apparently does not have a perovskite-type structure. This result parallels the stability range found for oxide perovskites where $0.8 \lesssim t \leq 1$.

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Crystal and Molecular Structure of an Unusual Five-Coordinated Aminecarboxylic Acid Nickel(II) Chelate

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Abstract: The complex 1,5-diazacyclooctane-*N,N'*-diacetatoaquonickel(II) dihydrate ($NiO_7N_2C_{10}H_{22}$) crystallizes in the monoclinic space group $P2_1/c$ with a = 14.412 (5), b = 7.316 (5), c = 14.431 (5) Å, β = 112.90 (4)°, and Z = 4. The measured and calculated densities are, respectively, 1.59 and 1.616 g cm^{-3}. A single-crystal study was undertaken using a Picker diffractometer equipped with a GE single-crystal orienter. A full-matrix least-squares refinement on 1622 unique nonzero reflections resulted in a final value of R = 0.083 without the inclusion of hydrogen atoms. The tetradentate aminecarboxylate ligand is coordinated in a plane with a water molecule occupying an apical position to form an approximate square pyramid. The unique aspect of the structure is a sterically forced five-coordination sphere about the nickel atom with a methylene hydrogen blocking the sixth coordination position. Complexes of this ligand are of particular interest since they appear to maintain their five-coordinate geometry in aqueous solution, a property seldom encountered for five-coordinate complexes.

The ability to stabilize various geometries by steric hinderance offers an approach to the study of metal ions in less common coordination geometries and oxidation states.[1,2] Recent studies of the complexes of a novel tetradentate ligand, 1,5-diazacyclooctane-*N,N'*-diacetic acid (DACODA), synthesized in this laboratory, have indicated that one of the normal octahedral sites is not available for coordination.[3] The approach was to design a tetradentate ligand which would coordinate in a plane and force a portion of the chelate framework across one of the axial coordination positions. By adding two acetic acid arms to the nitrogen of 1,5-diazacyclooctane (DACO), such a ligand is obtained. On coordination the two glycinate rings must be nearly coplanar, thus fixing a planar coordination for the tetradentate ligand, as shown in Figure 1. The eight-membered diazacyclooctane ring's geometry is then brought into play, as illustrated in Figure 1. Carbon atoms 3 and 7 of the DACO ring may be positioned in one of three ways: (1) both carbons over the central metal ion, (2) one carbon over the metal and one away from the metal ion, or (3) both carbon atoms away from the central metal ion. From space-filling models, (3) is not expected because hydrogen atoms from different methylene groups are forced into the same location. Both of the remaining two configurations are possible; however, the one with only one carbon forward over the metal might be favored because it allows a solvent molecule to coordinate at one of the axial sites, presumably fixing a square-pyramidal geometry. Because of the unusual properties observed for various metal ion complexes of DACODA and because of the similarity of the solid- and solution-state geometries,[3] the structure of the nickel(II) complex was undertaken, and the results of this study are given in this report.

Experimental Section

Unit Cell and Data Collection. The compound was made by mixing $NiSO_4$ with the barium salt of 1,5-diazacyclooctane-*N,N'*-diacetic acid,[4] filtering off the $BaSO_4$, and evaporating the resulting solution to form the blue-green crystals of 1,5-diazacyclooctane-*N,N'*-diacetatoaquonickel(II) dihydrate ($NiO_7N_2C_{10}H_{22}$). From $h0l$, $h1l$, and $h2l$ Weissenberg photographs and a $0kl$ precision photograph, the systematic absences of $k = 2n + 1$ for $0k0$ and $l = 2n + 1$ for $h0l$ fixed the space group as $P2_1/c$.[5] A crystal 0.20 × 0.17 × 0.14 mm in size was mounted along its b axis and aligned on a GE single-crystal orienter, using a Picker diffractometer. The lattice constants at room temperature were measured directly as a = 14.412 (5), b = 7.316 (5), c = 14.431 (5) Å, β = 112.92 (4)°. The observed density (from flotation ρ_{obsd} = 1.59 g cm^{-3}) is in good agreement with the calculated density (ρ_{calcd} = 1.616 g cm^{-3} for Z = 4, M = 341.01 g mol^{-1}).

The previously mentioned crystal was used to collect the data with Zr-filtered Mo Kα radiation. A θ–2θ scan rate of 2°/min was used. A 4-sec background was recorded on each side of the scan, and a 40-sec peak scan was employed. Data were collected in the form of hkl and $hk\bar{l}$ out to 2θ = 45°. Those reflections with a net count of less than 6% of background were considered unobserved. Of

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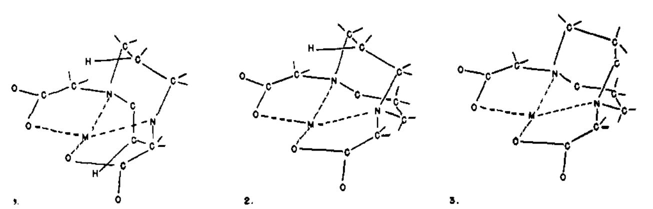

Figure 1. Possible configurations for coordination of 1,5-diazacyclooctane-*N*,*N*′-diacetate to a metal ion.

the 1845 reflections measured, 1662 were considered observed. The weighting scheme of

$$\sigma = 1/2\sqrt{\frac{(\text{total count}) + (\text{background}) + 0.01(\text{net count})^2 + 0.01(\text{background})^2}{(\text{net count})}}$$

was used to assign a weight to each reflection.[6] No absorption corrections were made.

Elucidation and Refinement of the Structure. A three-dimensional Patterson function[7] was computed from the reduced data and the fractional coordinates for nickel of $x = 0.237$, $y = 0.1875$, and $z = 0.131$ were obtained from the Harker sections. A structure factor calculation gave a value of $R = 0.35$ for the 491 strongest reflections. The nickel positional and isotropic temperature factor parameters were refined by one cycle of least squares ($R = 0.30$),[8] and a three-dimensional Fourier map was generated with phases based on the nickel position only. From this Fourier map, the positions of the four ligand oxygens, the coordinated water oxygen, and the two nitrogen atoms were found and refined *via* least squares. A difference Fourier map based on these positions was calculated, and the remaining nonhydrogen atoms were located. The positional and anisotropic thermal parameters were refined by the least-squares method and the results converged to $R_3 = 0.083$ (R_3. $[\Sigma_{hkl}w_{hkl}(|F_o| - |F_c|)^2/\Sigma_{hkl}w_{hkl}|F_o|^2]^{1/2}$). The scattering factor tables were obtained from ref 9. Anomalous dispersion corrections were not made.

The locations of all hydrogen atoms bonded to the carbon atoms of the ligand were found from a difference Fourier map. Some, but not all, of the remaining hydrogen atoms were also located. No remaining peaks above 0.4 e/Å^3 were found. Each hydrogen atom was assigned an isotropic thermal parameter of $B = 4.0$, and the positional parameters only were refined by least squares. The final hydrogen–carbon bond lengths varied from 0.98 to 1.26 Å. The hydrogen–oxygen bond distances refined either to very short bond lengths (0.4 Å) or to very long bond lengths (1.4 Å). These were then excluded from the final structure factor calculation. A final value of $R = 0.074$ was obtained with all reflections included.[10] The atomic positions with their estimated standard deviations are collected in Tables I and II. The interatomic distances with their estimated standard deviations are collected in Table III;[11] bond angles with their estimated standard deviations are shown in Table IV.[11]

The Crystal and Molecular Structure

Table I. Atomic Positions

Atom	*x*	*y*	*z*
Ni	0.76636 (8)	0.68790 (16)	0.37302 (8)
O(1)	0.8438 (5)	0.4548 (9)	0.4132 (5)
O(2)	0.6575 (5)	0.6232 (10)	0.4188 (5)
O(3)	0.9683 (6)	0.3033 (12)	0.3946 (5)
O(4)	0.5139 (5)	0.7300 (13)	0.4186 (6)
O(5)	0.8579 (5)	0.8416 (10)	0.4876 (5)
O(6)	0.6269 (5)	0.2859 (10)	0.4927 (5)
O(7)	0.8259 (5)	0.1797 (10)	0.5356 (5)
N(1)	0.8370 (6)	0.7100 (11)	0.2766 (6)
N(2)	0.6649 (5)	0.8738 (10)	0.2868 (5)
C(1)	0.8691 (7)	0.8981 (16)	0.2646 (8)
C(2)	0.7804 (8)	1.0263 (16)	0.2160 (7)
C(3)	0.7102 (7)	1.0544 (14)	0.2727 (8)
C(4)	0.6077 (7)	0.7800 (14)	0.1876 (7)
C(5)	0.6600 (8)	0.6054 (15)	0.1764 (8)
C(6)	0.7698 (8)	0.6268 (15)	0.1811 (7)
C(7)	0.9323 (7)	0.5987 (16)	0.3225 (9)
C(8)	0.9128 (8)	0.4380 (15)	0.3804 (8)
C(9)	0.5879 (8)	0.7409 (17)	0.3967 (8)
C(10)	0.5972 (7)	0.9153 (16)	0.3409 (8)
H(1,1)	0.918 (6)	0.863 (13)	0.230 (7)
H(2,1)	0.912 (6)	0.941 (13)	0.336 (6)
H(1,2)	0.828 (6)	1.155 (13)	0.218 (6)
H(2,2)	0.727 (6)	0.974 (13)	0.132 (7)
H(1,3)	0.752 (7)	1.215 (14)	0.307 (7)
H(2,3)	0.643 (7)	1.164 (14)	0.236 (7)
H(1,4)	0.603 (7)	0.884 (13)	0.131 (7)
H(2,4)	0.526 (7)	0.779 (14)	0.153 (7)
H(1,5)	0.659 (7)	0.520 (14)	0.216 (7)
H(2,5)	0.617 (7)	0.549 (13)	0.087 (7)
H(1,6)	0.792 (7)	0.494 (14)	0.191 (7)
H(2,6)	0.764 (7)	0.695 (14)	0.121 (6)
H(1,7)	0.989 (7)	0.654 (13)	0.377 (7)
H(2,7)	0.949 (7)	0.529 (13)	0.268 (7)
H(1,10)	0.624 (7)	1.032 (14)	0.393 (7)
H(2,10)	0.521 (7)	0.890 (14)	0.280 (6)

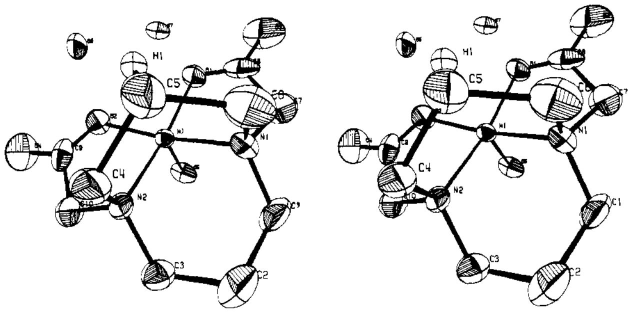

Figure 2. Stereographic illustration of the $Ni(C_{10}H_{16}N_2O_4)(H_2O)$ molecule.

The basic structure of NiDACODA is a five-coordinated square-pyramidal nickel(II) ion. From Table V it is seen that the nickel is 0.36 Å above the base of the square pyramid, which is within the reported values of 0.34–0.36 Å.[2] The Ni–N bond distances of 2.025 (7) and 2.030 (7) are at the middle of the reported range 1.95–2.11 Å.[1,12] The carboxylate oxygens in the basal plane are 1.997 (7) and 1.983 (6) Å from the nickel, while the apical water oxygen is 2.011 (7) Å. These distances are again within the reported range of 1.90–2.014 Å.[13-15] The increase of the apical Ni–O bond

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(6) Data reduction program was written locally by R. Bushey and D. N. Anderson.

(7) Patterson and Fourier maps were calculated using a program by F. R. Ahmed, National Research Council, Feb 1966, and were locally modified by D. N. Anderson.

(8) Least-squares program was written locally by D. N. Anderson.

(9) Reference 5, Vol. III, 1968, pp 202–205.

(10) A compilation of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(11) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Function and Error Program," Oak Ridge National Laboratory, locally modified by D. N. Anderson.

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Table II. Anisotropic Thermal Parameters[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	32.1 (5)	87.1 (21)	33.0 (5)	8.3 (13)	14.6 (5)	10.6 (13)
O(1)	53 (5)	113 (15)	70 (5)	34 (7)	25 (4)	24 (7)
O(2)	57 (5)	183 (18)	62 (5)	9 (8)	37 (4)	41 (7)
O(3)	58 (5)	208 (21)	114 (7)	57 (10)	3 (5)	9 (11)
O(4)	66 (5)	398 (29)	82 (6)	−1 (10)	52 (5)	−3 (10)
O(5)	59 (5)	165 (18)	44 (4)	17 (8)	−3 (4)	−14 (7)
O(6)	48 (4)	227 (20)	77 (5)	−7 (8)	28 (4)	1 (9)
O(7)	81 (5)	140 (16)	55 (4)	7 (9)	24 (4)	−21 (8)
N(1)	42 (5)	114 (18)	64 (6)	12 (9)	27 (5)	−4 (9)
N(2)	29 (4)	96 (17)	40 (5)	−4 (7)	12 (4)	−10 (7)
C(1)	45 (7)	208 (28)	84 (9)	−6 (12)	39 (7)	54 (13)
C(2)	62 (8)	181 (27)	55 (7)	−31 (12)	28 (6)	22 (11)
C(3)	49 (7)	111 (24)	70 (8)	−9 (11)	17 (6)	21 (10)
C(4)	38 (6)	95 (22)	67 (7)	1 (10)	2 (5)	−17 (10)
C(5)	49 (7)	167 (25)	57 (7)	−1 (11)	20 (6)	−19 (10)
C(6)	56 (7)	164 (26)	46 (7)	9 (11)	12 (6)	−8 (10)
C(7)	35 (6)	178 (28)	9 (10)	23 (11)	33 (7)	17 (14)
C(8)	47 (7)	112 (26)	65 (8)	10 (12)	−11 (6)	−23 (11)
C(9)	35 (6)	278 (36)	59 (7)	−22 (12)	25 (6)	−33 (12)
C(10)	48 (7)	181 (27)	79 (8)	16 (12)	41 (6)	14 (12)

[a] $\times 10^4$.

Table III. Bond Distances, Å

Ni–O(1)	1.997 (7)	C(4)–C(5)	1.52 (1)
Ni–O(2)	1.983 (6)	C(5)–C(6)	1.57 (1)
Ni–N(1)	2.025 (7)	C(1)–C(2)	1.52 (2)
Ni–N(2)	2.030 (7)	C(2)–C(3)	1.54 (1)
O(1)–C(8)	1.26 (1)	O(1)–O(7)	2.76 (1)
O(2)–C(9)	1.27 (1)	O(2)–O(6)	2.79 (1)
O(3)–C(8)	1.24 (1)	Ni–O(5)	2.011 (7)
O(4)–C(9)	1.23 (1)	Ni–H(1,5)	2.51 (9)
N(1)–C(7)	1.51 (1)	C(5)–H(1,5)[a]	0.88 (10)
N(2)–C(10)	1.50 (1)	C(5)–H(2,5)	1.27 (9)
N(1)–C(6)	1.47 (1)	O(5)–O(3)$_t$[b]	2.64 (1)
N(2)–C(4)	1.51 (1)	O(5)–O(7)$_t$[c]	2.657 (9)
N(1)–C(1)	1.49 (1)		
N(2)–C(3)	1.52 (1)		

[a] H(1,5) is for the H(1) attached to carbon atom 5. [b] Coordinates of O(3)$_t$ are related to those in Table I by the transformation $2 - x$, $1 - y$, $1 - z$. [c] Coordinates of O(7)$_t$ are related to those in Table I by the transformation x, $1 + y$, z.

Table IV. Bond Angles, Deg

N(1)–Ni–N(2)	87.7 (3)	O(1)–C(8)–C(7)	117.9 (9)
O(1)–Ni–O(2)	97.2 (3)	O(2)–C(9)–C(10)	118.3 (8)
N(1)–Ni–O(5)	100.2 (3)	N(1)–C(6)–C(5)	111.6 (8)
N(2)–Ni–O(5)	102.4 (3)	N(2)–C(4)–C(5)	111.8 (8)
N(1)–Ni–O(1)	83.9 (3)	N(1)–C(1)–C(2)	112.4 (8)
N(2)–Ni–O(2)	83.7 (3)	N(2)–C(3)–C(2)	111.0 (8)
O(1)–Ni–O(5)	97.2 (3)	C(1)–C(2)–C(3)	116.5 (8)
O(2)–Ni–O(5)	102.1 (3)	C(4)–C(5)–C(6)	116.4 (8)
Ni–O(1)–C(8)	114.0 (7)	N(1)–C(7)–C(8)	108.9 (8)
Ni–O(2)–C(9)	113.9 (6)	N(2)–C(10)–C(9)	108.1 (8)
Ni–N(1)–C(7)	105.7 (6)	C(6)–C(5)–H(1,5)	109 (6)
Ni–N(2)–C(10)	106.0 (6)	C(4)–C(5)–H(1,5)	112 (6)
Ni–N(1)–C(6)	106.7 (6)	C(6)–C(5)–H(2,5)	106 (6)
Ni–N(2)–C(4)	105.9 (6)	C(4)–C(5)–H(2,5)	114 (6)
Ni–N(2)–C(3)	114.8 (5)	O(5)–Ni–H(1,5)	173 (2)
Ni–N(1)–C(1)	114.7 (6)		
		Ni–H(1,5)–C(5)	94 (7)
O(1)–C(8)–O(3)	124.7 (11)		
O(2)–C(9)–O(4)	125.0 (11)	H(1,5)–C(5)–H(2,5)	113 (9)

Table V[a]

Atom	Distance from plane, Å
Plane 1. Basal Plane of Square Pyramid	
$0.3043x + 0.5942y + 0.7446z - 9.0406 = 0$	
O(1)*	0.020 (6)
O(2)*	−0.020 (7)
N(1)*	−0.020 (8)
N(2)*	−0.021 (7)
Ni	0.364 (1)
Plane 2. Metal–Acetate Ring No. 1	
$0.3679x + 0.5409y + 0.7563z - 9.6611 = 0$	
Ni*	0.103 (1)
O(1)*	−0.087 (6)
C(8)*	−0.051 (10)
C(7)*	0.227 (12)
N(1)*	−0.205 (8)
O(3)	−0.176 (8)
Plane 3. Metal–Acetate Ring No. 2	
$0.2578x + 0.5705y + 0.7798z - 0.8786 = 0$	
Ni*	0.166 (1)
O(2)*	−0.100 (7)
C(9)*	−0.066 (11)
C(10)*	0.199 (11)
N(2)*	−0.205 (7)
O(4)	−0.190 (8)

[a] Atoms used to define the plane are marked by an asterisk. Equation of plane in rectangular coordinates.

length over the basal Ni–O distance is probably due to hydrogen bonding, *vide infra*.

The point group symmetry about the nickel is nearly C_s, with hydrogen bonding probably accounting for deviations from this symmetry. The 1,5-diazacyclooctane portion of the ligand is bent such that half of the ring is back away from the central nickel, and the other half is bent forward over the nickel, forcing a hydrogen atom to be a distance of 2.51 (9) Å from the nickel and forming an angle of 137 (2)° for O(5)–Ni–H(1,5), as shown in Figure 2. Thus this methylene hydrogen effectively blocks the sixth coordination position to give this unusual five-coordinate nickel complex. The two waters of hydration are more than 4.1 Å from the nickel ion, thus precluding any possibility of coordination to form a six-coordinate complex.

Also shown in Table V are the data for the two glycinate chelate planes which force the square-planar base about the nickel. The two five-membered rings containing the acetate arms of the DACODA are planar within ±0.2 Å.

The hydrogen bonding in the molecule is composed of three weak and two strong oxygen–hydrogen–oxygen

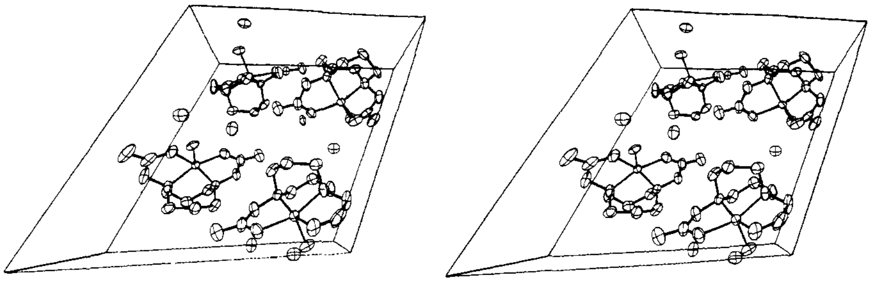

Figure 3. Stereographic illustration of packing in the unit cell.

bonds. The three bonds of O(1)–O(7), O(4)–O(6)$_t$, and O(6)–O(7) have distances of 2.76–2.80 Å, which are at the upper limit of bonds of this type.[16–18] The two shorter bonds of O(5)–O(3)$_t$ and O(5)–O(7)$_t$ at 2.64 (1) and 2.66 (1) Å correspond to moderately strong hydrogen bonds. The three weak bonds and the last strong hydrogen bonds are responsible for the packing of the two hydrated water molecules in the crystal lattice. This is illustrated in Figure 3. From a model of the nickel DACODA molecule a mirror plane containing the Ni–O(5) bond and bisecting the O(1)–Ni–O(2) angle would be expected. The bond distances and bond angles support this model except for those of O(5). The O(1)–Ni–O(5) and the O(2)–Ni–O(5) bond angles differ by 4.9 (3)° and the N(1)–Ni–O(5) and N(2)–Ni–O(5) angles differ by 2.5 (3)°. Apparently these two short hydrogen bonds are sufficiently strong to distort these bond angles and distort the complex from C_s symmetry.

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