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An Aziridine Ligand Reaction Intermediate. Crystal and Molecular Structure of $[Ni(C_{22}H_{27}N_4O_2)]Br\cdot 2H_2O$

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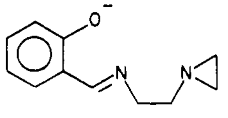
The tan intermediate formed during the reaction of bis[*N*-[2-(1-aziridinyl)ethyl]salicylaldimino]nickel(II) with hydrobromic acid to give [bis(salicylidene)ethylenediamino]nickel(II) has been characterized by X-ray crystallography. It is shown to be [2-[[[2-[[2-[2-[[[2-(1-aziridinyl)ethyl]imino]methyl]phenoxy]ethyl]amino]ethyl]imino]methyl]phenolato]nickel(II) bromide dihydrate, $[Ni(C_{22}H_{27}N_4O_2)]Br\cdot 2H_2O$. The hexadentate ligand of this complex is formed by the reaction of a phenol with an aziridine ring within the coordination sphere of a nickel(II) ion, thus constituting a template synthesis. The crystal and molecular structures were determined from single-crystal X-ray data collected in the $\theta/2\theta$ mode on an automated diffractometer. The bromide ions are 7.72 (1) Å from the Ni(II) ions. The complex crystallizes in the orthorhombic space group $P2_1cn$ with lattice constants a = 10.793 (2) Å, b = 12.478 (4) Å, and c = 18.04 (1) Å. Full-matrix least-squares refinement gave a conventional R of 0.063. The Schiff base nitrogens are mutually trans, the aziridine nitrogen is trans to the ether oxygen, and the phenolate oxygen and secondary amine nitrogen are mutually trans. The Ni–N(aziridine) distance is 2.07 (1) Å. The observed density of 1.503 g cm^{-3} agrees with the calculated value of 1.514 g cm^{-3} for Z = 4.

Introduction

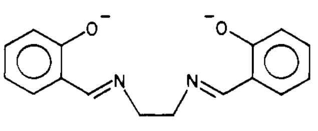
During our study of the reaction of bis[*N*-[2-(1-aziridinyl)ethyl]salicylaldimino]nickel(II), $Ni(SalAEA)_2$, with hydrobromic acid, we isolated and partially characterized a tan intermediate whose structure we now report as determined by X-ray crystallographic techniques.[2-4] The overall scheme of this reaction is presented in eq 1. The tan intermediate has an absorption at 3120 cm^{-1} indicating a secondary amine.[4]

$$Ni(SalAEA)_2 \xrightarrow{HBr} \text{green intermediate} \rightarrow \text{tan intermediate} \rightarrow Ni(Sal_2en) \quad (1)$$

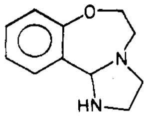
SalAEA$^-$ =



Sal$_2$en^{2-} =



Isolation of 1,2,3,5,6,11b-hexahydroimidazo[1,2-*d*][1,4]-benzoxazepine (**1**) by demetalation of the tan intermediate also



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supports the contention that at least one aziridine ring has been opened but there is no additional evidence to indicate whether the benzoxazepine is a ligand in the intermediate.[3,4] Therefore, it was of interest to study the structure of the tan intermediate by X-ray methods. The results reported here show that the two tridentate SalAEA$^-$ ligands in the starting complex are joined to form a hexadentate ligand that binds to all six coordination sites of the metal ion. The complex is a bromide salt and contains two water molecules in its lattice. The current *Chemical Abstracts* name for the compound is [2-[[[2-[[2-[2-[[[2-(1-aziridinyl)ethyl]imino]methyl]phenoxy]ethyl]amino]ethyl]imino]methyl]phenolato]nickel(II) bromide dihydrate, $[Ni(C_{22}H_{27}N_4O_2)]Br\cdot 2H_2O$.

Experimental Section

Preparation of Complex. The title compound was synthesized as previously noted.[3,4] The complex was recrystallized by gravity filtering a saturated *n*-BuOH solution at 70 °C. After the solution was allowed to stand unperturbed for 3 days, crystals suitable for X-ray analysis were filtered.

Collection and Reduction of X-ray Intensity Data. Data were collected on a Syntex P$\bar{1}$ automated diffractometer. After mounting and optical centering, automatic centering of 15 reflections with 2θ between 10 and 20° was performed. Least-squares analysis of the setting angles for these reflections yielded the orthorhombic lattice parameters (Table I). Axial photographs confirmed the chosen cell and *mmm* Laue symmetry. Crystal singularity was ensured by several ω scans of strong reflections. All data in the $+h,+k,+l$ octant of reciprocal space for which $2\theta < 50°$ were collected. No significant crystal decay was observed as shown by the standard reflections. Details of the crystal data are given in Table I.

Solution and Refinement of Structure. The following systematic absences were noted during data collection: $0k0$ ($k = 2n + 1$), $hk0$ ($h + k = 2n + 1$), and $h0l$ ($l = 2n + 1$). These absences indicate

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(1) (a) University of California at Los Angeles. (b) Bucknell University.

(2) Root, C. A.; Rising, B. A.; VanDerveer, M. C.; Hellmuth, C. F. *Inorg. Chem.* **1972**, *11*, 1489.

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Table I. Crystallographic Data for $[Ni(C_{22}H_{27}N_4O_2)]Br\cdot 2H_2O$

mol formula	$C_{22}H_{31}N_4O_4BrNi$
mol wt	554.135
a, Å	10.793 (2)
b, Å	12.478 (4)
c, Å	18.04 (1)
d(obsd), g cm^{-3}	1.503
d(calcd), g cm^{-3}	1.514
V, Å^3	2430 (2)
Z	4
space group	$P2_1cn$
abs coeff, cm^{-1}	25.33
color	light brown
habit	irreg parallelepiped
dimens, mm	0.20 × 0.25 × 0.08
λ(Mo Kα), Å	0.7107
method	$\theta/2\theta$
scan speed, deg min^{-1}	2.00
monochromator	graphite
bkgd time/scan time	1.0
stds	040, 212, 220 (measd every 97 reflcns)
2θ limits, deg	$0 < 2\theta < 50$
no. of data ($>2\sigma$)	1652
R, R_w, GOF	0.063, 0.067, 1.808
temp, °C	25

either the noncentrosymmetric space group $P2_1cn$ (nonstandard setting of $Pna2_1$, No. 33, ref 5) or the centrosymmetric space group $Pamn$ (nonstandard setting of $Pnma$, No. 62, ref 5). A statistical plot of the observed structure factor magnitudes indicated that the structure is noncentrosymmetric. Successful refinement in space group $P2_1cn$ confirmed this choice. Data were corrected for absorption with minimum and maximum transmission coefficients of 0.7244 and 0.8649, respectively.

A three-dimensional Patterson map yielded the positions of the nickel and bromine atoms. A Fourier synthesis phased by these two atoms followed by several difference Fourier maps and intermittent least-squares refinements located all non-hydrogen atoms. Hydrogen atom positions were then calculated by assuming idealized geometries with a bond distance of 1.00 Å and the isotropic thermal parameters fixed at 4.00 Å^2. Neither the positional nor thermal parameters of the hydrogens were refined. Atomic scattering factors for neutral atoms were used, and corrections for anomalous scattering were also included.[6] Anisotropic refinement of the positions and temperature factors for all non-hydrogen atoms was performed, and the convergence residuals were $R = 0.063$ and $R_w = 0.067$. A final difference Fourier map revealed peaks no larger than 0.65 e Å^{-3}. The hydrogens bonded to the two lattice waters were not located. The refined atomic coordinates were plotted with the ORTEP program of Johnson[7] (Figures 1 and 2). The final coordinates for non-hydrogen atoms are given in Table II. The hydrogen atom coordinates, thermal parameters for all atoms, and all distances and angles are in Tables IV–VIII in the supplementary material. All calculations were performed on a DEC VAX 11/780 computer.[8]

Results and Discussion

Description of Structure. The asymmetric unit consists of hexadentate $N_4O_2Ni^{II}$ cations with cis oxygen donors (see Figure 1), bromide counterions, and two lattice waters. The Ni(II) to bromide distance is 7.72 (1) Å. The shortest bromide nonbonding contact is 2.627 (6) Å with the secondary amine hydrogen, H(N4). The shortest nonbonding contact of either lattice water is the O(4) to H(8B) distance of 2.472 (13) Å. The coordination sphere of the Ni(II) ion is distorted octahedral (see Figure 2). Important bond distances and angles involving the coordination sphere are given in Table III.

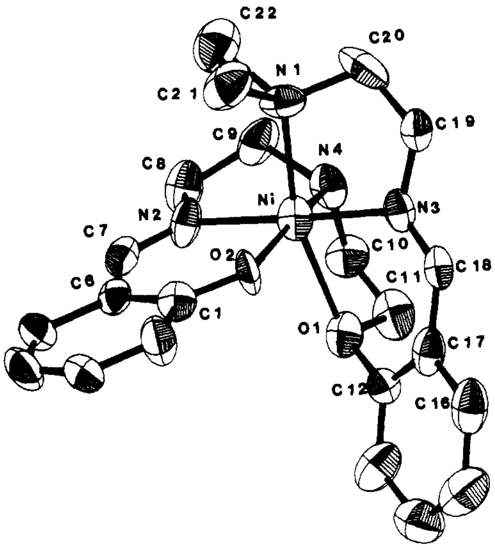


Figure 1. Molecular structure of $[Ni(C_{22}H_{27}N_4O_2)]Br\cdot 2H_2O$ with H atoms omitted. The 30% probability ellipsoids are shown.

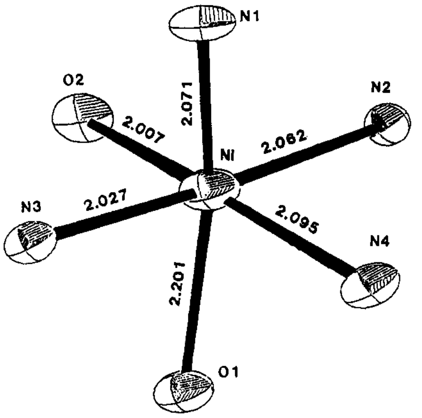
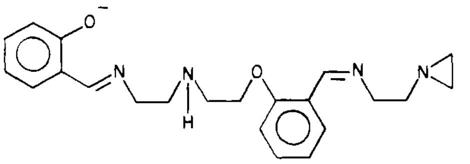


Figure 2. Coordination sphere about the Ni(II) ion in $[Ni(C_{22}H_{27}N_4O_2)]Br\cdot 2H_2O$ showing the distorted octahedral geometry and metal–donor bond lengths in angstroms.

Discussion of Structure. The ligand of the tan intermediate is the hexadentate **2**. It is easily seen that **2** can be formed by the attack of the phenol of a SalAEAH on an aziridine ring carbon of another SalAEA$^-$. The phenolate oxygen–nickel(II) distance, 2.01 Å, and the Schiff base nitrogen–nickel(II) distances, 2.03 and 2.06 Å, are within 0.02 Å of the values for the corresponding bonds in bis[N-[γ-(dimethylamino)propyl]salicylaldimino]nickel(II).[9] The ether oxygen–nickel(II) distance, 2.20 Å, agrees with the longer bond lengths found for aryl alkyl ether-to-nickel distances reported. Structural data on several N_2O_2 macrocyclic complexes have shown these bonds to have lengths of either 2.09 ± 0.02 or 2.22 ± 0.03 Å.[10-12] The aziridine nitrogen–nickel(II) bond,



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[7] Johnson, C. K. "ORTEP", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

[8] The programs used in this work included modified versions of the following: DATRED (Bell and Murphy)—processes intensities; applies Lorentz and polarization corrections as well as calculates a Wilson plot and applies statistical tests for centric or acentric cells. ORFLS (Busing, Martin, and Levy)—structure factor calculation and full-matrix, least-squares refinement. ORFFE (Busing, Martin, and Levy)—distance, angle, and error calculation. ABSORB (Coppens, Edwards, and Hamilton)—absorption correction calculation. MULTAN (Main)—package of programs including direct methods, structure factor normalization, Fourier transform, and peak search.

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Table II. Positional Parameters for the Non-Hydrogen Atoms of $[Ni(C_{22}H_{27}N_4O_2)]Br\cdot 2H_2O$

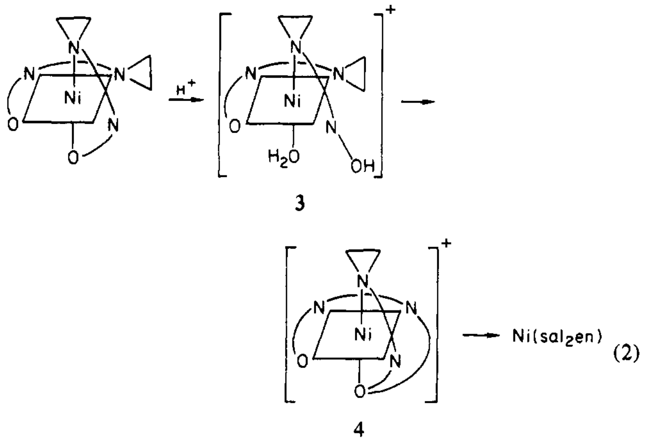
atom	*x*	*y*	*z*
Ni(1)	0.2139 (3)	0.2365 (1)	0.7280 (1)
N(1)	0.1896 (13)	0.0780 (9)	0.6971 (7)
N(2)	0.3814 (12)	0.2577 (9)	0.6751 (7)
N(3)	0.0531 (11)	0.2070 (9)	0.7824 (7)
N(4)	0.1538 (11)	0.3048 (10)	0.6282 (6)
O(1)	0.1825 (9)	0.4028 (7)	0.7640 (5)
O(2)	0.3029 (7)	0.2039 (8)	0.8230 (5)
O(3)	0.1836 (11)	1.0439 (10)	0.9162 (6)
O(4)	0.4291 (13)	0.9519 (11)	1.0473 (7)
Br(1)	0.3250 (0)	0.7959 (1)	0.8988 (1)
C(1)	0.4213 (15)	0.2076 (12)	0.8370 (9)
C(2)	0.4619 (15)	0.1861 (15)	0.9102 (9)
C(3)	0.5854 (16)	0.1890 (12)	0.9291 (9)
C(4)	0.6744 (15)	0.2146 (13)	0.8768 (12)
C(5)	0.6414 (14)	0.2344 (13)	0.8071 (10)
C(6)	0.5137 (12)	0.2327 (10)	0.7839 (7)
C(7)	0.4888 (14)	0.2556 (11)	0.7045 (8)
C(8)	0.3721 (16)	0.2843 (14)	0.5964 (9)
C(9)	0.2437 (16)	0.2669 (14)	0.5709 (8)
C(10)	0.1510 (15)	0.4192 (11)	0.6321 (9)
C(11)	0.1019 (16)	0.4509 (11)	0.7066 (10)
C(12)	0.1412 (13)	0.4231 (11)	0.8367 (9)
C(13)	0.1793 (17)	0.5178 (13)	0.8674 (10)
C(14)	0.1356 (18)	0.5443 (13)	0.9389 (11)
C(15)	0.0567 (21)	0.4772 (16)	0.9744 (9)
C(16)	0.0172 (15)	0.3785 (15)	0.9409 (9)
C(17)	0.0603 (15)	0.3496 (14)	0.8703 (8)
C(18)	0.0143 (14)	0.2529 (14)	0.8398 (10)
C(19)	−0.0024 (14)	0.1041 (12)	0.7646 (9)
C(20)	0.0550 (18)	0.0594 (13)	0.6937 (11)
C(21)	0.2663 (18)	−0.0060 (13)	0.7328 (12)
C(22)	0.2686 (17)	0.0095 (14)	0.6527 (12)

Table III. Bond Distances (Å) and Angles (deg) Involving the Coordination Sphere of the Ni(II) Ion

Ni-O(1)	2.201 (9)	Ni-N(2)	2.062 (12)
Ni-O(2)	2.007 (9)	Ni-N(3)	2.027 (12)
Ni-N(1)	2.071 (11)	Ni-N(4)	2.095 (11)
O(2)-Ni-N(3)	87.67 (41)	N(3)-Ni-N(4)	103.04 (46)
O(2)-Ni-N(2)	90.10 (42)	N(3)-Ni-O(1)	84.06 (42)
O(2)-Ni-N(1)	95.57 (43)	N(2)-Ni-N(1)	96.23 (52)
O(2)-Ni-N(4)	164.74 (47)	N(2)-Ni-N(4)	79.68 (50)
O(2)-Ni-O(1)	90.72 (38)	N(2)-Ni-O(1)	98.68 (41)
N(3)-Ni-N(2)	176.49 (47)	N(1)-Ni-N(4)	96.78 (48)
N(3)-Ni-N(1)	81.31 (52)	N(1)-Ni-O(1)	163.80 (45)

2.07 Å, is considerably shorter than the tertiary amine-nickel(II) bonds in the *N*-[γ-(dimethylamino)propyl]salicylaldimine complex, 2.32 and 2.28 Å.[9] We feel that the lower steric requirement for the aziridine ring overcomes the fact that, electronically, the aziridine is the weaker base. It is this difference in metal-ligand bond strength that we feel is responsible for the fact that $Ni(SalAEA)_2$ is protonated at a phenolate oxygen,[4] while $Ni(Saldmen)_2$[13] is protonated at the tertiary amine.[14] Other metal-nitrogen (aziridine) distances that are known are 1.98 Å (Mn-N),[15] 1.97 Å (Ga-N),[16] 1.93 Å (average of three Al-N distances),[17] 1.99 Å (Rh-N),[18] and 2.03, 1.85, 2.04 Å (Pt-N).[19]

Discussion of Chemical System. The structural data reported here are of great value in understanding the chemical transformation occurring in eq 2. The first step in the reaction



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4

(2)

involves protonation of the phenol and its replacement in the coordination sphere by water. This is the green intermediate, **3**, previously characterized.[4] The next step involves attack of the phenol on the aziridine ring adjacent to it in the coordination sphere of the metal ion. It is not known whether the aziridine is coordinated or not at the time of reaction or whether protonation of the aziridine by the phenol plays any role in the sequence. The formation of a carbon-oxygen bond and opening of the aziridine ring occur, followed by coordination of the ether oxygen in the same site it occupied as a phenolate ion. This constitutes a template synthesis in which the original geometric distribution of donor atoms is conserved. The resulting complex is **4**, [2-[[[2-[[2-[2-[[[2-(1-aziridinyl)ethyl]imino]methyl]phenoxy]ethyl]amino]ethyl]imino]methyl]phenolato]nickel(II) ion, the structure of which is reported herein. It is significant that the overall transformation has been found to occur only with labile metal ions, Ni(II), Cu(II), Co(II), and Zn(II).[2] There is no evidence for this kind of a ligand reaction in the absence of a metal ion, however.[4] Aziridine ring opening has not been observed when $[Co^{III}(SalAEA)_2]^+$ is reacted with acid. We are continuing to study the decomposition of **4** to give $Ni(Sal_2en)$.

Acknowledgment. We acknowledge the assistance of Mr. Kurt L. Loening, Nomenclature Director, Chemical Abstracts Service, in naming complex **4**. Also, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No. **4**, 84393-95-3; $Ni(SalAEA)_2$, 38966-31-3.

Supplementary Material Available: Tables IV–VIII, listing thermal parameters for non-hydrogen atoms, positional and thermal parameters for hydrogen atoms, observed and calculated structure factors, internuclear distances, and angles for $[Ni(C_{22}H_{27}N_4O_2)]Br\cdot 2H_2O$ (26 pages). Ordering information is given on any current masthead page.

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