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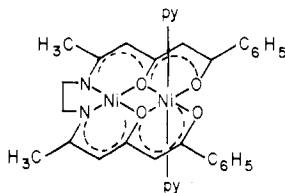
Complexes of Binucleating Ligands with Two Different Coordinating Environments. 3. Crystal and Molecular Structure of a Binuclear Nickel(II) Mixed Spin State Complex, $\text{Ni}_2(\text{py})_2(\text{BAA})_2\text{en-py}$

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The crystal and molecular structure of $\text{Ni}_2(\text{py})_2(\text{BAA})_2\text{en-py}$ is reported, where $(\text{BAA})_2\text{en}$ is the tetraanion of the Schiff base formed from ethylenediamine and 1-phenyl-1,3,5-hexanetrione. The crystals are monoclinic, $P2_1/c$, $a = 10.971$ (3), $b = 16.005$ (5) Å, $c = 21.759$ (4) Å, $\beta = 104.24$ (2)°, $Z = 4$. The structure was solved by Patterson-Fourier techniques with $R = 0.045$ for 2950 observed diffractometer data. The structure comprises two nickels coordinated as shown.



The nickel at the $\text{N}_2\text{-O}_2$ site is square planar low spin, whereas the nickel at the O_2O_2 site is octahedral high spin.

Introduction

In the first paper of this series,¹ we reported the preparation and characterization of a number of binuclear complexes of the first transition series metals and the Schiff-base ligand formed from ethylenediamine and 1-phenyl-1,3,5-hexanetrione, abbreviated $\text{H}_4(\text{BAA})_2\text{en}$. In that paper a preparative procedure was presented which was used to produce pure heterobinuclear complexes. The basis for the procedure is the presence of two different coordination sites in the ligand, which imparts a good deal of selectivity with respect to the coordination position occupied by different metal ions.

The second paper² reported the structures of two heterobinuclear complexes, $\text{NiZn}(\text{py})(\text{BAA})_2\text{en}$ and $\text{NiVO}(\text{BAA})_2\text{en}$, both of which have the nickel atom coordinated to two nitrogens and two carbonyl oxygens and the second metal coordinated to the four $(\text{BAA})_2\text{en}^{4-}$ carbonyl oxygens. The two central carbonyl oxygens are, therefore, bonded to both metals forming two one-atom bridges between the two different metal atoms.

While the underlying reason for using ligands such as $\text{H}_4(\text{BAA})_2\text{en}$ to prepare heteronuclear complexes is the presence of two different coordination sites, there are other interesting uses for this ligand based on the presence of the different sites. If the two sites represent environments of significantly different ligand field strengths, the opportunity exists to systematically prepare molecular, binuclear complexes containing two of the same metal ions in different spin states or oxidation states. Mixed spin state or mixed valence state molecular complexes in which the metal atoms are in juxtaposition and, hence, may experience strong interactions are relatively rare. This paper reports the crystal and molecular structure of a molecular, binuclear complex containing a low spin Ni(II) and a high spin Ni(II) bridged by carbonyl oxygens.

Experimental Section

The preparations of the ligand and $\text{Ni}_2(\text{py})_2(\text{BAA})_2\text{en}$ have been reported.³

Single crystals were obtained by recrystallization from pyridine. The crystals were found to be air stable and did not appear to decompose by loss of solvent from the crystal lattice. A well formed crystal, bound by the (100), (011), and (011) planes, had dimensions 0.304, 0.112, and 0.228 mm with respect to these faces.

Rotation and axial photographs of the crystal on a Syntex $P2_1$ four-circle diffractometer, together with a small data set, were consistent with the monoclinic space group $P2_1/c$. Fifteen reflections

with 2θ between 10 and 22° were centered automatically and used in a least-squares refinement of cell parameters (λ 0.71069 Å): $a = 10.971$ (3), $b = 16.005$ (5), $c = 21.759$ (4) Å, $\beta = 104.24$ (2)°, $U = 3704$ (2), $Z = 4$, $\rho_{\text{calcd}} = 1.404$ g cm^{-3} , $\rho_{\text{(floatation)}} = 1.41$ g cm^{-3} , $\mu = 10.7$ cm^{-1} .

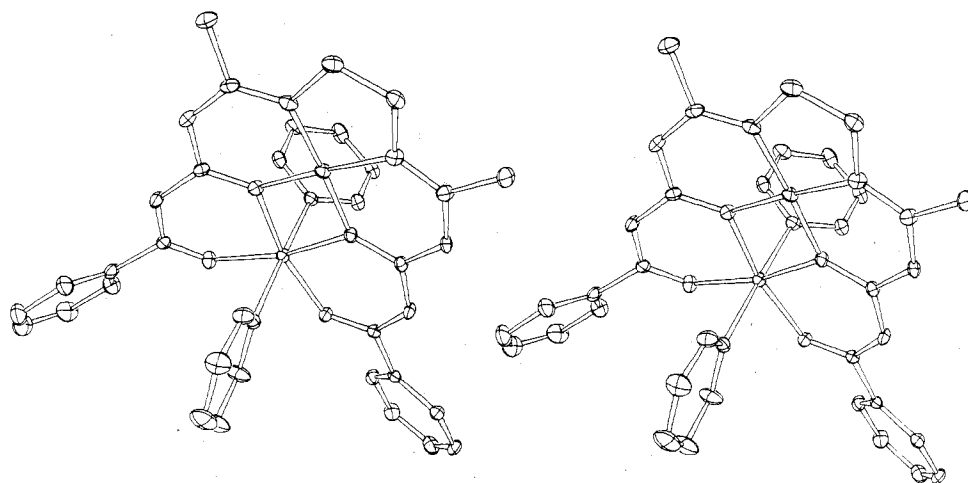
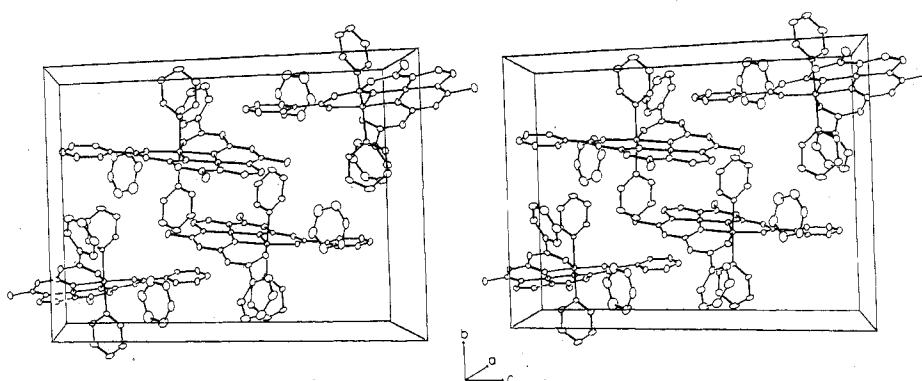
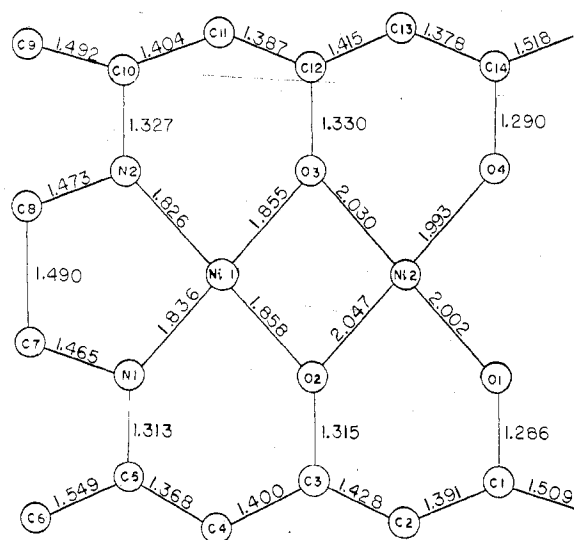
Intensity data were collected with Mo $K\alpha$ radiation which had been diffracted from a highly oriented graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. The θ - 2θ scan technique was used with a constant scan speed of 2°/min. The 2θ scan range was $K_{\alpha 1} - 1.0^\circ$ to $K_{\alpha 2} + 1.0^\circ$ and the ratio of background time/scan time was 0.5. During data collection, the intensities of three reflections were measured every 100 reflections with no indication of crystal movement or decomposition. A total of 5404 independent data were collected to $\sin \theta/\lambda < 0.54$. Standard deviations⁴ were assigned as: $\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (pI)^2]^{1/2}$ where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counts, K is the ratio of scan time to background time (2.0), and p equals 0.04. Corrections for Lorentz and polarization factors and absorption were applied. No correction was made for extinction. There were 2957 data with $I > 2.5\sigma(I)$; 2950 of these were used for the solution and refinement of the structure, and seven reflections were poorly determined because of instrumental difficulties.

Solution and Refinement of Structure. A three-dimensional Patterson synthesis yielded the position of the two independent nickel atoms. Structure factors based upon these coordinates gave an unweighted discrepancy index of 0.397 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). A subsequent three-dimensional Fourier synthesis allowed the determination of all but the atoms of the noncoordinated pyridine molecule. A difference Fourier synthesis then yielded the positions of these additional atoms. Full-matrix least-squares refinement of the nonhydrogen atoms and isotropic thermal parameters resulted in an unweighted discrepancy index of 0.093 and a weighted discrepancy index of 0.104 ($wR = \{ \sum w(|F_o| - |F_c|)^2 / \sum wF_o^2 \}^{1/2}$). The coordinates of the hydrogen atoms were calculated with C-H distances of 0.97 Å and isotropic temperature factors set at 10% greater than the equivalent isotropic temperature factor of the carbon atom to which it is bonded.

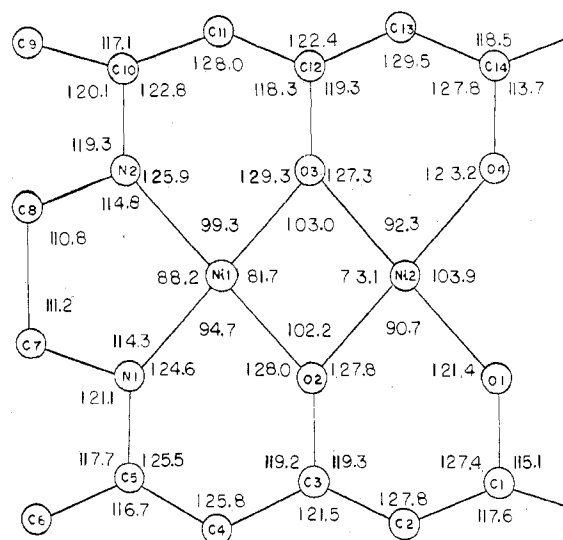
Several cycles of block diagonal least-squares refinement of the anisotropic thermal parameters and coordinates of all nonhydrogen atoms were carried out followed by recalculation of hydrogen atom positions and temperature factors. This process was repeated twice more until the refinement converged with discrepancy factors: $R = 0.045$ and $wR = 0.048$. The error of a measurement of unit weight (error of fit) was 1.69. The highest residual in the final difference Fourier map was 0.32 $e^-/\text{Å}^3$. Atomic parameters are given in Table I.

Results and Discussion

The structure of one molecule of $\text{Ni}_2(\text{py})_2(\text{BAA})_2\text{en}$ is shown in Figure 1. The molecule contains the $(\text{BAA})_2\text{en}^{4-}$

Figure 1. A stereoscopic view of the $\text{Ni}_2(\text{py})_2(\text{BAA})_2\text{en}$ molecule.Figure 2. A stereoscopic view of the packing of $\text{Ni}_2(\text{py})_2(\text{BAA})_2\text{en}\cdot\text{py}$.Figure 3. Significant bond distances in $\text{Ni}_2(\text{py})_2(\text{BAA})_2\text{en}\cdot\text{py}$. Estimated standard deviations are 0.005 Å for distances involving Ni and 0.007 Å for all other distances.

ligand with one of the nickel atoms four coordinated to two nitrogens from the ethylenediamine moiety and two carbonyl oxygens in typical square-planar manner. The other nickel atom is bonded to four equatorial carbonyl oxygens and two axial pyridine nitrogens in a distorted octahedral geometry. The unit cell contains four binuclear molecules and four uncoordinated pyridines of solvation. A stereoscopic view of the unit cell is shown in Figure 2. The distances and angles in the binuclear molecule, excluding the adducted pyridines,

Figure 4. Significant bond angles in $\text{Ni}_2(\text{py})_2(\text{BAA})_2\text{en}\cdot\text{py}$. Estimated standard deviations are 0.3° for angles about the Ni and $0.3\text{--}0.5^\circ$ for all other angles.

are presented in Figures 3 and 4. The Ni-pyridine N distance is 2.12 Å and the N-Ni-N angle is 177.2° . It is noteworthy that the planes of the two coordinated pyridines are essentially perpendicular to one another. This fact does not appear to be due to packing forces and, therefore, may be a bonding phenomenon.

The environment of the N_2O_2 bound Ni is essentially identical to that found in $\text{NiZn}(\text{py})(\text{BAA})_2\text{en}^2$ and $\text{NiVO}(\text{BAA})_2\text{en}^2$ which indicates that the second metal ion has a

Table I. Atomic Parameters for Ni₂(py)₂(BAA)₂en·py^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni(1)	0.070 30 (8)	0.634 03 (6)	0.472 04 (4)	C(15)phenyl 14	-0.0089 (6)	0.6836 (4)	0.1777 (3)
Ni(2)	0.205 42 (8)	0.681 38 (5)	0.370 57 (4)	C(16)phenyl 14	-0.1295 (6)	0.7027 (4)	0.1420 (3)
O(1)	0.383 2 (4)	0.720 6 (3)	0.383 7 (2)	C(17)phenyl 14	-0.1507 (6)	0.7037 (5)	0.0764 (3)
O(2)	0.229 0 (4)	0.668 4 (3)	0.466 4 (2)	C(18)phenyl 14	-0.0555 (7)	0.6865 (5)	0.0474 (3)
O(3)	0.037 0 (3)	0.645 1 (3)	0.384 6 (2)	C(19)phenyl 14	0.0612 (6)	0.6694 (5)	0.0820 (3)
O(4)	0.138 3 (3)	0.684 3 (3)	0.276 8 (2)	C(20)phenyl 14	0.0858 (6)	0.6679 (4)	0.1489 (3)
N(1)	0.113 2 (5)	0.625 4 (3)	0.558 8 (2)	C(21)phenyl 1	0.5444 (6)	0.8153 (4)	0.4305 (3)
N(2)	-0.089 3 (5)	0.603 1 (3)	0.473 2 (2)	C(22)phenyl 1	0.6157 (6)	0.7986 (5)	0.3876 (3)
N(3)pyr 1	0.155 5 (4)	0.808 9 (3)	0.372 9 (2)	C(23)phenyl 1	0.7078 (7)	0.8564 (5)	0.3810 (4)
N(4)pyr 2	0.257 3 (5)	0.554 5 (3)	0.363 8 (2)	C(24)phenyl 1	0.7257 (8)	0.9267 (5)	0.4157 (4)
N(5)pyr 3	0.428 3 (6)	0.177 5 (4)	0.320 8 (3)	C(25)phenyl 1	0.6575 (7)	0.9441 (5)	0.4564 (4)
C(1)	0.442 4 (6)	0.754 6 (4)	0.436 1 (3)	C(26)phenyl 1	0.5654 (7)	0.8873 (5)	0.4646 (3)
C(2)	0.421 8 (6)	0.742 1 (4)	0.496 0 (3)	C(27)pyr 1 A	0.1078 (7)	0.8443 (4)	0.4177 (3)
C(3)	0.321 5 (5)	0.697 1 (4)	0.512 0 (3)	C(28)pyr 1 A	0.0815 (8)	0.9257 (5)	0.4195 (4)
C(4)	0.318 8 (6)	0.683 4 (4)	0.575 2 (3)	C(29)pyr 1 A	0.1011 (8)	0.9768 (5)	0.3741 (4)
C(5)	0.222 7 (6)	0.646 9 (4)	0.595 3 (3)	C(30)pyr 1 A	0.1480 (9)	0.9431 (5)	0.3258 (4)
C(6)	0.246 2 (7)	0.629 7 (5)	0.667 3 (3)	C(31)pyr 1 A	0.1744 (8)	0.8601 (4)	0.3285 (3)
C(7)	0.013 8 (6)	0.591 2 (4)	0.585 7 (3)	C(32)pyr 2 B	0.1906 (6)	0.5021 (4)	0.3216 (3)
C(8)	-0.107 2 (6)	0.584 0 (4)	0.536 6 (3)	C(33)pyr 2 B	0.2243 (7)	0.4207 (4)	0.3170 (3)
C(9)	-0.313 5 (6)	0.575 4 (5)	0.431 7 (3)	C(34)pyr 2 B	0.3308 (7)	0.3907 (4)	0.3550 (4)
C(10)	-0.187 4 (6)	0.600 0 (4)	0.423 4 (3)	C(35)pyr 2 B	0.3995 (6)	0.4425 (4)	0.3997 (3)
C(11)	-0.178 5 (5)	0.617 9 (4)	0.361 5 (3)	C(36)pyr 2 B	0.3610 (6)	0.5236 (4)	0.4029 (3)
C(12)	-0.072 3 (5)	0.640 3 (4)	0.341 5 (3)	C(37)pyr 3 C	0.4923 (9)	0.1927 (5)	0.2754 (3)
C(13)	-0.076 0 (6)	0.656 2 (4)	0.277 1 (3)	C(38)pyr 3 C	0.5460 (8)	0.1340 (7)	0.2497 (4)
C(14)	0.020 8 (5)	0.674 7 (4)	0.249 3 (3)	C(39)pyr 3 C	0.5370 (9)	0.0524 (6)	0.2663 (4)
				C(40)pyr 3 C	0.4749 (9)	0.0352 (6)	0.3114 (4)
				C(41)pyr 3 C	0.4237 (8)	0.1014 (6)	0.3341 (4)
Atom	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	2 <i>B</i> ₁₂	2 <i>B</i> ₁₃	2 <i>B</i> ₂₃	<i>B</i> _{iso}
Ni(1)	2.67 (4)	2.77 (4)	2.67 (3)	0.14 (7)	1.08 (6)	0.27 (7)	2.59 (5)
Ni(2)	2.22 (3)	2.87 (4)	2.49 (3)	-0.07 (7)	0.81 (5)	0.0 (7)	2.46 (5)
O(1)	3.0 (2)	4.2 (2)	3.6 (2)	-0.5 (4)	1.3 (3)	-0.7 (4)	3.4 (2)
O(2)	2.7 (2)	3.4 (2)	2.8 (2)	0.2 (4)	0.8 (3)	0.1 (3)	2.9 (2)
O(3)	1.9 (2)	3.2 (2)	3.4 (2)	-0.3 (3)	0.9 (3)	0.1 (3)	2.7 (2)
O(4)	2.6 (2)	3.4 (2)	2.5 (2)	-0.1 (4)	0.7 (3)	0.0 (3)	2.8 (2)
N(1)	3.8 (3)	2.6 (3)	3.2 (2)	0.3 (5)	1.9 (4)	0.3 (4)	2.9 (3)
N(2)	2.9 (3)	3.2 (3)	3.6 (2)	0.8 (4)	1.3 (4)	0.1 (4)	3.0 (2)
N(3)	3.3 (3)	2.3 (3)	3.2 (2)	-0.1 (4)	0.8 (4)	-0.1 (4)	2.9 (2)
N(4)	2.4 (3)	2.9 (3)	3.7 (3)	0.1 (4)	1.1 (4)	0.3 (4)	2.9 (2)
N(5)	7.5 (4)	7.7 (4)	4.1 (4)	-1.2 (7)	1.9 (7)	-0.5 (7)	6.0 (4)
C(1)	2.2 (3)	2.9 (4)	3.7 (3)	0.2 (5)	0.4 (5)	0.7 (6)	2.9 (3)
C(2)	2.3 (3)	4.9 (4)	2.7 (3)	-0.3 (6)	-0.1 (5)	0.0 (6)	3.2 (3)
C(3)	2.3 (3)	2.9 (3)	2.7 (3)	0.8 (5)	0.5 (5)	0.4 (5)	2.5 (2)
C(4)	5.2 (3)	4.4 (4)	2.1 (3)	0.7 (6)	-0.1 (5)	-0.4 (6)	3.1 (4)
C(5)	4.3 (3)	2.7 (4)	2.5 (3)	1.0 (6)	0.5 (5)	0.4 (5)	3.0 (3)
C(6)	5.6 (4)	6.1 (4)	2.7 (4)	-0.5 (8)	0.4 (6)	1.1 (7)	4.5 (4)
C(7)	4.3 (4)	4.4 (4)	3.4 (3)	0.3 (6)	2.2 (6)	0.8 (6)	3.5 (3)
C(8)	3.3 (4)	3.4 (4)	4.3 (3)	0.1 (6)	1.9 (6)	0.4 (6)	3.4 (3)
C(9)	2.4 (3)	6.6 (5)	5.0 (4)	-0.3 (7)	1.3 (6)	1.4 (7)	4.0 (4)
C(10)	3.0 (3)	3.7 (4)	3.0 (3)	0.5 (5)	1.0 (5)	0.5 (5)	3.1 (3)
C(11)	1.4 (3)	4.0 (4)	4.1 (3)	-0.7 (5)	0.7 (5)	0.3 (6)	2.7 (3)
C(12)	2.5 (3)	2.3 (3)	3.0 (3)	-0.1 (5)	0.8 (5)	-0.3 (5)	2.5 (3)
C(13)	1.9 (3)	3.9 (4)	2.8 (3)	-0.3 (5)	0.1 (5)	-0.3 (5)	2.8 (2)
C(14)	2.6 (3)	2.5 (3)	2.5 (3)	0.1 (5)	0.9 (5)	0.0 (5)	2.4 (3)
C(15)	3.5 (3)	2.2 (3)	1.8 (3)	-0.7 (5)	0.4 (5)	-0.1 (5)	2.4 (3)
C(16)	3.3 (3)	2.6 (3)	3.4 (3)	0.0 (6)	0.4 (5)	-0.1 (5)	3.1 (3)
C(17)	3.4 (4)	5.2 (5)	2.5 (3)	-0.7 (6)	-0.9 (6)	0.8 (6)	3.4 (3)
C(18)	6.4 (5)	4.8 (4)	3.2 (3)	-1.8 (8)	1.3 (6)	0.0 (6)	4.4 (4)
C(19)	4.9 (4)	5.6 (4)	2.7 (3)	-1.3 (7)	1.3 (6)	-0.3 (6)	4.0 (4)
C(20)	3.7 (3)	4.0 (4)	2.7 (3)	-0.7 (6)	0.4 (5)	-0.4 (6)	3.4 (3)
C(21)	2.0 (3)	4.7 (3)	3.4 (3)	-0.1 (6)	-0.1 (5)	0.8 (6)	3.2 (4)
C(22)	3.8 (4)	5.3 (5)	5.9 (4)	-1.0 (7)	2.3 (6)	0.1 (7)	4.4 (3)
C(23)	3.6 (4)	7.6 (5)	8.0 (4)	-0.3 (9)	2.7 (7)	2.3 (8)	5.3 (5)
C(24)	3.6 (5)	7.1 (5)	7.8 (7)	-1.0 (8)	1.4 (9)	1.4 (10)	5.6 (5)
C(25)	4.6 (5)	4.5 (4)	8.7 (5)	-1.5 (7)	-0.6 (8)	-0.1 (7)	5.5 (4)
C(26)	4.0 (4)	4.5 (5)	6.0 (4)	-1.0 (7)	0.8 (6)	0.4 (7)	4.7 (4)
C(27)	5.0 (4)	4.1 (4)	3.2 (4)	0.4 (6)	1.7 (7)	0.5 (6)	3.8 (2)
C(28)	6.8 (5)	4.3 (4)	5.5 (5)	1.2 (8)	2.9 (9)	-0.4 (7)	4.9 (4)
C(29)	7.5 (6)	2.8 (4)	9.6 (5)	1.5 (8)	2.9 (8)	0.8 (7)	5.5 (5)
C(30)	11.9 (7)	3.5 (4)	5.7 (5)	-0.1 (9)	3.9 (10)	1.2 (7)	5.6 (5)
C(31)	9.0 (5)	3.1 (3)	3.9 (4)	0.3 (7)	3.8 (7)	0.7 (6)	4.0 (4)
C(32)	3.5 (4)	3.5 (4)	4.3 (4)	-0.3 (6)	1.3 (6)	-0.3 (6)	3.7 (3)
C(33)	4.2 (4)	3.4 (4)	6.4 (4)	-1.1 (7)	2.1 (7)	-0.9 (7)	4.2 (4)
C(34)	4.9 (4)	3.4 (4)	7.5 (5)	-0.3 (7)	2.7 (8)	-1.4 (7)	4.6 (4)
C(35)	3.5 (3)	3.4 (4)	7.1 (4)	1.2 (6)	1.9 (6)	1.1 (7)	4.1 (4)
C(36)	3.3 (4)	3.6 (4)	4.1 (3)	-0.7 (6)	1.7 (6)	-0.7 (6)	3.4 (3)
C(37)	5.8 (6)	10.2 (6)	6.0 (4)	-3.2 (10)	0.4 (8)	0.3 (8)	6.8 (5)

Table I (Continued)

Atom	B ₁₁	B ₂₂	B ₃₃	2B ₁₂	2B ₁₃	2B ₂₃	B _{iso}
C(38)	4.9 (5)	11.1 (8)	6.2 (5)	-1.2 (11)	2.4 (8)	-2.0 (11)	6.5 (6)
C(39)	6.4 (7)	13.3 (7)	8.9 (6)	2.4 (11)	4.8 (11)	-0.5 (11)	7.5 (5)
C(40)	7.1 (6)	8.6 (6)	7.7 (6)	2.7 (10)	1.1 (10)	1.9 (10)	7.5 (6)
C(41)	5.2 (5)	11.2 (6)	3.6 (5)	1.4 (9)	1.5 (8)	0.3 (8)	5.7 (4)

^a Thermal parameters have units of Å² and are of the form $T = \exp[-1/4 \sum (B_{ij} H_i^2 a_j^{*2} + \dots + 2B_{ij} H_i H_j a_i^* a_j^* + \dots)]$ for the anisotropic case and $T = \exp[-B(\sin \theta/\lambda)^2]$ for the isotropic case.

Table II. Some Intramolecular Nonbonded Distances in NiM(BAA)₂en Complexes

Nonbonded atoms	Distance, Å		
	NiNi(py) ₂ -(BAA) ₂ en ^a	NiZn(py) ₂ -(BAA) ₂ en ^b	NiVO-(BAA) ₂ en ^b
Ni-M	3.04	3.12	2.99
N ₁ -N ₂	2.55	2.57	2.58
O ₁ -O ₂	2.88	2.82	2.71
O ₂ -N ₁	2.72	2.74	2.74
N ₂ -O ₃	2.72	2.76	2.66
O ₃ -O ₄	2.90	2.84	2.69
O ₁ -O ₄	3.15	3.06	2.70
O ₂ -O ₃	2.43	2.37	2.36

^a Estimated standard deviations are 0.005 Å for distances involving Ni and 0.007 Å for all other distances. ^b See ref 2. Estimated standard deviations are 0.005 Å for distances involving Ni and 0.007 Å for all other distances for the NiZn and NiVO structures, respectively.

negligible effect on the environment of the first. The Ni(1)-N and Ni(1)-O bond lengths of the N₂O₂ bound Ni are typical of square-planar Ni(II) and approximately 0.2 Å shorter than the bond lengths in octahedral Ni(II). For example, the bond lengths of 1.83 Å (Ni(1)-N) and 1.86 Å (Ni(1)-O) are comparable to those found in the square-planar complex bis(*N*-methylsalicylaldiminato)nickel(II) in which the coordination sphere also contains two nitrogen and two oxygen donors.⁵

The octahedrally coordinated Ni which is bound to four equatorial ketonic oxygens has bond distances typical of mononuclear, octahedral complexes. In bis(2,4-pentanedionato)diaquanickel(II), for example, the equatorial Ni-O bond distances are 2.02 and 2.01 Å. These values are very similar to Ni(2)-terminal O and Ni(2)-bridging O distances of 2.00 and 2.04 Å for NiNi(py)₂(BAA)₂en. The Ni-pyridine N distance of 2.12 Å is also comparable to the Ni-water O distance of 2.14 Å in bis(2,4-pentanedionato)diaquanickel(II).⁶ Therefore, essentially all six Ni donor atom bond lengths are the same in the two octahedral complexes.

The coordination spheres of the two Ni atoms explain the magnetic properties of the binuclear complex which were reported in a previous paper.¹ The magnetic moment of the molecule is 3.16 BM at 300 K and 3.00 BM at 77 K which is consistent with one diamagnetic, planar Ni(II) and one paramagnetic, octahedral Ni(II) per molecule.

Certain nonbonded distances in NiNi(py)₂(BAA)₂en, such as the chelate ring "bites", are of interest since they define the coordination sphere of the metal ions. In addition, the metal-metal distance and the distance between the bridging oxygens are of interest from the standpoint of potential interactions between the metal ions in the four-membered Ni₂O₂ ring. These distances are given in Table II and are compared to the analogous values in the Ni, Zn and Ni, VO complexes. Most of the analogous distances are similar for the three compounds and any significant differences are most likely due to the fact that the five-coordinate Zn and V atoms are above the plane of the ketonic oxygens, while the six-coordinate Ni is in the plane.

One of our purposes in preparing the ethylenediamine Schiff-base derivatives of triketonates is to synthesize poly-

Table III. Comparison of Bond Angles in NiNi(py)₂(BAA)₂en and Ni₂(DBA)₂(py)₄

	Bond angles, deg ^a	
	NiNi(py) ₂ (BAA) ₂ en	Ni ₂ (DBA) ₂ (py) ₄ ^b
α ₁	88.2	102.3 (av)
α ₂	95.0 (av)	89.5 (av)
α ₃	81.7	78.5 (av)
α ₄	102.6 (av)	101.5 (av)
α ₅	73.1	78.5 ≡ α ₃
α ₆	91.5 (av)	89.5 ≡ α ₂
α ₇	103.9	102.3 ≡ α ₁

^a Bond angle errors are in the range 0.2 to 0.3°. ^b See ref 8.

nuclear complexes with unusual magnetic properties. It was our belief that one effect of the ethylenediamine ring would be to constrain the system in such a way that the M-O-M bridging angle would be close to 90°. Support for this postulate was derived from the observed planarity of the triketonate moiety in binuclear 1,3,5-triketonates of Co(II),⁷ Ni(II),⁸ and Cu(II).⁹ Since the M-O-M bridging angles in these compounds are all about 103° and the compounds exhibit antiferromagnetic exchange,⁶⁻⁸ it would be interesting to design very similar binuclear compounds with 90° bridging angles. Currently accepted superexchange theories would predict that the exchange in the 90° case would be ferromagnetic due to the presence of a plane orthogonality bisecting the bridging oxygens.¹⁰

Unfortunately it is found that the least flexible angle in the metal atom and donor atom region of the molecule appears to be the M-O-M bridging angle. The average value of 102.6° in NiNi(py)₂(BAA)₂en is very similar to the values reported for the simple binuclear triketonates.⁷⁻⁹ The constraints of the ethylenediamine ring are manifested in other parts of the molecule, however, as is seen in the comparison between the bond angles in NiNi(py)₂(BAA)₂en and in the simpler triketonate Ni₂(DBA)₂(py)₄⁸ in Table III. The most obvious change that accompanies addition of the ethylenediamine ring is the decrease in α₁ from 102.3 to 88.2°. One might have expected that a secondary result of this would be equatorial bond angles of nearly 90° around the Ni. If this were true, a value of 90° for the bridging angle α₄ would be necessary to maintain planarity of the molecule. This is not the case, however. Rather, the change is compensated for by increases in α₂ from 89.5 to 95.0° and in α₃ from 78.5 to 81.7°. The net effect on the bridging angle, α₄, is small. The environment around the octahedral Ni is not greatly altered by the addition of the ethylenediamine, except for α₅ which decreases from 78.5 to 73.1°.

How much the effects of the ethylenediamine ring on bond angles are due to the short bond lengths in low spin Ni(II) is not known. However, they undoubtedly contribute. It would be instructive in this regard to study complexes of H₄(BAA)₂en in which the spin state of the metal ion does not change in

Table IV. Analysis of Mean Planes

Atom	Deviation from planes, ^b Å		
	I	II	III
O(1)	-0.039*	-0.142*	
O(2)	0.018*	0.016*	
O(3)	0.031*		0.021*
O(4)	-0.035*		-0.021*
N(1)	-0.010*	0.119*	
N(2)	0.035*		0.000*
Ni(1)	0.013	0.354	-0.117
Ni(2)	0.023	0.202	-0.151
C(1)		0.097*	
C(2)		0.102*	
C(3)		0.002*	
C(4)		-0.099*	
C(5)		-0.095*	
C(6)		-0.370	
C(7)	0.153	0.180	
C(8)	0.013		0.007
C(9)			0.090
C(10)			0.023*
C(11)			0.009*
C(12)			-0.022*
C(13)			-0.025*
C(14)			-0.015*

^a Equations of planes in the form $AX + BY + CZ = D$. The orthonormal basis set for these equations corresponds to a^* , b , and

	a	b	c	d
Plane I	0.2949	-0.9534	-0.0634	-10.8369
Plane II	-0.4685	0.8814	-0.0602	8.8130
Plane III	0.2045	-0.9696	-0.1312	-11.4168

c , respectively. ^b The atoms that define the plane are marked with an asterisk. The estimated errors are about 0.008 Å.

going from the binuclear 1,3,5-triketionate to the ethylenediamine Schiff-base derivative.

Another aspect of the structure worthy of mention is the planarity. The donor atoms and the carbon atoms in the ligand "backbone" are all approximately sp^2 hybridized which imparts a planar configuration to the triketonate moiety. The results of the planes calculations are given in Table IV. Plane I is the donor atom mean plane, in which the greatest deviation is 0.039 Å. In addition, the deviations of the metal atoms and the carbon atoms of the ethylenediamine group are only 0.013, 0.023, 0.153, and 0.013 Å, respectively. Planes II and III are the donor atoms and "backbone" carbons from one triketonate moiety. Each moiety is essentially planar, but the dihedral angle between the two planes is 10.4°.

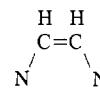
The coplanarity of the ethylenediamine carbons, C(7) and C(8), is surprising since they are saturated and would be expected to have a staggered configuration. The eclipsed configuration of C(7) and C(8) is further demonstrated by the fact that the dihedral angle described by the atoms of the ethylenediamine linkage, N(1), C(7), C(8), N(2), is only 7.3°. A related structure, aquo- N,N' -ethylenediaminebis(acetylacetonate)iminato)copper(II) abbreviated $Cu(acac)_2en(H_2O)$, reported by Clark, Hall, and Waters,¹¹ also contains eclipsed ethylene carbons. However, as they pointed out, anhydrous $Cu(acac)_2en$ has the ethylene carbons in the more normal staggered configuration. This configuration is also present in the N,N' -ethylenediaminebis(salicylidiniminato)salen complexes of Cu(II) and Fe(III). In the other two NiM(BAA)₂en complexes whose structures have been completed, one has staggered ethylene carbons and the other has cis eclipsed carbons. These results, in the manner of Clark, Hall, and Waters,¹¹ are summarized in Table V. In addition to the displacements of the ethylene carbons from the coordination plane, the carbon-carbon distances are given for various en complexes in Table V. The distances are shortened considerably from the

Table V. Deviation of the Ethylenediamine Carbons from the Coordination Plane and the Carbon-Carbon Distances

Compd	Coord No.	Deviation (Å) from coord plane		C-C bond distance, Å	Ref
		1st C	2nd C		
$Cu(acac)_2en$	4	-0.44	0.12	1.43	12
$Cu(acac)_2en \cdot 1/2 H_2O$	4	-0.11	0.10	1.51	13
$Cu(acac)_2en(H_2O)$	5	0.11	0.14	1.50	14
$Cu(salen)CHCl_3$	5	-0.44	0.12	1.62	15
$Fe(salen)Cl$	5	-0.40	0.38	1.50	16
$[Fe(salen)Cl]_2$	6	-0.44	0.22	1.46	2
$NiZn(py)(BAA)_2en$	4	-0.13	0.20	1.46	2
$NiVO(BAA)_2en$	4	0.22	0.18	1.49	This work
$NiNi(py)_2(BAA)_2en$	4	0.15	0.01		

1.53 Å value found in the uncoordinated ethylenediamine.¹

The presence of eclipsed carbons and shortened C(7)-C(8) bond distance must result in a significant strain in this part of the molecule. The strain could perhaps be relieved by loss of two hydrogen atoms to give an unsaturated, planar



linkage. This may explain the facile mass spectral dehydrogenation of the molecular ion which was discussed in the first paper of the series.¹

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Registry No. $Ni_2(py)_2(BAA)_2en \cdot py$, 59751-86-9.

Supplementary Material Available: Listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

References and Notes

- R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic, and D. P. Gavel, *Inorg. Chem.*, **15**, 1646 (1976).
- M. D. Glick, R. L. Lintvedt, D. P. Gavel, and B. K. Tomlonovic, *Inorg. Chem.*, **15**, 1654 (1976).
- R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic, D. P. Gavel, and J. M. Kuszaj, *Inorg. Chem.*, **15**, 1633 (1976).
- (a) Local versions of the following programs were used: (i) SYNCOR, W. Schmonsees' program for data reduction; (ii) FORDAP, A. Zalkins' Fourier program; (iii) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; (iv) ORTEP, C. K. Johnson's program for drawing crystal models; (v) HFINDR, A. Zalkins' program for calculating idealized hydrogen coordinates; (vi) REFINE, J. J. Park's block-diagonal least-squares program; (vii) ABSORB, D. and L. Templeton's absorption correction program modified by T.J.A. (b) Scattering factors, including anomalous dispersion corrections for Ni, were taken from "The International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., Kynoch Press, Birmingham, England, 1974.
- J. M. Stewart and E. C. Lingafelter, *Acta Crystallogr.*, **12**, 842 (1959).
- H. Montgomery and E. C. Lingafelter, *Acta Crystallogr.*, **17**, 1481 (1964).
- J. Kuszaj, B. K. Tomlonovic, D. P. Murtha, R. L. Lintvedt, and M. D. Glick, *Inorg. Chem.*, **12**, 1297 (1973).
- R. L. Lintvedt, L. L. Borer, D. P. Murtha, J. M. Kuszaj, and M. D. Glick, *Inorg. Chem.*, **13**, 18 (1974).
- A. B. Blake and L. R. Fraser, *J. Chem. Soc., Dalton Trans.*, 2254 (1974).
- See, for example, P. W. Anderson, "Magnetism", Vol. 1, G. T. Rado and H. Suhl, Ed., Academic Press, New York, N.Y., 1963, Chapter 2; J. B. Goodenough, "Magnetism and the Chemical Bond", Interscience, New York, N.Y., 1963; J. Kanamori, *Phys. Chem. Solids*, **10**, 87 (1959).
- G. R. Clark, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 823 (1969).
- D. Hall, A. D. Rae, and T. N. Waters, *J. Chem. Soc. A*, 5897 (1963).
- G. R. Clark, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 223 (1968).
- E. N. Baker, D. Hall, A. J. McKinnon, and T. N. Waters, *Chem. Commun.*, 134 (1967).
- M. Gerlock and F. E. Mabbs, *J. Chem. Soc. A*, 1598 (1967).
- M. Gerlock and F. E. Mabbs, *J. Chem. Soc. A*, 1900 (1967).