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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

By E. B. FLEISCHER and S. W. HAWKINSON

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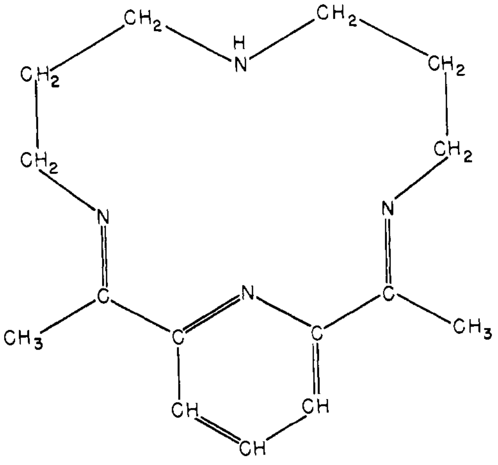
The structure of bromo(2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene)nickel(II) bromide monohydrate, $Ni(C_{15}H_{22}N_4)Br_2 \cdot H_2O$, has been determined by three-dimensional X-ray analysis. The diffractmeter data were refined by full-matrix least-squares procedures 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, $\alpha = 105.5°$, $\beta = 98.6°$, $\gamma = 91.5°$, $Z = 2$, ρ_c = 1.80 g/cm^3, ρ_o = 1.79 g/cm^3, with space group P$\bar{1}$. 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),2,11,13,15-pentaene, $C_{15}H_{22}N_4$, hereafter referred to as CR (structure I), forms a number of interesting nickel(II) complexes.[1] Of particular interest is the fact that while $Ni(CR)Cl_2$, $Ni(CR)(NCS)_2$, and $Ni(CR)(H_2O)_2(ClO_4)_2$ are paramagnetic species which exhibit normal Curie–Weiss temperature dependencies, the complex $Ni(CR)Br_2 \cdot H_2O$ is diamagnetic. Karn and Busch postulated from chemical evidence that the complex $Ni(CR)Br_2 \cdot H_2O$ 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.



I

Collection and Reduction of the X-Ray Data

Dark blue-black crystals of $Ni(CR)Br_2 \cdot H_2O$ were graciously supplied by Professor D. H. Busch of The 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$\bar{1}$. The space group P$\bar{1}$ was confirmed by subsequent solution and refinement of the structure. From a least-squares refinement of 2θ measurements made using the General Electric XRD-5 spectrogoniometer and Mo Kα radiation (zirconium filtered, λ 0.7107 Å) at ambient room temperature, the unit cell dimensions were found to be a = 6.642 ± 0.006 Å, b = 10.83 ± 0.01 Å, c = 13.38 ± 0.01 Å, $\alpha = 105.48 \pm 0.06°$, $\beta = 98.59 \pm 0.07°$, $\gamma = 91.51 \pm 0.06°$, with cell volume of 914.6 ± 1.74 Å^3. The experimental density of 1.79 g/cm^3 obtained by neutral bouyancy in a mixture of carbon tetrachloride and methyl iodide agrees well with the density of 1.80 g/cm^3 calculated on the basis of two formula units per unit cell.

A crystal fragment of dimensions 0.40 × 0.31 × 0.15 mm^3 was mounted along the longest dimension and the a^* axis was aligned so as to coincide with the ϕ axis of the goniostat. The intensity data were collected using Mo Kα 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 $2\theta = 38°$ (or $d \geq 1.1$ Å). Background was observed at $2\theta = \pm 2°$ 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 ($0\bar{3}2$ and $1\overline{14}$) were monitored at frequent intervals and showed only random fluctuations.

Absorption effects were observed to be particularly large (μ = 57.2 cm^{-1}) and an empirical method[2] was used to correct the observed intensities. A plot of the intensity of the 400 reflection, whose scattering vector

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

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

TABLE I

ATOMIC PARAMETERS[a] AFTER FINAL REFINEMENT

Atom	x	y	z	B, Å^2
Br(1)	0.80601 (31)	0.29589 (21)	0.15890 (16)	3.9[c]
Br(2)	0.32209 (36)	0.17003 (21)	0.74639 (17)	4.4[c]
O	0.2394 (24)	0.8542 (13)	0.6542 (11)	5.4 (5)
Ni	0.22337 (35)	0.32838 (21)	0.23702 (17)	2.2[c]
N(1)	0.2317 (20)	0.3833 (13)	0.3777 (10)	2.2 (4)
N(2)	0.2237 (19)	0.5097 (12)	0.2491 (9)	1.6 (3)
N(3)	0.2974 (24)	0.2773 (15)	0.0983 (12)	3.9 (5)
N(4)	0.2385 (21)	0.1654 (13)	0.2632 (11)	2.5 (4)
C(1)	0.2371 (28)	0.5093 (18)	0.4269 (14)	3.1 (5)
C(2)	0.2240 (27)	0.5830 (17)	0.3509 (14)	2.9 (5)
C(3)	0.2004 (32)	0.5712 (20)	0.1666 (16)	4.4 (6)
C(4)	0.3128 (34)	0.5002 (21)	0.0774 (17)	4.8 (7)
C(5)	0.2265 (31)	0.3606 (19)	0.0273 (16)	3.9 (6)
C(6)	0.2320 (29)	0.1388 (18)	0.0361 (15)	3.4 (5)
C(7)	0.3230 (31)	0.0459 (19)	0.0937 (16)	4.0 (6)
C(8)	0.2172 (31)	0.0367 (19)	0.1887 (16)	3.9 (6)
C(9)	0.2390 (26)	0.1654 (16)	0.3603 (14)	2.6 (5)
C(10)	0.2432 (27)	0.2951 (17)	0.4330 (14)	2.7 (5)
C(11)	0.2591 (28)	0.3315 (17)	0.5490 (14)	2.9 (5)
C(12)	0.2653 (28)	0.4646 (17)	0.5912 (14)	3.0 (5)
C(13)	0.2522 (26)	0.5552 (16)	0.5363 (13)	2.5 (5)
C(14)	0.2105 (29)	0.7261 (18)	0.3760 (15)	3.5 (6)
C(15)	0.2434 (30)	0.0504 (19)	0.4055 (15)	3.7 (6)

Atom	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
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-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

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

was parallel to the goniometer ϕ 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.[3]

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$\bar{1}$ 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 least-squares procedure in which the function minimized was $\Sigma w(|F_o| - |F_c|)$.[2] Atomic scattering factors[4] for Ni^{2+}, 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 ($R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$) 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-

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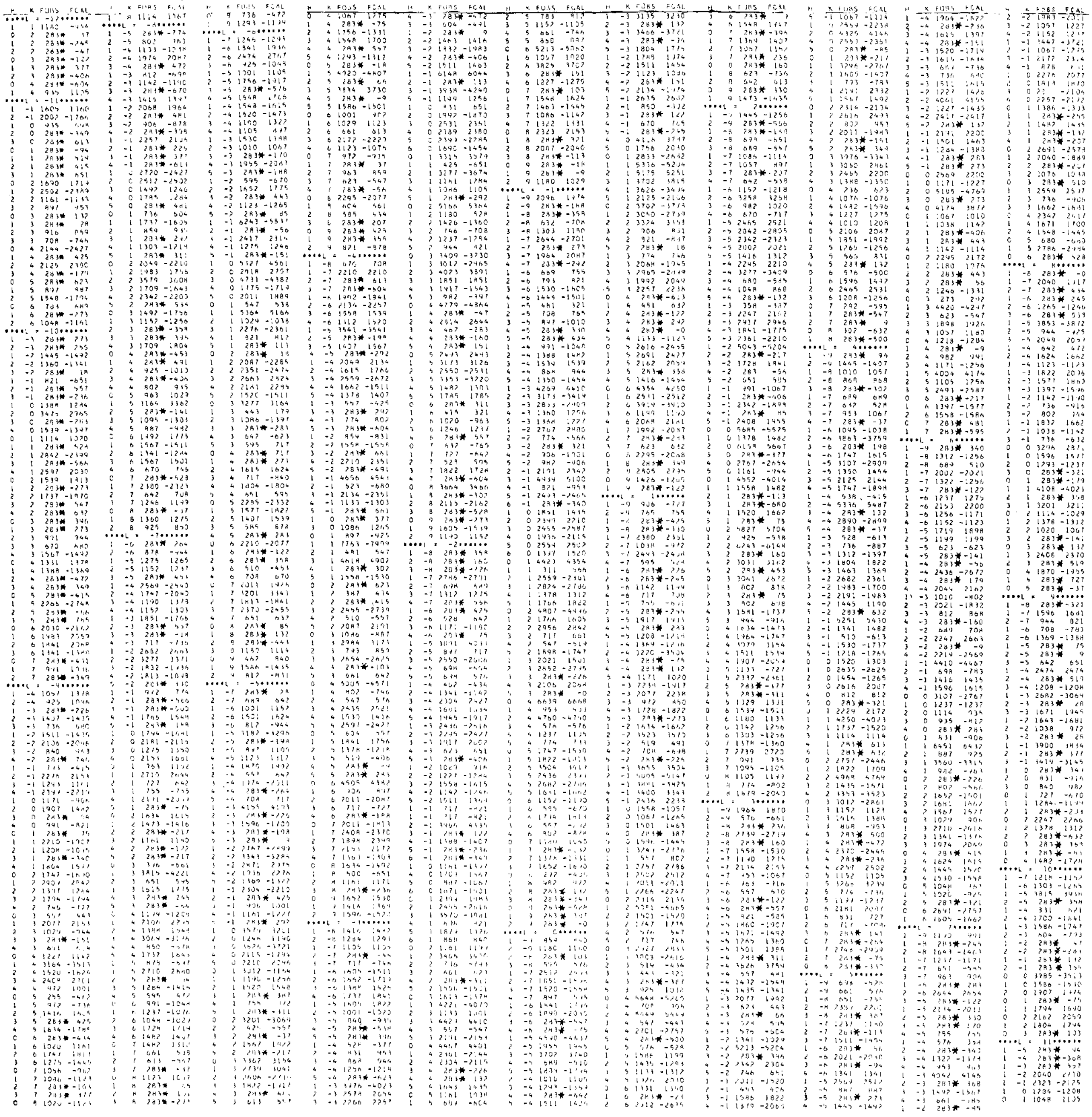
(3) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

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

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]



[a] 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

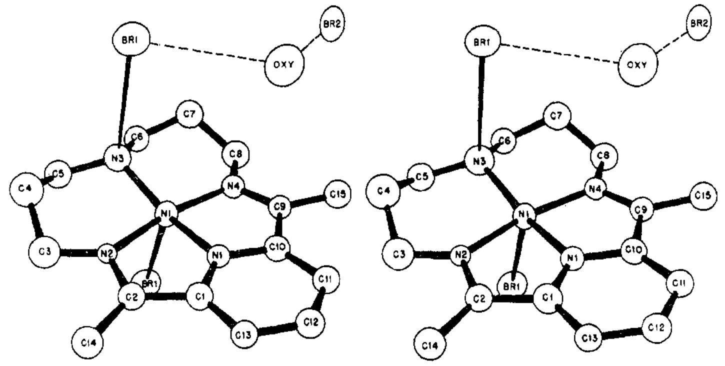


Figure 1.—Stereoscopic view of the molecule show labeling of the atoms. The ellipsoids show the relative magnitudes of thermal vibration; only the Ni and Br atoms were refined anisotropically.

TABLE III

INTERATOMIC DISTANCES,[a] 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)		

[a] 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 $-a$.

TABLE IV

INTERATOMIC ANGLES,[a] 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)		

[a] 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 ±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[5] 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[1] was correct that the complex is five-coordinate, the N–H group

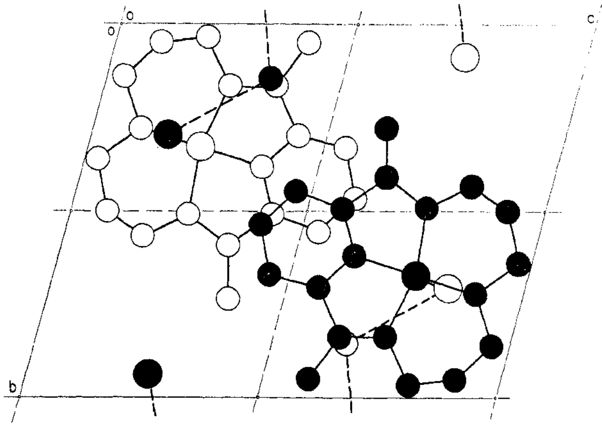


Figure 2.—Projection of the contents of the unit cell down the [100] axis. (The shaded atoms are in the upper half of the cell.)

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(5) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960 ,p 260.

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[5] 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) dibromide[6] 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 $NiBr_2$·triars[7] (triars = triarsine = $(CH_3)_2As(CH_2)_3As(CH_3)(CH_2)_3As(CH_3)_2$) 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.

The observation that $Ni(CR)Br_2 \cdot H_2O$ is diamagnetic can now be more reasonably explained, especially in the light of the crystal field model calculated for square-pyramidal nickel(II) complexes by Ciampolini.[8] 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 out-of-plane distortion.

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

(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), $Ni(AA)_2(py)_2$, was determined by X-ray methods using an automated diffractometer to collect 1641 independent data. The compound crystallizes in the monoclinic space group $P2_1/c$. 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 $\beta = 117.06 \pm 0.01°$. 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_{2h} symmetry, with the two pyridine ligands in an eclipsed configuration. All atoms including hydrogen were refined. Packing calculations on this compound and *trans*-$Co(AA)_2(py)_2$, which has a staggered configuration, account for the folding of the acetylacetone ligands and indicate that the configurational differences are the result of crystal forces and not metal–ligand π bonding.

Introduction

The determination of the crystal structure of *trans*-bis(2,4-pentanedionato)dipyridinecobalt(II),[1] $Co(AA)_2(py)_2$, revealed that the two *trans*-pyridine ligands are staggered with respect to one another. Symmetry arguments[2] based on unit cell and space group data indicate that such a configuration is not possible for *trans*-bis(2,4-pentanedionato)dipyridinenickel(II), $Ni(AA)_2(py)_2$, 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 π bonding between metals and pyridine[3-5] although some of these claims have been disputed[6] and other experiments[7] have been found to show no evidence for π bonding to aromatic heterocycles. This paper reports a single-crystal X-ray analysis which was undertaken to provide detailed information on the structure of $Ni(AA)_2(py)_2$ and the results of a series of packing calculations which were performed to learn if the con-

(1) R. C. Elder, *Inorg. Chem.*, **7**, 1117 (1968).

(2) J. T. Hashagen and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **87**, 2821 (1965).

(3) P. Ford, D. P. Rudd, R. Gaunder, and H. Taube, *ibid.*, **90**, 1187 (1968).

(4) J. E. Falk, J. N. Phillips, and E. A. Magnusson, *Nature*, **212**, 1531 (1966).

(5) J. deO. Cabral, H. C. A. King, T. M. Shepherd, and E. Koros, *J. Chem. Soc.*, 859 (1966).

(6) D. P. Graddon and E. C. Watton, *Australian J. Chem.*, **18**, 507 (1965).

(7) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).