.1176 (4)	0.4585 (3)	0.1087 (1)	3.0 (1)
N(1)	0.0409 (4)	0.5249 (4)	0.2116 (2)	2.8 (2)
N(2)	0.3326 (5)	0.3806 (4)	0.0795 (2)	2.7 (2)
N(3)	−0.0816 (5)	0.1639 (4)	0.1160 (2)	3.2 (2)
C(1)	0.1352 (6)	0.6386 (5)	0.2083 (2)	3.6 (2)
C(2)	0.1220 (6)	0.6828 (5)	0.1481 (3)	3.6 (2)
C(3)	0.3255 (5)	0.6064 (5)	0.1039 (2)	3.0 (2)
C(4)	0.3527 (6)	0.5113 (5)	0.0605 (2)	3.4 (2)
C(5)	0.4612 (5)	0.3683 (4)	0.1820 (2)	2.8 (2)
C(6)	0.4664 (5)	0.3405 (5)	0.1199 (2)	3.0 (2)
C(7)	0.3063 (6)	0.2978 (5)	0.0289 (2)	3.5 (2)
C(8)	0.1497 (7)	0.3114 (6)	−0.0030 (2)	4.0 (3)
C(9)	0.1643 (5)	0.0595 (5)	0.1143 (2)	3.0 (2)
C(10)	−0.0021 (6)	0.0434 (5)	0.1113 (3)	4.2 (3)
C(11)	−0.0769 (7)	0.2169 (6)	0.0156 (3)	4.8 (3)
C(12)	−0.1736 (6)	0.1967 (6)	0.0610 (3)	4.2 (3)
C(13)	−0.1709 (6)	0.1598 (5)	0.1626 (3)	4.1 (3)
C(14)	−0.0700 (7)	0.1584 (6)	0.2193 (3)	4.5 (3)
C(15)	−0.1825 (5)	0.5403 (5)	0.1357 (2)	3.0 (2)
C(16)	−0.1178 (6)	0.5584 (5)	0.1985 (2)	3.4 (2)
C(17)	−0.0020 (7)	0.3472 (6)	0.2728 (2)	4.2 (3)
C(18)	0.0778 (6)	0.4697 (6)	0.2693 (2)	3.9 (2)

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(1) Lauffer, R. C. *Chem. Rev.* **1987**, *87*, 901.

(2) Furmanski, P.; Longley, C. *Cancer Res.* **1988**, *48*, 4604.

(3) Plehwe, W. E.; McRobbie, D. W.; Lerski, R. A.; Kohner, E. M. *Invest. Opthamol. Visual Sci.* **1988**, *29*, 663.

(4) Graf, E.; Lehn, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 5022.

(5) Beer, P. D.; Crowe, D. B.; Main, B. XIVth International Symposium on Macrocyclic Chemistry, June 25–28, 1989, Townsville, Queensland, Australia; Paper P12/T.

(6) Bogatskii, A. V.; Luk'yanenko, N. G.; Kinichenko, T. I. *Zh. Org. Khim.* **1980**, *16*, 1301.

(7) Deitrich, B.; Hosseini, M. W.; Lehn, J. M.; Sessions, R. B. *Helv. Chim. Acta* **1985**, *68*, 289.

(8) Kahwa, I. A.; Folkes, S.; Williams, D. J.; Ley, S. V.; O'Mahoney, C. A.; McPherson, G. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1531.

0020-1669/90/1329-4366$02.50/0