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## The Structure of a Five-Coordinate Nickel(II) Macrocyclic Complex: Bromo(2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene)nickel(II) Bromide Monohydrate

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The structure of bromo(2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene)nickel(II) bromide monohydrate, Ni( $C_{16}H_{22}N_4$ ) $Br_2 \cdot H_2O$ , has been determined by three-dimensional X-ray analysis. The diffractmeter data were refined by full-matrix least-squares procedures to a conventional *R* factor of 0.09. The unit cell dimensions are a = 6.64 Å, b = 10.83 Å, c = 13.38 Å,  $\alpha = 105.5^{\circ}$ ,  $\beta = 98.6^{\circ}$ ,  $\gamma = 91.5^{\circ}$ , Z = 2,  $\rho_o = 1.80$  g/cm<sup>3</sup>,  $\rho_o = 1.79$  g/cm<sup>3</sup>, with space group P1. The structure consists of macrocyclic molecules, connected together by N-H···Br-Ni linkages, in which the nickel coordination polyhedron can be described as approximately square pyramidal with four nitrogen atoms forming the basal plane and a bromide ion at the apex. The water molecule is held tightly between the coordinated and free bromide ions.

### Introduction

The tetradentate macrocycle 2,12-dimethyl-3,7,11,-17 - tetraazabicyclo[11.3.1]heptadeca - 1(17),2,11,13,15pentaene,  $C_{1b}H_{22}N_4$ , hereafter referred to as CR (structure I), forms a number of interesting nickel(II) complexes.<sup>1</sup> Of particular interest is the fact that while



Ni(CR)Cl<sub>2</sub>, Ni(CR)(NCS)<sub>2</sub>, and Ni(CR)(H<sub>2</sub>O)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> are paramagnetic species which exhibit normal Curie– Weiss temperature dependencies, the complex Ni(CR)-Br<sub>2</sub>·H<sub>2</sub>O is diamagnetic. Karn and Busch postulated from chemical evidence that the complex Ni(CR)Br<sub>2</sub>· H<sub>2</sub>O was five-coordinate and that the water molecule was involved in hydrogen bonding with the coordinated bromide and N–H group in such a way as to diminish the donor strength of the bromide ligand. The structural investigation of this complex by single-crystal X-ray diffraction methods has been carried out in order to explain more fully the nickel(II) coordination and to determine the role played by water in this complex.

#### Collection and Reduction of the X-Ray Data

Dark blue-black crystals of  $Ni(CR)Br_2 H_2O$  were graciously supplied by Professor D. H. Busch of The

(1) J. L. Karn and D. H. Busch, Nature, 211, 160 (1966).

Ohio State University. Examination of suitable crystals by use of a precession camera indicated that they belonged to the triclinic system, space group either P1 or  $P\overline{1}$ . The space group  $P\overline{1}$  was confirmed by subsequent solution and refinement of the structure. From a least-squares refinement of  $2\theta$  measurements made using the General Electric XRD-5 spectrogoniometer and Mo K $\alpha$  radiation (zirconium filtered,  $\lambda$  0.7107 Å) at ambient room temperature, the unit cell dimensions were found to be  $a = 6.642 \pm 0.006$  Å,  $b = 10.83 \pm$  $0.01 \text{ Å}, c = 13.38 \pm 0.01 \text{ Å}, \alpha = 105.48 \pm 0.06^{\circ}, \beta =$  $98.59 \pm 0.07^{\circ}$ ,  $\gamma = 91.51 \pm 0.06^{\circ}$ , with cell volume of 914.6  $\pm$  1.74 Å<sup>3</sup>. The experimental density of  $1.79 \text{ g/cm}^3$  obtained by neutral bouyancy in a mixture of carbon tetrachloride and methyl iodide agrees well with the density of  $1.80 \text{ g/cm}^3$  calculated on the basis of two formula units per unit cell.

A crystal fragment of dimensions  $0.40 \times 0.31 \times$ 0.15 mm<sup>3</sup> was mounted along the longest dimension and the  $a^*$  axis was aligned so as to coincide with the  $\phi$  axis of the goniostat. The intensity data were collected using Mo K $\alpha$  radiation (zirconium filtered, using a scintillation counter and pulse-height discriminator) by the stationary-crystal, stationary-counter technique with all counting times fixed at 10 sec. A total of 1625 reflections were examined, comprising all of the data within a hemisphere of  $2\theta = 38^{\circ}$  (or  $d \ge 1.1$  Å). Background was observed at  $2\theta = \pm 2^{\circ}$  of peak and their average subtracted from the total peak counts. The observed intensities were corrected for Lorentz and polarization effects in the usual manner. Reflections were considered to be unobserved if the peak height was less than twice the background. Two reflections  $(0\overline{3}2)$ and 114) were monitored at frequent intervals and showed only random fluctuations.

Absorption effects were observed to be particularly large ( $\mu = 57.2 \text{ cm}^{-1}$ ) and an empirical method<sup>2</sup> was used to correct the observed intensities. A plot of the intensity of the 400 reflection, whose scattering vector

<sup>(2)</sup> U. W. Arndt and B. T. M. Willis, "Single Crystal Diffractometry," Cambridge University Press, Cambridge, England, 1966, p 241.

		Атоміс Р.	ARAMETERS <sup>a</sup> AB	FTER FINAL	REFINEMENT		
Atom		x	У			Z	<i>B</i> , Å <sup>2</sup>
Br(1)	0.8	0601(31)	0.2958	9(21)	0.158	390 (16)	3.90
Br(2)	0.3	2209(36)	0.1700	3(21)	0.74	639(17)	$4.4^{\circ}$
0	0.2	394(24)	0.8542	(13)	0.654	42 (11)	5.4(5)
Ni	0.22	2337(35)	0.32838	8(21)	0.237	'02(17)	$2.2^{\circ}$
N(1)	0.2	317 (20)	0.3833	(13)	0.373	77 (10)	2.2(4)
N(2)	0.2	237(19)	0.5097	(12)	0.249	91 (9)	1.6(3)
N(3)	0.2	974(24)	0.2773	(15)	0,098	<b>33</b> (12)	3.9(5)
N(4)	0.2	385(21)	0.1654	(13)	0.263	B2(11)	2.5(4)
C(1)	0.2	371(28)	0.5093	(18)	0.426	39(14)	3.1(5)
C(2)	0.2	240(27)	0.5830	(17)	0.350	09(14)	2.9(5)
C(3)	0.2	004(32)	0.5712	(20)	0.160	36 (16)	4.4(6)
C(4)	0.3	128(34)	0.5002	(21)	0.073	74(17)	4.8(7)
C(5)	0.2	265(31)	0.3606	(19)	0.021	73 (16)	3.9(6)
C(6)	0.2	320 (29)	0.1388	(18)	0.03	31 (15)	3.4(5)
C(7)	0.3	230 (31)	0.0459	(19)	0.093	37 (16)	4.0(6)
C(8)	0.2	172(31)	0.0367	(19)	0.188	87 (16)	3.9(6)
C(9)	0.2	390 (26)	0.1654	(16)	0.360	03 (14)	2.6(5)
C(10)	0.2	432(27)	0.2951	(17)	0.433	30 (14)	2.7(5)
C(11)	0.2	591 (28)	0.3315	(17)	0.549	90 (14)	2.9(5)
C(12)	0,2	653(28)	0.4646	(17)	0,593	12 (14)	3,0(5)
C(13)	0.2	522(26)	0.5552	(16)	0.536	33 (13)	2.5(5)
C(14)	0.2	105(29)	0.7261	(18)	0.37	30(15)	3.5(6)
C(15)	0.2	434 (30)	0.0504	(19)	0.40	55(15)	3.7(6)
Atom	$\beta_{11}^{b}$	$\beta_{22}$	<i>β</i> 83		$\beta_{12}$	<b>\$</b> 13	<b>\$</b> 28
Br(1)	0.0180(7)	0.0102(3)	0.0052 (	(2)	-0.0018(3)	-0.0008(3)	0.0004(2)
Br(2)	0.0331(7)	0.0096(3)	0.0050 (	(2)	-0.0007(3)	0,0002(3)	0.0020 (2)
Ni	0.0155(7)	0.0052(3)	0.0022 (	(2)	-0.0017(3)	-0.0011(3)	0.0002(2)
			Root-mean-squ	Root-mean-square amplitudes of vibration, Å			
		Atom	1	2	3		
		Br(1)	0.168	0.228	0.263		
		Br(2)	0.194	0.225	0,287		
		Ni	0.118	0.178	0.205		

TABLE I

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits. <sup>b</sup> The anisotropic temperature factor is defined as  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ . Calculated from the anisotropic temperature factors by the  $= \text{equation } B = (4/6) \{ (\beta_{11}/a^{*2}) + (\beta_{22}/b^{*2}) + (\beta_{33}/c^{*2}) + (\beta_{12}/a^{*}b^{*}) \cos \gamma^{*} + (\beta_{13}/a^{*}c^{*}) \cos \beta^{*} + (\beta_{23}/b^{*}c^{*}) \sin \alpha^{*} \}.$ 

was parallel to the goniometer  $\phi$  axis, was used in scaling all of the observed reflections as a function of azimuthal angle.

After the averaging of symmetry-related reflections, there were 1074 observed and 364 unobserved reflections. The  $F_{o}$  values were then approximately placed on an absolute scale using Wilson's method.<sup>3</sup>

#### Determination of the Structure

From a sharpened three-dimensional Patterson function several trial structures were found corresponding to the four bromine atoms and two nickel atoms in the triclinic cell, assuming space group P1. The best set of positions (R = 0.3) was used to calculate a Fourier map which immediately showed the two molecules related by a center of symmetry. A new structure factor calculation based on two bromine atoms and one nickel atom in the space group  $P\overline{1}$  gave satisfactory agreement (R = 0.4) and a subsequent difference Fourier map revealed the positions of the remaining nonhydrogen atoms.

The trial structure was refined by a full-matrix leastsquares procedure in which the function minimized was  $\Sigma w(|F_{o}| - |F_{c}|)^{2}$  Atomic scattering factors<sup>4</sup> for Ni<sup>2+</sup>,

(3) A. J. C. Wilson, Nature, 150, 152 (1942).

Br-, O, N, and C were used without correction for anomalous dispersion; such correction would alter the scattering factor for bromine by a maximum of 2%. The effects of extinction were also neglected.

Initial refinement was carried out with all atoms assigned isotropic thermal parameters and only the observed data included. This refinement converged to a conventional R factor  $(R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|)$  of 0.108 and to a weighted R factor  $(R' = [\Sigma w(|F_o| |F_{\rm o}|^2 / \Sigma w |F_{\rm o}|^2$  of 0.117.

The unobserved reflections were included in the subsequent refinement with amplitudes equal to the mean  $F_{c}$  for all such reflections. Observed reflections were given unit weights while unobserved reflections were given weights of 1/4.

The refinement then converged to values of R =0.121 and R' = 0.109 for all reflections and the estimated errors in positional parameters were reduced substantially.

A difference Fourier map revealed the anisotropic motion of the heavy atoms and hence the Ni and Br atoms were refined with anisotropic thermal parameters while the thermal parameters of the light atoms were held constant. The final refinement produced the following agreement factors: R = 0.091 and R' =0.080 for all reflections and R = 0.066 for only the ob-

<sup>(4)</sup> J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

TABLE	П	

OBSERVED AND CALCULATED STRUCTURE FACTORS<sup>4</sup>

K FUILS FCAL		0 9 736 -472	0 4 1067 1275	4 -1 2898 -172	2 5 783 912	1 -3 3135 3230	3 6 233	H <u>K FURS</u> FCAL 5 -1 1067 -1114	H <u>x FUSS FUAL</u>	
1 1 1140 -444	· · · · · · · · · · · · · · · · · · ·	9 1293 -11 24	1 4 283 4 • 75	5 -3 604 -49L	3 5 1152 -1105	2 -3 263# 132	4 5 1548 1747 0 7 283-4 - 204	1 1/2459 =2238	2 -4 201#-756	3 -2 1057 122
2 2 2834 1	2 -5 802 763	1 -1 1245 -1245	3 4 1548 1700	2 -2 1463 1416	5 5 850 097	4 -3 283# -74	1 7 1364 1407	4 0 2551 -2351	3 -4 1615 1997 4 -4 28347-151	1 -1 1447 -172
2 2 263# -4	1 -4 1133 -1218     2 -4 1026 2082     2 -4 1026 2082     1	1 -6 1341 1910	6 6 283# 557 5 6 2243 -3312	3 -2 1932 -1983 4 -2 283# -406	C 6 5213 -5052	5 -3 1804 1775	2 7 1057 1157 1 7 291# 236	5 C 281# -85	1 -3 1520 -1719	2 -L 1067 -124
3 2934 37	7 3 -4 285# 472	1 -6 425 -1043	0 5 283 <b>% •</b> LA	5 -2 1511 1663	2 6 3825 3702	2 -2 1511 1454	0 8 283# 160	1 1 1296 -2767	3 -3 667 -736	4 -1 A78 P
2 3 283# -404	5 1 -3 K12 -698	2 -5 1701 1105	1 5 4020 -4807	1 -1 6148 6044	3 6 281# 151 4 6 1227 #1279	3 -2 1123 1036 4 -2 263¥ [3]	1 8 623 -736	2 1 1605 -1407	4 -3 736 630	1 0 2274 201
1 4 945 11.7	3 -3 2115# -670	s -5 283₩ -576	3 5 1914 3730	3 -1 3938 -4240	0 7 283# 103	5 -2 2134 -: 124	D 9 283# 330	4 1 2141 2332	1 -2 1227 1426	<ul> <li>4 0 20 -210</li> </ul>
	4 -3 1415 134*	4 -5 (548 1765 1 -5 1568 -1015	4 5 283₩ -9 5 5 1586 +1501	5 -1 1194 1256	1 7 1548 1624 2 7 1461 #1665	1 -1 2635 2632	1 9 1473 -1435	5 1 1567 1402 0 2 2416 - 2136	2 -2 4061 4195	4 0 2257 -212
2 -1 2007 -176/	2 -2 2A3# 4HI	2 -4 1520 -1473	0 6 1001 902	2 0 1942 -1870	3 7 1086 -1142	3 -1 283# 122	1 -> 14+5 -1256	1 2 2616 2493	4 -2 24 1 -2417	1 2434 -2
1 0 035 644	n 3 −2 906 −878 N 6 −2 243¥ −308	3 -4 1100 1327 4 -4 1105 847	2 6 661 613	3 0 2531 2351 4 0 2389 2380	4 7 1322 1331 0 8 2323 2153	4 -1 610 745 5 -1 283¥-245	2 -9 283★-956 1 -8 283★-113	2 2 802 951	5 -2 243 <b>H</b> 137	2 1 1462 141
3 C 2054 01	1 -1 2257 2134	1 -3 L53C L3AH	3 6 5:25 -5553	5 0 2393 -2285	1 8 2H 5# 921	4 0 41.8 1747	2 -8 893 -851	4 2 283 <b>¥</b> −141	2 -1 1501 1463	4   2H3¥-2
0 1 283# -94	2 -1 285 <del>7</del> 225	3 -3 283# -1/0	0 7 972 -735	0 1 3315 3579	3 8 2834 -113	0 1 2833 ~2642	1 -7 1085 -1114	0 3 3976 - 334 3	J -1 1284 -1388 A -1 283 ₩ 263	0 2 2691 -251 1 2 2040 -18r
2 1 2814 91	4 -1 281# -611	4 -3 1955 -2067 6 -3 783 <b>4</b> -148	1 7 783 # 37	1 1 425 -851	Q 9 283₩ ~18	1 1 5336 -5234	2 -7 1057 H97	1 3 3050 2461	5 -1 283# 273	2 2 283#-2
3 1 263# 651 0 2 1690 L71-	2 C 2512 +2502	1 -2 595 -670	3 7 621 -547	3 1 11h1 1784	2 9 1180 1029	3 1 3702 3815	4 -7 642 -538	4 3 L3K8 -135C	0 0 2569 2200	0 3 2834 5
1 2 2502 -2183	a 3 C 1492 1246	2 -2 1652 1775	4 / 283美 -56 0 6 2295 -2027	-4 1 1086 1105 4 5 1 283₩ =292	1 49 2096 La74	4 6 3626 - 3474 5 1 2125 - 3166	1 -6 1152 -1218 2 -6 3258 3258	0 4 236 623	2 0 5105 -4769	1 1 2559 25
3 2 847 45	5 Q 281# 441	4 -2 1123 -1265	1 9 404 461	0 2 5166 5364	2 -9 283# -168	C 2 1702 -17/3	3 -6 982 1020	2 4 1442 -1545	4 0 4174 38/2	3 3 1662 - 16
0 3 283# 132	0 1 736 504	5 -2 283 d5 1 -1 6243 -583'	2 8 585 434 3 L 283 # 207	1 2 1180 578	1 -8 283# -355 2 -8 637 -706	2 2 3050 -2759	4 -6 670 -717	3 4 1227 1275 4 4 1010 1208	0 1 1067 1010	C 4 2347 241
2 3 915 859	2 1 849 98	2 -1 2834 -56	0 9 2834 425	3 2 746 -708	3 -8 1303 1180	3 2 906 831	2 -> 2842 -2805	0 5 2:06 2047	2 1 283#-406	2 4 1548 -144
3 3 708 -74/	4 1 1303 -1214	4 -1 1275 1246	2 9 28314 115	5 2 944 921	2 -7 2014 271	4 2 321 -837 5 7 783★ 18	4 -5 2022 2021	2 5 1255 -1256	3 1 263 2 443	C 5 680 -67
4 2834 42	5 1 283# 311	5 -L 283 # -151	****[ = -4,,,,,,	0 3 3409 - 3230	3 -7 1964 2087	1 3 774 746	5 -5 1416 1312	3 5 565 811	0 2 2245 2172	0 6 283# 52
3 4 2674 -17	1 2 1983 1755	2 0 2918 2757	1 -7 2210 2210	2 3 4023 3891	1 -6 659 755	3 3 2965 -20149	2 -4 3277 -3409	0 6 5 6 -50C	2 2 283 4 443	-8 283 <b>*</b>
0 5 283# 623	2 2 3579 3608	3 0 4731 -4382	2 -7 283# 613	3 3 1851 1851 6 3 1917 -1563	2 -6 794 821	4 3 1992 2044	3 -4 680 -545	L 6 L595 1447	3 2 283# 56	1 -7 2040 11
2 5 1548 -1794	4 2 2342 - 2203	5 C 2011 1889	1 -6 1992 -1941	5 3 982 - 997	4 -6 1445 -150L	D 4 243¥ -613	5 -4 283# -132	3 6 1208 -1256	4 2 1246 - 1341 C 3 273 242	2 =7 203 ¥ 31 1 =6 283 ¥ 20
C 6 701 ARS	5 5 2 24346 554 C 3 1492 -1755	0   547 536	2 -6 2134 -2257	0 6 6779 - 4864	1 =5 481 321	1 4 451 632	1 -3 358 -387 2 -5 7267 2162	0 7 292 -595	1 3 4420 -4247	2 -6 1265 -126
2 6 1048 -1161	1 3 1157 -1256	2 1 1024 -1038	4 -6 1112 1520	2 4 25.4 2644	3 -5 847 -1010	3 4 283 242	3 -3 2917 2946	2 7 283 🗰 9	3 3 1898 1925	1 -5 3853 -38
L = 3 26346 273	2 3 283 <b>00 - 3</b> 59 3 3 283 <b>00 - 3</b> 59	3 1 7276 -2361 4 1 821 HL?	1 -5 1941 -3541 2 -5 283# -199	, 4 467 −263 4 4 283# −160	-5 283₩ 340 5 -5 283₩ 434	4 283 ★ -0 5 4 1133 -1123	1 1841 -1775 5 - 3 2361 -2210	J R 302 -632 1 R 283₩-500	4 3 1057 1160 0 4 1219 -1284	2 -5 944 -22
2 -3 2434 255	4 3 1709 1804	5 1 283# 111 0 2 2014 10	3 -5 1407 1567	5 4 283# 151	1 -4 991 -1040	0 > 2616 - 24 - 5	1 -2 5043 -5204	••••L • •••••	1 4 281# -9	- 642 4
2 -2 1360 -1341	1 4 241# 491	1 2 2087 -2285	-4 2049 2134	1 5 31/1 3126	2 -4 1388 1482 3 -4 1534 1539	2 5 2162 2054	2 -2 283 - 217 3 -2 1728 1941	2 -9 1645 -1407	2 4 982 991 3 4 1171 -1256	2 -4 1624 16A J -4 1123 -112
3 -2 2834 14	2 4 925 -LOID	2 2 2351 -2474	2 -4 1015 1766	2 5 2550 -2531	4 -4 85X 944	3 5 283-4 558	4 -2 283 -55	1 -8 1010 1057	1 5 4034 4174	1 -3 1822 20
2 -1 2614 551	4 4 802 915	4 2 2141 2245	4 -4 1662 -1511	4 5 1+82 1303	1 -3 4269 4410	6 6 4354 4250	1 -1 +91 -1067	3 -8 283# -302	≤ 5 1105 1756 3 5 2493 =2587	
B −1 263∰ −236 1 0.3 kan 1244	, G 5 963 1029 I 5 1164 3162	5 2 152C -L511 0 3 3277 3164	5 -4 1578 1407 1 -3 547 -429	5 5 1745 1785 C 6 283# 311	2 +3 3175 -3419 3 -3 2855 -2969	L 6 2511 -2512 2 6 3914 -1415	2 -L 283第-406 3 -1 2342 -1899	1 -7 689 689 7 -7 642 524	0 6 283# -217	L -2 1142 -11-
2 0 3415 2365	2 5 28)#-141	1 3 443 179	3 -3 283# 242	1 6 615 321	4 -3 1360 1256	3 6 L199 L190	4 <b>- 283★</b> 85	3 -7 953 1067	2 6 1558 -1586	3 -2 802 34
3 C 2634 -283 5 0 1519 -1343	4 5 987 -442	2 1 1046 -1397 3 3 261# -283		2 6 1020 -963 3 6 1246 1237	5 -3 1364 1227 1 -2 2767 2485	4 6 2068 2161 1 7 1992 -2087	5 -1 2408 1955 0 0 5685 -5525	4 =7 283₩ -37 1 =6 1095 =1038	C 7 263# 481	1 -1 1832 166
0 1 1114 1020	0 6 1492 1775	4 3 647 -623	1 -2 954 -931	5 6 283 <b>#</b> 557	2 -2 114 -566	2 7 243#-243	1 0 1378 1482	2 -6 3863 -3759		3 -1 736 -61
2 1 2834 524	2 8 1141 -1244	0 4 283# 717	2 =7 1550 =1550 3 -2 241₩ 661	1 1 121 -642	3 -2 203 321 4 -2 935 -1131	0 5 2295 -2Ca8	2 U 0154 5667 3 0 283 🖶 - 177	3 -6 20347 198 4 -6 1747 1615	1 -9 283# 340 1 -8 1312 -1256	0 0 3296 237
3 1 2A3# -564	, 3 6 1567 15JL	1 4 283# 271 2 6 1616 1626	4 -2 2210 2351 5 -2 283 <b>8</b> -491	2 7 529 505	5 -2 982 -906	1 6 2H 5# 54-1	4 0 2767 -2654	L -5 3107 -2909	2 -8 689 510	2 0 1293 -123
0 2 1539 1413	C 7 283#+528	3 4 717 -840	1 -1 4056 4541	4 7 2×3¥ -504	3 -1 4434 5100	0 4 1426 -1205	0 1 4552 -4014	3 -5 2125 2144	2 -7 1322 -2021	0 1 283#-1/
1 2 2030 -271	2 7 642 708	4 4 1804 +1804	2 -1 523 -680	0 8 3664 3466	4 -1 871 -953 5 -1 7433 -7445	1 4 283 <b>1</b> 122	L 1 1558 1482	4 -5 1747 -L89H	3 -7 281# -122	1 1 4108 -402
3 2 283# 541	3 7 1246 1199	0 5 2255 -2332	<ul> <li>+1 1133 -1303</li> </ul>	2 8 2115 -2162	6 -1 231# -340	1 -0 936 -777	3 L 2H3+ -680	2 -4 5336 5487	2 ~6 2153 2200	3 3201 321
4 2 28314 642 C 3 28344 397	1 8 1360 12/5	2 5 1407 1539	1 0 281 377	3 8 28377-528 0 9 24377-528	2 0 2349 2210	2 -9 765 755	4 1 1520 1662 5 1 283 ₩ 75	3 -4 283 <b>*</b> 132 4 -4 2890 -2899	3 -6 1256 -1171	0 2 1114 -102
3 2634 273	2 8 925 850	3 5 5K5 678	3 0 1086 1265	1 9 1805 -1519	3 0 2455 -2587	3 -6 283#-150	0 2 1827 5704	5 -4 283 <b>#</b> -37	1 -5 1719 1898	2 2 1020 100
3 3 670 680	1 -6 281# 204	0 4 2210 -2077	1 1 1763 - 7999	1 4 4 8   2 -21 3 4 1 4 4	5 0 2554 2502	2 -7 1018 -972	2 2 0243 -0144	2 -1 736 -887	2 -5 1199 1199	3 2 281 <b>7</b> - 14 9 3 281 <b>7</b> - 14
4 3 1567 -1492	2 -6 878 -944	1 6 243#-122 2 6 283# 158	2 1 481 547	L -8 283 # 358 2 -8 284 # 165	6 0 1377 1520 0 1 6623 6356	3 -1 2443 -2438	3 2 283₩ 160	3 -3 1312 -1397	4 -5 283 -141	1 3 2405 237
1 4 1388 +1349	2 -5 1152 1217	3 6 510 -451	4 L 281# 302	а -н 283∰ -226	1 1 111 100	1 -6 261# 226	5 2 2+3 🗮 453	5 -3 1463 1369	2 -4 2436 -7672	0 4 1870 -195
2 283 - 472	a 1 -4 2569 -2540	0 7 2011 1425	0 2 2414 623	2 -7 698 589	3 1 2824 -2760	2 -6 283 # -245	0 3 3041 2672 1 N 8C2 878	1 -2 2662 2361 2 -2 1983 -1700	3 -4 283# 179	1 4 283 4 72
0 5 283# -41	5 2 -4 1747 -2040	1 7 1201 3343	1 2 3H7 434 2 2 2234 AIS	3 -7 1312 1275	4 1 1478 1312	4 -6 717 735	2 3 2H3 ₩ 75	3 -2 2191 -1983	1 -3 1010 -802	
2 5 2539 -64	4 -4 1157 1903	3 7 2370 -2455	\$ 2 2455 - 2739	1 -6 201# 425	0 2 4907 -4476	2 -5 281#-255	4 3 15H1 -1737	• -2 1445 1190 5 -2 283 <b>#</b> 632	2 -3 2021 -1832 3 -3 812 868	1 -8 283#*~32
3 5 2634 765	4 1 −3 1851 −1766 1 2 −3 283¥ 537	4 7 651 632 0 8 283¥ 85	4 2 510 -551 5 2 2087 2591	2 -6 528 642	1 2 1766 1605 2 2 2056 2062	3 -5 1917 1919	5 3 944 -916	1 -1 5251 5430	4 -3 283#-160	2 -7 944 82
1 6 1983 205	3 -3 283# -14	1 8 283 # 132	0 1046 -887	4 -A 201# 75	3 2 717 661	5 -5 1208 -1215	4 1964 -1747	3 -1 510 -613	2 -2 2247 2663	2 -6 1369 -135
2 6 1441 20N	1 -2 2552 2403	3 8 1187 1114	2 1 7+3 850	2 -5 847 717	5 2 1898 -1747	2 -4 1369 -1216	2 4 1070 3354	4 -1 1530 -1737 5 -1 1218 -1265	3 -2 283# -9	1 -5 283 # /
C 7 243M +43	2 -2 3277 3371	0 4 467 940	3 3 2654 -2625 4 3 283¥+103	3 -5 2550 -2606	3 2021 1501	-4 2:3 🗰 - 75	4 4 1907 -2014	0 0 1520 1303	1 -1 4410 -4467	3 -5 642 65
2 7 28340 - 347	4 -2 813 -1648	2 4 812 -811	5 7 6AL 642	5 -5 614 576	3 2834 -226	5 -4 1171 1020	L 5 2317 -2461	2 0 1454 -1265	2 -1 698 -783	1 -4 2474 247 Z -4 283₩ 5L
****( : -4****** 1 -4 1057 137	• 5 -2 201₩ 130 4 1 -1 972 774	1 -/ 2a3# 2ª	1 4 402 -746	2 -4 462 -434	4 3 2105 2054 5 3 2834 -0	L - 3 7738 - 1417 2 - 1 2077 - 7218	2 5 263 🛱 = 477	3 0 2616 2007	4 -1 1596 1615	3 -4 :208 -120
2 -4 925 109	. 2 -1 281₩-hes	2 -7 ANR 642	2 4 547 576	3 -4 2304 2427	0 4 6639 6668	3 -3 472 850	5 1 3 2 9 1 3 3 1	5 0 283¥-321	1 0 1237 -1237	2 -3 283# 2
2 -1 1437 -143	4 -1 1765 1544	2 -6 1501 1624	4 4 1535 1416	5 -4 1945 -1917	2 4 4760 -4110	5 -3 7*3¥ -273	1 6 1180 1133	J 1 2229 2172 1 1 4250 -4023	2 0 1114 935	3 -3 1671 194
3 -3 736 687	n 5 +L 265∰ 149 c 1 0 1799 -L64L	3 -6 812 -944 1 -5 3182 -6295	0 5 604 157	1 -3 2436 -2516	3 4 576 -576	1 -2 1616 +1662	2 6 1142 1256 3 6 1353 -1256	2 1 1737 -1520	4 0 283# 283	2 -2 1038 97
2 -7 2106 -2014	2 0 2181 -2115	2 -5 283# -19A	1 5 1841 1756	3 -1 1917 2002	5 6 774 733	3 -2 519 441	0 / 1378 -1360	1 293 🗰 613	1 1 6451 6432	L -1 3900 IN 5
1 -2 R40 -1 4 -2 201∰ 744	, 4 0 2155 Iost	4 -5 1123 1312	1 5 519 -405	► -3 023 A51 5 -3 265# -406	0 5 1822 -1-03	→ -2 7020 -648 5 -2 253 ¥ -225	2 7 2739 2723	5 l 283∯ 632 0 2 2757 -2446	2 1 887 925	2 -1 283 # 57
1 -1 111 -41	5 2 2 761 1192 1 1 2715 2044	1 -4 (475 (492 2 -4 563 A42	4 5 283∯ -4 5 5 283∰ 245	1 -2 1027 916	2 5 1504 1417	1 +1 3655 3504	3 7 1095 -1105 U B 1105 -1105	1 2 1422 1709	4 1 972 -763	1 0 2H3# 34
3 -1 1293 112	1 2 1 127 642	3 -4 1274 -7311	0 6 4505 4187	3 -2 1558 -1615	5 2682 -27.05	5 -1 3891 -3425	1 4 774 -802	1 2 1435 -15/1	U 2 283∰-226 1 2 802 -566	3 0 831 -91 3 0 840 98
<ul> <li>-1 2194 -2711</li> <li>1 0 1171 -404</li> </ul>	, , , , , , , , , , , , , , , , , , ,	5 -4 703 717	2 6 2011 -2047	<ul> <li>-2 1142 -1246</li> <li>-2 1511 1364</li> </ul>	0 6 1152 -1170	1 1400 3343 5 -1 2436 2233	2 8 16/9 -2040 ****L : 3*****	<ul> <li>2 1353 - 3523</li> <li>0 3 3012 - 2841</li> </ul>	2 2 1652 -1501	0 1 121 -61
2 0 1907 144	p 5 1 283# −75 6 0 2 1836 3615	1 -3 4155 4103 2 -3 28 <b>3#</b> -725	3 6 717 -727 4 8 281₩-198	1 -1 717 -971	1 6 595 -670 2 6 1746 1-14	1 U 1558 -1057 2 D 1067 -1445	1 -9 1964 1870	1 3 1152 1123	4 2 1567 1577	2 1 283# -2.1
0 941 -82	1 2 1473 -1416	1 -1 1946 -1700	0 7 2011 -1413	2 - 3466 4335	6 557 -112	3 0 1501 1463	1 -1 213 # 234	3 3 858 - 151	0 4 1029 905 1 3 2710 -2616	1 2 1378 131
U I 263₩ 7 I 1.2210 -100	y 2 2 2 201 <del>4</del> 77217 γ 3 2 1161 1160	3 203₩-107	2 7 1898 2399	3 -1 2814 122 4 -1 1308 -1407	- 6 802 -828 - 0 7 1148 1045	4 0 2214∰ 387 5 0 1596 −1445	2 -8 2139 -2739 3 -8 223 # 160	4 3 293¥ 500 ; 4 283¥-472	2 3 1341 -1575	2 2 283 * - 63
2 1 1204 -107	6 4 2 2×349 −122 6 5 2 2×349 −122	1 -2 2167 -2493 2 -2 1368 -120-	3 7 2151 2172	5 -1 283 + -236	7 243# - 52	0 1 1247 -2716	-7 1558 -1530	2 6 2310 -2445	0 4 281# 414	283 🐳 - 1
	1 0 3 376 -561	3 -2 287. 2015	C 8 1535 -1592	1 0 1161 -1177	1 1 1652 - Le /0	2 1 2/57 2/96	2 -7 1190 1275	s = 283∰ -236 4 = 2257 2502	2 4 1624 1415	C 4 1482 -177
0 2 1747 -16 8	0 i 33815 +4221 2 2 3 651 595	4 -2 1736 2278 5 -2 1369 -1377	1 P 500 +651 2 A LLAS LL71	A C 1/67 1567 5 C 847 -1667	19 6 212 -435 11 8 982 972	3 1 2502 2512 4 1 2051 -2013	4 -7 -53 -:067	0 5 1152 1105	3 4 1530 -1558	1 -7 1218 -115
2 2 13/11 124	4 1 3 1515 1775	1 -1 2304 -2210	3 8 243# -230	6 C 1071 -1001	2 8 2814 112	5 1 2766 +2247	7 -6 557 510	2 5 774 -134	1 5 1020 -925	1 -5 3815 391
<ul> <li>3 2 1714 - 174</li> <li>4 2 745 - 12</li> </ul>	283#	5 -L 906 Lool	1 2 1414 1354	2 L 2495 -25L6	3 H 2015€-541 3 U 251€-528	0 2 2114 2114	3 ~6 28 <b>1₩-1</b> 22 4 ~0 2n1 <b>₩</b> -557	3 5 1199 -1237 0 6 2181 2007	2 5 281#-121	2 -5 283# 35
0 3 557 54	x 0 4 1174 -1205 1 1 4 2105 2275	<ul> <li>トート しいれーレンフィート</li> <li>トレート シャレーシャン</li> </ul>	2 3 1596 -1522	3 1 3570 - Mail	1 1 2014 102	2 2 1501 -1520	1 -5 921 -585	1 5 531 727	1 1 1505 - 1662	2 -4 1700 -164
2 3 1029 - 74	4 2 4 1388 1948	1 0 1579 3201	1 -6 1414 :4-2	5 1 187 + 1926		4 2 9/6 547	3 -5 1671 -1492	3 6 263₩ 141	2 = 9 22 /0 997	1 ~3 1586 -174 2 -3 604 -79
1 3 2814 - 15 4 3 601 A.	1 N 306-1 H3176 N N A 450 -578	5 1524 - 1721	2 -8 1284 1291 1 -7 1105 1105	5 1 850 840 0 2 1.61 1177	2 -0 450 840 2 -0 1180 1140	5 2 727 746 0 1 2 127 2433	k ~5 1265 1360 5 ~5 1501 1388	C 7 2834 -254 1 7 2764 -2454	L -5 28.5#-745	-2 283 <b>€</b> 5
0 4 1221 114	2 6 6 1737 6665 1 5 6 875 -847	4 0.2115 -1794 5 0.2210 2094	2 -7 241# -55 1 -7 717 -766	2 2 2466 3456	-/ -E 203★ 105 3 -E 505 50	1 1003 -2415	1 -4 241 # 311	2 1 2414 - 76	1 -1 1237 -1171	-1 -1 263¥ 11
2 4 1520 -162	4 1 5 2710 2h-0	0 1 3012 -3154	-6 (605 -1511	3 2 661 -21	1 -1 2512 2475	3 3 443 = 123	1 -4 557 4×1	• 5 /31# -310 ••••	2 -7 651 -555	2 -1 283 🕊 15 0 0 3785 -351
3 4 2404 270	i 2 3 285∰ 14 i 3 5 1286 -14is	2 1 1520 1548	2 -6 1962 -1713	マージーンの3番~511 5 2 1556 -1523	2 -7 1051 -1195 3 -7 1520 -1558	4 3 2×3₩-387 5 3 925 1012	4 -4 1472 -1549 5 -4 1435 -1341	1 - N 698 - N2A 2 - N 661 574	1 -5 283# 283	L C 1586 - 15 H
0 5 255 -41	2 4 5 545 477	3 1 281# 381 6 1 755 172	4 -6 1737 1841	C 1 1613 -1174	4 -7 847 545	0 4 5544 5725	-1 2011 1992	1 -8 651 -755	7 -6 2644 2654 3 -6 285 <b>4</b> -122	0 L 283# -/
2 5,1414 16.	4 I N 1237 -1076	1 203# - 111	2 -> 2001 -1020	2 3 1133 1001	2 -6 1840 -2010	1 4 708 995 2 4 5449 9464	7 -3 574 443 3 -3 281₩ 66	2 -H 2357 2265 3 -B 243¥ 367	1 -5 2214 -2011	1 1 1794 1640
3 5 263 H 42 4 5 LA34 -17H	<ul> <li>5 2 6 1048 −3027</li> <li>4 3 6 1728 1718</li> </ul>	2 2 421 - 3069 2 2 421 - 551	3 -5 840 -935 4 -5 289∰ -558	3 3 4423 4410 4 3 557 -547	1 -6 243# -547 4 -6 243# -75	3 4 547 -441	4 -4 524 545	1 -1 1237 1150	4 -1 2H1# 170	1 2 1804 174
C 6 2834 -41	4 6 6 1462 1447 6 7 1245 1447	3 2 2814 -37 6 2 1667 1677	5 -5 28348 396	5 3 2191 -2153	1 -5 4540 -4637	5 - 2×1+ -500	1 -2 1341 -1029	3 -7 1511 -1959	4 -5 755 755 1 -4 576 357	
2 6 1747 181	1 661 513	2 2034 -217	2 -4 431 953	1 4 2101 -2144	3 -5 3702 3/40	U 5 576 -528 1 5 5566 1199	2 -2 5213 -5204 3 -2 283 <b>4</b> 346	L =6 283∰ 56 2 =6 2021 =2040	2 -4 283# -343	L -5 293 # 94
3 6 1275 -144 0 7 1056 -05	5 2 7 613 −557 2 3 7 283∰ +42	0 1 1167 3154	s −6 868 966 4 −4 125h +1254	2 4 2304 -2115 3 - 2234 -226	4 = 5 589 -510 5 -5 1834 -1774	2 5 1415 -1294	2 2342 2304	3 -8 281# -94	4 -4 953 963	1 -3 263 - 39
1 7 1046 -117	1 U H 1123 1C/7	2 1 2606 -271-	5 -4 2434 -623	293# 132	-4 1010 110h	4 h 1126 2010	2 746 651 0571- 1107 1- 1	N =0 1341 1341 1 ≥5 2569 2512	1 -3 4042 4145 2 -3 283番 468	L -2 2040 2710 L -2 2323 -2125
2 7 283#-10 3 7 283# 17	v L 0 26178 55 7 7 15 2834€ L/r	3 2011 41	2 -3 2578 2654	0 5 1053 1035 0 5 1061 1038	3 -4 1299 -1559 4 -6 283★ -442	0 6 1131 L150 1 6 283∰ -24	2 -1 443 406 3 -1 1586 1831	2 -5 887 µ47 3 -5 201¥ 221	3 -3 1492 -1567	1 0 1234 -120
0 9 1020 -112	i 1 6 283%-271	5 3 613 517	3 -4 2266 2257	1 5 657 -664	6 +4 1511 1426	2 5 2112 -2515	5 -L 18/9 -2065	A -1 1465 -1463	<ul> <li>1 e61 = 185</li> </ul>	0 1 1048 1105

<sup>a</sup> An asterisk indicates unobserved reflections.

served reflections. The standard deviation of an observation of unit weight was 0.87.

Table I gives the final positional and thermal parameters obtained from the last cycle of least-squares refinement along with their standard deviations as estimated from the full-matrix procedure. The final calculated structure factors as well as the observed ones are given in Table II. The values given are to be multiplied by 0.0212 to be placed on an absolute scale.

#### **Results and Discussion**

A stereoscopic view of the molecule is shown in Figure 1, and the labeling of the atoms is indicated. Interatomic distances and angles are presented in

Tables III and IV. The crystal is composed of macrocyclic molecules connected by N-H···Br-Ni linkages in such a way as to form infinite chains. Between the macrocyclic planes the water molecule is held tightly between the coordinated and free bromide ions. The contents of the unit cell are shown in projection in Figure 2.

The coordination polyhedron about the Ni atom is only approximately a square pyramid. The mean plane of the Ni atom and four nitrogen atoms has the equation 6.37X + 0.33Y + 1.45Z = 2.01 (referred to the triclinic coordinates) and the distances of the atoms out of this plane are: N(1), +0.14 Å; N(2), -0.064 Å; N(3), +0.12 Å; N(4), -0.06 Å; Ni, -0.14 Å (with



Figure 1.—Stereoscopic view of the molecule show labeling of the atoms. The ellipsoids show the relative magnitudes of thermal vibration; only the Ni and Br atoms were refined anisotropically.

TABLE III							
Interatomic Distances, <sup>a</sup> Å							
Ni-N(1)	1.808 (14)	C(6)-C(7)	1.509(27)				
Ni-N(2)	1.927(13)	C(7)-C(8)	1.567(28				
Ni-N(3)	1.932(16)	C(9)-C(10)	1.476(24				
Ni-N(4)	1.892(14)	C(9)-C(15)	1.523(26				
N(1)-C(1)	1.345(21)	C(10)-C(11)	1,417 (24				
N(1)-C(10)	1.353(21)	C(11)-C(12)	1.408 (24				
N(2)-C(2)	1.381(20)	C(12)-C(13)	1.372(23				
N(2)-C(3)	1.427(23)	Br(1)'-Ni	2.791(4)				
N(3)-C(5)	1.512(24)	Br(1)–Ni	4.156(5)				
N(3)-C(6)	1.524(24)	Br(1)-N(3)	3.342(16				
N(4)-C(8)	1.470(23)	Br(1)O	3.373 (15				
N(4)-C(9)	1.298(20)	Br(2)-O	3.312(14)				
C(1)-C(13)	1.400(24)	Br(1)'-N(1)	3.657 (14				
C(1)-C(2)	1.466(24)	Br(1)'-N(2)	3.419(13)				
C(2)-C(14)	1.504(26)	Br(1)'-N(3)	3.477(16)				
C(3)-C(4)	1,542 (29)	Br(1)'-N(4)	3.503(14)				
C(4)-C(5)	1.537(28)						

<sup>a</sup> Standard deviations from the final least-squares cycle are given in parentheses. The atoms designated with a prime are related to the unprimed atoms by the translation -a.

estimated errors of  $\pm 0.05$  Å). Thus it can be seen that the nitrogen atoms actually lie on a saddle-shaped surface with the Ni atom about 0.17 Å below toward the coordinated bromide ion Br(1)'. This nonplanarity of the macrocyclic ligand can also be seen in the angles across the molecule, N-Ni-N, of 163.7 and 165.2°.

Although hydrogen atoms could not be located with any certainty on the final difference map, there appear to be three hydrogen bonds of importance in the structure. Br(1), which is coordinated to the Ni atom at 1 + X in the crystal, is only 3.34 Å away from N(3), compared to the sum of van der Waals radii<sup>5</sup> of 3.45 Å for the group N-Br. The angle Ni-N(3)-Br(1) of 72.9 is 36.6° away from the otherwise nearly tetrahedral angles about N(3), indicating that the N-H bond is pointing in the direction of Br(1). Thus Br(1) is probably involved in hydrogen bonding which links the molecules together in the crystal. The two other probable hydrogen bonds involve the water molecule; the Br(1)-O distance is 3.37 Å while the Br(2)-O distance is 3.31 Å and the Br(1)-O-Br(2) angle is 115.3°. Although the prediction of Busch and Karn<sup>1</sup> was correct that the complex is five-coordinate, the N-H group

(5) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. V., 1960 ,p 280.

## TABLE IV

INTERATOMIC ANGLES," DEG

Macrocycle							
Ni-N(1)-C(1) 120.8 (1.2) $C(8)-N(4)-C(9)$	114.3 (1.5)						
Ni-N(1)-C(10) 118.4 (1.1) $N(4)-C(9)-C(10)$	113.7 (1.5)						
Ni-N(2)-C(2) 112.8 (1.0) $C(9)-C(10)-N(1)$	109.4(1.5)						
Ni-N(2)-C(3) 128.0 (1.2) $N(1)-C(10)-C(11)$	121.6(1.6)						
Ni-N(4)-C(8) 129.7 (1.2) $C(10)-C(11)-C(12)$	115.2(1.6)						
Ni-N(4)-C(9) 115.2 (1.2) $C(11)-C(12)-C(13)$	123.9 (1.7)						
N(1)-C(1)-C(2) 109.9 (1.5) $C(12)-C(13)-C(1)$	116.4(1.6)						
C(1)-C(2)-N(2) 113.9 (1.5) $C(13)-C(1)-N(1)$	122.2(1.6)						
C(2)-N(2)-C(3) 118.8 (1.4) $C(1)-N(1)-C(10)$	120.7(1.5)						
N(2)-C(3)-C(4) 110.0 (1.7) $C(13)-C(1)-C(2)$	127.9(1.7)						
C(3)-C(4)-C(5) 112.5 (1.7) $C(9)-C(10)-C(11)$	129.0(1.6)						
C(4)-C(5)-N(3) 110.5 (1.6) $C(1)-C(2)-C(14)$	125.0(1.6)						
N(3)-C(6)-C(7) 111, 1 (1,5) $C(10)-C(9)-C(15)$	118.5(1.5)						
C(6)-C(7)-C(8) 114.2 (1.6) $N(2)-C(2)-C(14)$	121.1(1.5)						
C(7)-C(8)-N(4) 107.3 (1.5) $N(4)-C(9)-C(15)$	127.8(1.6)						
Nickel Coordination							
N(1)-Ni-N(3) 163.7 (0.6) $Br(1)-Ni-Br(1)'$	145.2(0.1)						
N(2)-Ni-N(4) 165.2 (0.6) $Br(1)-Ni-N(3)$	52.2(0.5)						
N(1)-Ni-N(2) 82.5 (0.6) $Br(1)'-Ni-N(3)$	93.0 (0.5)						
N(1)-Ni-N(4) 83.0 (0.6) $Br(1)'-Ni-N(1)$	103.2(0.4)						
N(3)-Ni-N(2) 96.6 (0.6) $Br(1)'-Ni-N(2)$	90.9(0.4)						
N(3)-Ni-N(4) 96.9 (0.6) $Br(1)'-Ni-N(4)$	94.9 (0.4)						
About N(3)							
C(6)-N(3)-Br(1) 106.7 (1.0) $Br(1)-N(3)-Ni$	72.9(0.5)						
C(5)-N(3)-Br(1) 111.6 (1.1) $C(5)-N(3)-Ni$	115, 6(1, 2)						
C(5)-N(3)-C(6) 106.8 (1.4) $C(6)-N(3)-Ni$	115.1 (1.1)						

#### About the Water

Br(1)-O-Br(2) 115.3 (0.4)

<sup>a</sup> Standard deviations from the final least-squares cycle are given in parentheses. The atoms designated with a prime are related to the unprimed atoms by the translation -a.



Figure 2.—Projection of the contents of the unit cell down the [100] axis. (The shaded atoms are in the upper half of the cell.)

is not hydrogen bonded to the water but to the coordinated bromide of another molecule.

The coordinated bromide ion shows normal contact distances to the nitrogen atoms; their average of 3.52 Å was compared to the sum of the van der Waals radii<sup>5</sup> of 3.45 Å. The distance Br(1)'-Ni is 2.79 Å which is significantly longer than that found in the octahedral complex tetrapyridinenickel(II) dibromide6 where the Ni–Br distance was found to be 2.58 Å. The distance is also longer than in the five-coordinate nickel-(II) complex NiBr<sub>2</sub> triars<sup>7</sup> (triars = triarsine =  $(CH_3)_2$ - $A_{s}(CH_{2})_{3}A_{s}(CH_{3})(CH_{2})_{3}A_{s}(CH_{3})_{2})$  which is a distorted square-pyramidal, diamagnetic complex of nickel(II) having an Ni-Br distance of 2.69 Å for the apical bromide ion. It should also be noted that the basal plane field strength is enhanced by the short distance Ni-N(1)of 1.81 Å which is about 0.1 Å shorter than the other three normal Ni-N distances of the complex.

(6) A. S. Antsyshkina and M. A. Porai-Koshits, Kristallografiya, **3**, 676 (1958).

The observation that  $Ni(CR)Br_2 H_2O$  is diamagnetic can now be more reasonably explained, especially in the light of the crystal field model calculated for squarepyramidal nickel(II) complexes by Ciampolini.<sup>8</sup> Specifically, it was found that spin pairing is favored by a decrease in the axial field strength and an increase in the basal plane field strength. On the other hand, spin pairing is disfavored by distortion of the metal atom out of the basal plane toward the axial ligand. Apparently in this case, a combination of diminished axial field strength and increased basal plane field strength promotes spin pairing over and above the effect of outof-plane distortion.

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(7) B. A. Mair, H. M. Powell, and D. E. Henn, Proc. Chem. Soc., 415 (1960).
(8) M. Ciampolini, Inorg. Chem., 5, 35 (1966).

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# Conformations and Crystal Packing. The Crystal and Molecular Structure of *trans*-Bis(2,4-pentanedionato)dipyridinenickel(II), Ni $(AA)_2(py)_2$

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The crystal structure of *trans*-bis(2,4-pentanedionato)dipyridinenickel(II), Ni(AA)<sub>2</sub>(py)<sub>2</sub>, was determined by X-ray methods using an automated diffractometer to collect 1641 independent data. The compound crystallizes in the monoclinic space group P2<sub>1</sub>/c. There are two molecules in the unit cell with  $a = 8.321 \pm 0.003$ ,  $b = 9.649 \pm 0.015$ ,  $c = 14.723 \pm 0.025$  Å, and  $\beta = 117.06 \pm 0.01^{\circ}$ . The structure was refined by full-matrix least squares to a conventional *R* factor for nonzero data of 0.050 and *wR* (all data) of 0.056. The molecule which is required to lie on a center of symmetry has nearly D<sub>2h</sub> symmetry, with the two pyridine ligands in an eclipsed configuration. All atoms including hydrogen were refined. Packing calculations on this compound and *trans*-Co(AA)<sub>2</sub>(py)<sub>2</sub>, which has a staggered configuration, account for the folding of the acetyl-acetone ligands and indicate that the configurational differences are the result of crystal forces and not metal-ligand  $\pi$  bonding.

#### Introduction

The determination of the crystal structure of trans-bis(2,4-pentanedionato)dipyridinecobalt(II),<sup>1</sup> Co-(AA)<sub>2</sub>(py)<sub>2</sub>, revealed that the two trans-pyridine ligands are staggered with respect to one another. Symmetry arguments<sup>2</sup> based on unit cell and space group data indicate that such a configuration is not possible for trans-bis(2,4-pentanedionato)dipyridinenickel(II), Ni(AA)<sub>2</sub>(py)<sub>2</sub>, and suggest instead an eclipsed configuration. If  $d\pi$ -p $\pi$  back-bonding were important in these compounds, the staggered configuration would be ideal, for it makes possible donation from two filled metal d orbitals, one for each pyridine ligand, whereas the eclipsed structure leads only to use of a single metal orbital to form bonds to both pyridine ligands.

Several experiments have been interpreted to show evidence of  $\pi$  bonding between metals and pyridine<sup>3-5</sup> although some of these claims have been disputed<sup>6</sup> and other experiments<sup>7</sup> have been found to show no evidence for  $\pi$  bonding to aromatic heterocycles. This paper reports a single-crystal X-ray analysis which was undertaken to provide detailed information on the structure of Ni(AA)<sub>2</sub>(py)<sub>2</sub> and the results of a series of packing calculations which were performed to learn if the con-

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