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Complexes of Binucleating Ligands with Two Different Coordinating Environments. 2. Crystal and Molecular Structures of Two Heterobinuclear Complexes, $NiZn(py)(BAA)_2en$ and $NiVO(BAA)_2en$

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The crystal structures of two heterobinuclear chelates containing the Schiff base ligand derived from ethylenediamine and 1-phenyl-1,3,5-hexanetrione, abbreviated $H_4(BAA)_2en$, have been determined by single-crystal x-ray techniques. The first compound, $NiZn(py)(BAA)_2en$, crystallizes in the space group $I2/c$ with unit cell dimensions of $a = 28.403$ (6) Å, $b = 8.465$ (3) Å, $c = 30.220$ (9) Å, $\beta = 108.86$ (2)°, and $Z = 8$. The second compound, $NiVO(BAA)_2en$, crystallizes in the space group $P2_1/c$ with unit cell dimensions of $a = 11.923$ (3) Å, $b = 15.868$ (4) Å, $c = 13.048$ (7) Å, $\beta = 102.93$ (3)°, and $Z = 4$. In both cases, the Ni(II) is coordinated to two nitrogens and two ketonic oxygens in a square-planar manner with bond lengths and angles similar to related Schiff base and macrocyclic complexes. The second metal, Zn or V, is coordinated to four ketonic oxygens, two of which are also bonded to the Ni atom. In addition, the Zn is bonded to a pyridine nitrogen and the V to a vanadyl oxygen. The environments of both Zn and V are very similar to those found in analogous 1,3-diketonate chelates.

Introduction

In previous papers we have reported the structural and magnetic properties of homobinuclear metal complexes of 1,3,5-triketonate type ligands.[1-3] The structural studies reported to date include a binuclear chelate of Co(II),[1] one of Ni(II),[2] and three of Cu(II).[3,4] One fundamental reason for the interest in this system stems from the strong magnetic superexchange between the metal ions, which are connected by bridging ketonic oxygens. Since the mechanism of superexchange interactions is believed to depend upon the value of the M–O–M bridging angle, structural information is imperative in a discussion of the magnetism. In all of the binuclear chelates studied to date the bridging M–O–M angles are very close to 103° and the magnetic exchange is strongly antiferromagnetic. In the ethylenediamine Schiff base derivatives of 1,3,5-triketonate chelates, the constraints of the diamine might be expected to cause a variation in the M–O–M angle and a resultant change in the magnetic properties. The structural studies of the Schiff base diamine 1,3,5-triketonate chelates were initially undertaken to investigate the relation between bridging angles and magnetic exchange interactions.

In the previous paper in this series[5] we described the synthesis and characterization of a number of heterobinuclear complexes containing Schiff base 1,3,5-triketonate type ligands. In this paper we report the crystal and molecular structures of two heterobinuclear complexes, $NiVO(BAA)_2en$ and $NiZn(py)(BAA)_2en$. The preliminary structure of $NiZn(py)(BAA)_2en$ has been communicated.[6]

Experimental Section

I. Synthesis. Syntheses of the ligand[3] and the complexes[5] have been presented in previous papers.

II. Structure Determination. 1. [*μ*-[[5,5′-(1,2-Ethanediyldinitrilo)bis[1-phenyl-1,3-hexanedionato]](4-)-N^5,$N^{5'}$,O^3,$O^{3'}$:O^1,$O^{1'}$,-O^3,$O^{3'}$]](nickel)pyridinezinc–Dipyridine, $NiZn(py)(BAA)_2en\cdot 2py$. The three-dimensional single-crystal structure determination was carried out on crystals obtained by the recrystallization of $NiZn(BAA)_2en$ from pyridine. Since the dark red-brown crystals decomposed on extended exposure to the air, they were sealed in a capillary with a touch of the mother liquor to maintain crystal stability. The flat platelike crystal used for data collection had the dimensions 0.6 × 0.15 × 0.075 mm. Crystal instability precluded an accurate density measurement. Qualitative determinations with an aqueous saturated potassium tartrate solution and with carbon tetrachloride placed the experimental density between 1.4 and 1.6 g/cm³. The calculated density is 1.501 g/cm³.

Rotation and axial photographs of the crystal on a Syntex $P2_1$ four-circle diffractometer, together with a small set of counter data, were consistent with the monoclinic space groups $I2/c$ and Ic. Fifteen reflections with 2θ between 15 and 22° were centered using a programmed centering routine. The cell constants and errors obtained by a least-squares refinement of these angles were $a = 28.403$ (6) Å, $b = 8.465$ (3) Å, $c = 30.220$ (9) Å, $\beta = 108.86$ (2)°, $V = 6989.2$ (32) Å³, and $Z = 8$. The nonconventional I-centered cell was used to maintain β as close to 90° as possible and thus reduce correlations. The direct cell transformation

$$\begin{bmatrix} 101 \\ 010 \\ -100 \end{bmatrix}$$

yields the conventional cell with symmetry $C2/c$ and lattice constants $a = 34.129$ Å, $b = 8.465$ Å, $c = 28.403$ Å, and $\beta = 123.08°$.

Intensity data were collected using Mo Kα radiation which had 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 scan speed inversely proportional to the peak height and ranging between 1.5 and 14°/min. The 2θ scan range was Kα_1 − 1.0° to Kα_2 + 1.0° and the ratio of the total background time to scan time was 1.0. During data collection, the intensities of four standard reflections were measured every 100 reflections, with no indication of decomposition. Independent data totaling 5055 reflections were collected to $(\sin\theta)/\lambda < 0.54$. Standard deviations[7] of intensities were assigned as $\sigma(I) = [\sigma_{\text{counter}} + (pI)^2]^{1/2}$ where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I is the net intensity, B is the total background counts, K is the ratio of scan time to background time, and p is an instability factor equal to 0.05 in this case. No extinction or absorption corrections was applied. A total of 2562 data with I

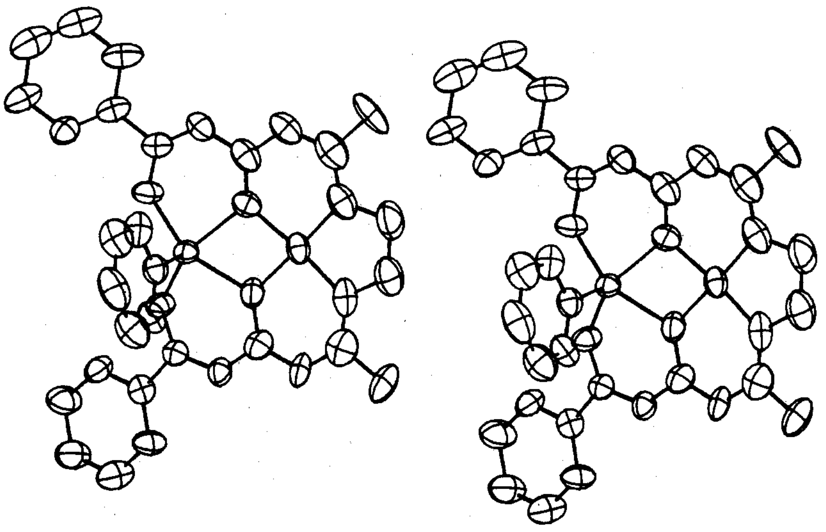


Figure 1. Stereoscopic view of NiZn(py)(BAA)$_2$en.

$> 3\sigma(I)$ were used in the solution and refinement of the structure.

Structure Solution and Refinement. The calculated density indicated eight binuclear molecules in the unit cell. The structure was solved and refined in the centrosymmetric space group $I2/c$. Three-dimensional Patterson techniques yielded the position of the two independent metal ions which gave an unweighted discrepancy factor of 0.468 ($R = \sum||F_o| - |F_c||/\sum|F_o|$). Subsequent three-dimensional Fourier maps allowed the positioning of the remaining nonhydrogen atoms. Full-matrix isotropic least-squares refinement on F of all nonhydrogen atoms resulted in an unweighted R value of 0.102 and a weighted discrepancy factor of $R_w = 0.179$ (where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$). Unambiguous assignment of nitrogen positions in the free pyridine molecules was impossible.

During the isotropic refinement several reflections had $(F_o - F_c)/\sigma > 10$. Three of these were axial ($\bar{2}00$, 002, and 200) and an examination of these data indicated highly asymmetric backgrounds. Therefore, these reflections were dropped from the data set resulting in discrepancy factors $R = 0.082$ and $R_w = 0.102$. Attempts to ascertain the hydrogen atom positions from a difference Fourier map were unsuccessful.

Six cycles of block-diagonal anisotropic least-squares refinement resulted in unweighted and weighted discrepancy factors of 0.057 and 0.071, respectively. However, there was a large shift:error ratio on several atoms,which prompted two cycles of full-matrix least-squares refinement varying x, y, and z to obtain more stable atom positions. A final cycle of anisotropic block-diagonal least-squares refinement resulted in small shift:error ratios, $R = 0.056$, $R_w = 0.070$, and an error of fit of 2.483. The highest residual electron density from the final difference Fourier map was 0.34. Positional coordinates and thermal parameters are listed in Table I. Observed and calculated structure factor amplitudes and an analysis of mean planes are available as supplementary material.

2. [μ-[[5,5′-(1,2-Ethanediyldinitrilo)bis[1-phenyl-1,3-hexanedionato]](4−)-$N^5,N^{5'},O^3,O^{3'}$:$O^1,O^{1'},O^3,O^{3'}$]](nickel)oxovanadium, NiVO(BAA)$_2$en. A single crystal with dimensions of 0.19 × 0.30 × 0.27 mm was mounted inside a thin-walled glass capillary with a glass fiber inserted to prevent the crystal from moving. Rotation and axial photographs on the Syntex diffractometer showed Laue symmetry of $2/m$ and were used to determine initial values of lattice parameters. Accurate lattice constants were obtained from the least-squares refinement of 14 reflections on the previously described diffractometer with Mo Kα radiation (λ 0.710 69 Å). The unit cell parameters are $a = 11.923$ (3) Å, $b = 15.868$ (4) Å, $c = 13.048$ (7) Å, $\beta = 102.93$ (3)°, $\rho_{\text{calcd}} = 1.53$ g/cm^3, $\rho_{\text{flotation}} = 1.53$ g/cm^3, $Z = 4$ molecules, and $\mu = 12.399$ cm^{-1}.

Intensity data to $(\sin\theta)/\lambda < 0.595$ were collected using Mo Kα radiation on the Syntex diffractometer by the θ–2θ technique. The scan rate was 2.02°/min and the scan range was 2θ(MoKα_1) − 1.0° to 2θ(Mo Kα_2) + 1.0°. Backgrounds were measured at each end of the scan for a total time equal to half the scan time. The intensities of three standard reflections measured following every 97 data showed no significant fluctuation. Upon examination of the intensity data the space group was found to be $P2_1/c$.

Standard deviations were assigned as previously given with $p = 0.03$. Of the 4529 independent data examined 2482 had $I \geq 3\sigma(I)$ and were used in the solution and refinement processes.

Analysis of a three-dimensional Patterson synthesis yielded the position of the independent nickel and vanadium atoms. A Fourier map phased on these atoms ($R = 0.396$) yielded the positions of the remaining nonhydrogen atoms. Two cycles of full-matrix least-squares refinement on all nonhydrogen atom coordinates with isotropic thermal parameters resulted in $R = 0.089$ and $R_w = 0.100$. The hydrogen atom positions were calculated at a distance of 0.97 Å from the carbon and verified from a difference Fourier map. Two cycles of block-diagonal least-squares refinement on all nonhydrogen atoms with anisotropic thermal parameters yielded $R = 0.058$ and $R_w = 0.061$. The hydrogen atoms were now recalculated and assigned isotropic thermal parameters of 5.0. This was followed by two cycles of full-matrix least-squares refinement on all nonhydrogen atom coordinates with anisotropic thermal parameters to give a final $R = 0.043$, $R_w = 0.046$, and an error of fit of 1.74. The highest residual electron density from the final difference map was 0.58 e/Å^3. A listing of atomic coordinates and thermal parameters is in Table II. A listing of calculated and observed structure factors and an analysis of mean planes are available as supplementary material.

Results

The structure of one molecule of NiZn(py)(BAA)$_2$en is shown in Figure 1. The molecule consists of the (BAA)$_2$en^{4-} ligand with Ni(II) coordinated to the two nitrogens and the two central oxygens while the Zn(II) is coordinated to the four ketonic oxygens and a nitrogen of pyridine. The Ni(II) is four-coordinate and square planar and the Zn(II) five-coordinate and square pyramidal. Although the x-ray results do not allow one to distinguish between Ni and Zn atoms, structural comparisons between NiZn(py)(BAA)$_2$en and related mononuclear complexes of Ni(II) and Zn(II) leave no doubt as to the positions of these atoms. These comparisons are discussed below. The unit cell contains eight binuclear molecules as well as two uncoordinated pyridine molecules per chelate molecule. A stereoscopic view of the unit cell is shown in Figure 2. The identity of the nitrogen atoms in the uncoordinated pyridines is indeterminate due to the high thermal motion of the atoms.

The important distances and angles in NiZn(py)(BAA)$_2$en are given in Figures 3 and 4. The most important deviation from planarity in the molecule is the zinc atom which is about 0.33 Å out of the mean plane described by the Ni, nitrogen, and oxygen atoms of the ligand.

The structure of a single molecule of the nickel–vanadyl complex, NiVO(BAA)$_2$en, is shown in Figure 5. The

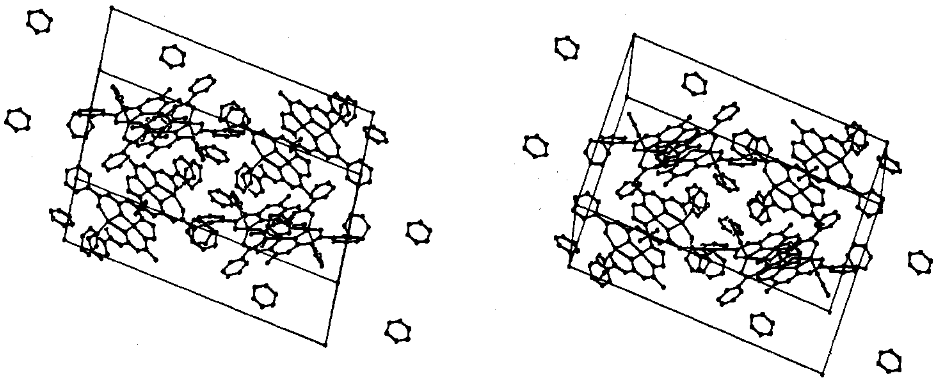


Figure 2. Stereoscopic view of the $NiZn(py)(BAA)_2en{\cdot}py$ unit cell.

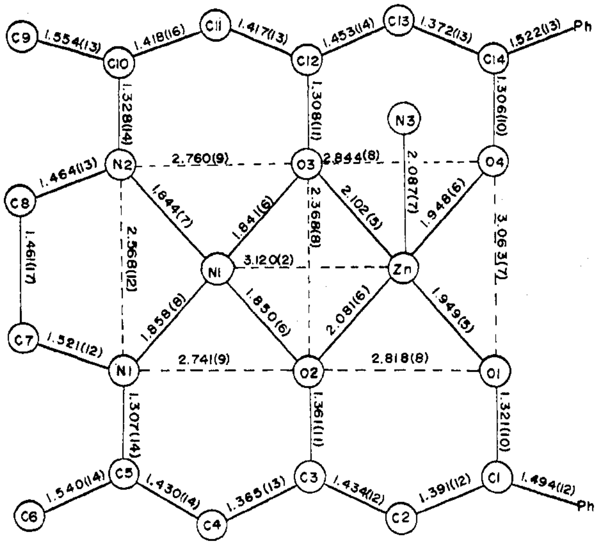


Figure 3. Distances in $NiZn(py)(BAA)_2en$.

structure is quite similar to that of $NiZn(py)(BAA)_2en$ with the Ni(II) coordinated to two nitrogens and the two central oxygens in a square-planar manner and the $V^{IV}O$ coordinated to four ketonic oxygens. A stereoscopic view of the unit cell is shown in Figure 6. Unlike the $NiZn(py)(BAA)_2en$ complex, the crystals of $NiVO(BAA)_2en$ do not contain adduct ligands or solvate molecules.

The important bonded and nonbonded distances in $NiVO(BAA)_2en$ are given in Figure 7. In addition to the values shown, the $N_1{\cdots}N_2$, $O_2{\cdots}O_3$, and $O_1{\cdots}O_4$ distances are 2.580, 2.357, and 2.703 Å, respectively. The bond distances and angles in the phenyl rings in both compounds are normal. The bond angles within the ligand framework are given in Figure 8. The bond lengths and angles for the coordination spheres of the metal atoms are given in Figure 9.

The $Ni(BAA)_2en$ moiety is approximately planar with the vanadium atom sitting 0.616 Å out of the mean plane described by the ketonic oxygens and the nitrogens in typical square-pyramidal fashion. In view of the fact that the vanadium atom is so far out of the plane of the donor atoms it is somewhat surprising that the Ni–V distance (2.991 Å) is the shortest metal–metal distance yet found in 1,3,5-triketonate type binuclear chelates.

Discussion

One of our purposes in undertaking structural studies of these heterobinuclear complexes has been to determine whether the structural features can be characterized as being built from the analogous mononuclear 1,3-diketonates and their Schiff base derivatives. In other words, can the structures of $M_AM_B(BAA)_2en$ complexes be treated as relatively straightforward combinations of the two parent compounds, I and II? If this approach is valid, then the occurrence and properties of the mononuclear chelates could be used to predict the occurrence and certain properties of the heterobinuclear complexes.

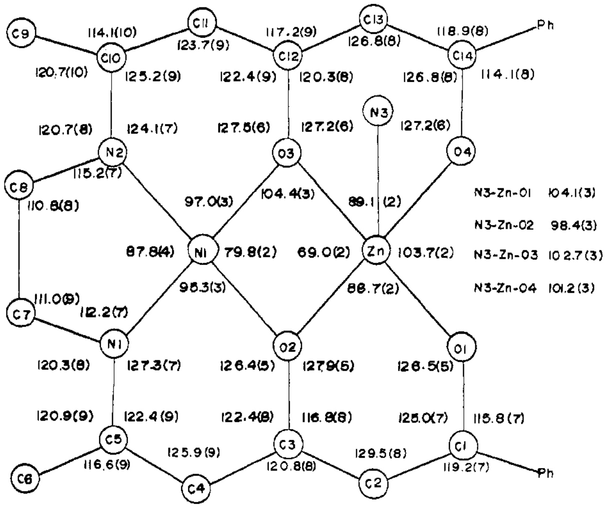
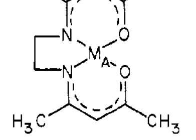
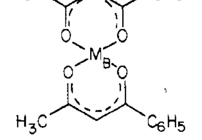


Figure 4. Angles in $NiZn(py)(BAA)_2en$.



$M_A(acac)_2en$

I



$M_B(BA)_2$

II

We have discussed in the previous paper[5] the similarities in spin state ($S = 0$) and d–d electronic spectrum (λ_{max} 565 nm) between $Ni(acac)_2en$ and the $NiH_2(BAA)_2en$. Unfortunately the single-crystal x-ray structure of $Ni(acac)_2en$ has not been reported. However, it is instructive to compare Ni–O and Ni–N distances in some other low-spin, square-planar Ni(II) complexes with the values found for $NiZn(py)(BAA)_2en$ and $NiVO(BAA)_2en$. The values in Table III clearly show that the Ni–O and Ni–N distances in the $(BAA)_2en^{4-}$ chelates are quite typical of square-planar Ni(II).

Since the nickel ions in the $NiM(BAA)_2en$ chelates are in a macrocyclic environment, albeit a rather strange one, we may compare the bond angles about the planar nickel atom to those found in a more usual macrocyclic complex. In the nickel(II)–tetramethylcyclam complex[11] which also contains five- and six-membered chelate rings the N–Ni–N angle in the six-membered ring is 93° while in the five-membered ring it is 87°. In the $NiM(BAA)_2en$ complexes the six-membered

Table I. Positional and Thermal Parameters for NiZn(py)$(BAA)_2$en·2py (Estimated Standard Deviations of the Last Digit in Parentheses)[a]

	x	y	z		x	y	z
Zn	0.3537 (1)	0.3620 (1)	0.3556	C(17)	0.2434 (4)	0.0219 (14)	0.5003 (4)
Ni	0.2825 (1)	0.4703 (2)	0.2625	C(18)	0.2836 (4)	0.0463 (15)	0.5387 (4)
O(1)	0.4199 (2)	0.2883 (7)	0.3604 (2)	C(19)	0.3272 (4)	0.1212 (14)	0.5337 (4)
O(2)	0.3485 (2)	0.4341 (8)	0.2886 (2)	C(20)	0.3284 (3)	0.1740 (12)	0.4895 (3)
O(3)	0.2803 (2)	0.3710 (7)	0.3161 (2)	C(21)	0.5018 (3)	0.2954 (10)	0.3541 (3)
O(4)	0.3336 (2)	0.2365 (7)	0.4013 (2)	C(22)	0.5156 (3)	0.2006 (12)	0.3941 (3)
N(1)	0.2907 (3)	0.5789 (9)	0.2117 (2)	C(23)	0.5641 (3)	0.1612 (14)	0.4140 (4)
N(2)	0.2160 (3)	0.4994 (9)	0.2390 (3)	C(24)	0.6011 (4)	0.2159 (14)	0.3932 (4)
N(3)	0.3639 (2)	0.5832 (9)	0.3873 (2)	C(25)	0.5880 (4)	0.3129 (13)	0.3540 (4)
C(1)	0.4490 (3)	0.3383 (10)	0.3359 (3)	C(26)	0.5383 (3)	0.3531 (11)	0.3345 (3)
C(2)	0.4338 (3)	0.4218 (11)	0.2948 (3)	C(27)	0.3345 (3)	0.6241 (12)	0.4150 (3)
C(3)	0.3856 (3)	0.4719 (12)	0.2700 (3)	C(28)	0.3406 (4)	0.7733 (13)	0.4380 (4)
C(4)	0.3781 (3)	0.5553 (12)	0.2300 (3)	C(29)	0.3755 (4)	0.8770 (13)	0.4300 (4)
C(5)	0.3319 (4)	0.6107 (12)	0.2022 (3)	C(30)	0.4055 (4)	0.8334 (13)	0.4010 (4)
C(6)	0.3326 (4)	0.7074 (14)	0.1592 (3)	C(31)	0.3984 (3)	0.8825 (12)	0.3807 (3)
C(7)	0.2428 (4)	0.6464 (13)	0.1821 (4)	SC(1)	0.4688 (4)	0.2040 (15)	0.4956 (4)
C(8)	0.2009 (4)	0.5747 (15)	0.1937 (4)	SC(2)	0.4435 (4)	0.3514 (15)	0.4806 (4)
C(9)	0.1274 (3)	0.4783 (15)	0.2370 (4)	SC(3)	0.4370 (4)	0.4593 (15)	0.5093 (4)
C(10)	0.1829 (4)	0.4519 (13)	0.2598 (4)	SC(4)	0.4412 (5)	0.4115 (17)	0.5554 (4)
C(11)	0.1935 (3)	0.3745 (12)	0.3030 (4)	SC(5)	0.4623 (5)	0.2550 (16)	0.5631 (4)
C(12)	0.2415 (3)	0.3370 (12)	0.3296 (3)	SC(6)	0.4738 (4)	0.1619 (14)	0.5388 (4)
C(13)	0.2465 (3)	0.2628 (12)	0.3740 (3)	SC(7)	0.0 (0)	0.1962 (14)	0.7500 (0)
C(14)	0.2803 (3)	0.2195 (11)	0.4054 (3)	SC(8)	−0.0039 (5)	0.2738 (14)	0.7132 (4)
C(15)	0.2872 (3)	0.1547 (10)	0.4518 (3)	SC(9)	−0.0054 (4)	0.4399 (15)	0.7097 (4)
C(16)	0.2440 (4)	0.0769 (13)	0.4553 (4)	SC(10)	0.0 (0)	0.5227 (20)	0.7500 (0)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.0011 (1)	0.0129 (2)	0.0010 (1)	0.0002 (1)	0.0004 (1)	−0.0001 (1)
Ni	0.0013 (1)	0.0141 (2)	0.0010 (1)	0.0010 (1)	0.0000 (1)	−0.0006 (1)
O(1)	0.0012 (1)	0.0182 (12)	0.0015 (1)	0.0009 (6)	0.0006 (2)	0.0011 (6)
O(2)	0.0014 (1)	0.0188 (12)	0.0010 (1)	0.0008 (6)	0.0000 (2)	0.0000 (6)
O(3)	0.0010 (1)	0.0199 (13)	0.0015 (1)	0.0007 (6)	0.0005 (2)	0.0002 (6)
O(4)	0.0012 (1)	0.0168 (12)	0.0018 (1)	0.0000 (6)	0.0007 (2)	0.0007 (6)
N(1)	0.0020 (2)	0.0168 (15)	0.0011 (1)	0.0015 (8)	−0.0003 (2)	−0.0006 (7)
N(2)	0.0016 (1)	0.0155 (16)	0.0017 (1)	0.0009 (8)	−0.0002 (2)	−0.0015 (8)
N(3)	0.0013 (1)	0.0146 (14)	0.0013 (1)	0.0004 (7)	0.0003 (2)	−0.0005 (7)
C(1)	0.0013 (1)	0.0120 (16)	0.0011 (1)	0.0001 (8)	0.0005 (2)	−0.0007 (8)
C(2)	0.0014 (2)	0.0151 (19)	0.0011 (1)	0.0005 (9)	0.0003 (2)	0.0002 (8)
C(3)	0.0022 (2)	0.0152 (19)	0.0012 (1)	0.0011 (10)	0.0007 (3)	−0.0002 (9)
C(4)	0.0022 (2)	0.0195 (21)	0.0007 (1)	0.0011 (10)	0.0001 (2)	0.0010 (9)
C(5)	0.0028 (2)	0.0154 (20)	0.0016 (2)	0.0003 (11)	0.0007 (3)	−0.0009 (10)
C(6)	0.0036 (3)	0.0238 (25)	0.0012 (2)	0.0020 (13)	0.0007 (3)	0.0028 (11)
C(7)	0.0019 (2)	0.0233 (24)	0.0019 (2)	0.0018 (12)	−0.0003 (3)	0.0008 (12)
C(8)	0.0023 (2)	0.0267 (27)	0.0015 (2)	0.0005 (13)	−0.0004 (3)	0.0019 (12)
C(9)	0.0008 (1)	0.0277 (26)	0.0031 (2)	0.0016 (11)	−0.0007 (3)	−0.0012 (14)
C(10)	0.0019 (2)	0.0146 (20)	0.0021 (2)	0.0002 (10)	0.0000 (3)	−0.0024 (11)
C(11)	0.0013 (2)	0.0171 (20)	0.0019 (2)	0.0001 (10)	0.0000 (3)	−0.0012 (10)
C(12)	0.0011 (2)	0.0176 (19)	0.0019 (2)	0.0003 (9)	0.0002 (3)	−0.0020 (10)
C(13)	0.0009 (1)	0.0169 (20)	0.0016 (2)	0.0001 (9)	0.0001 (2)	−0.0012 (10)
C(14)	0.0014 (2)	0.0119 (15)	0.0015 (2)	−0.0001 (8)	0.007 (3)	−0.0006 (9)
C(15)	0.0017 (2)	0.0090 (16)	0.0019 (2)	0.0099 (9)	0.0011 (3)	0.0000 (9)
C(16)	0.0019 (2)	0.0165 (21)	0.0028 (2)	−0.0010 (10)	0.0015 (4)	0.0000 (11)
C(17)	0.0028 (2)	0.0211 (24)	0.0028 (2)	0.0001 (13)	0.0018 (4)	0.0008 (13)
C(18)	0.0029 (2)	0.0240 (25)	0.0028 (2)	0.0020 (13)	0.0017 (4)	0.0026 (14)
C(19)	0.0026 (2)	0.0209 (24)	0.0023 (2)	0.0012 (12)	0.0016 (3)	0.0016 (12)
C(20)	0.0018 (2)	0.0156 (20)	0.0014 (1)	0.0012 (9)	0.0007 (3)	0.0002 (9)
C(21)	0.0015 (1)	0.0118 (15)	0.0013 (1)	0.0010 (8)	0.0004 (2)	−0.0004 (8)
C(22)	0.0016 (2)	0.0180 (19)	0.0012 (1)	0.0012 (9)	0.0006 (3)	0.0013 (9)
C(23)	0.0015 (2)	0.0247 (25)	0.0023 (2)	0.0011 (11)	0.0007 (3)	0.0019 (12)
C(24)	0.0015 (2)	0.0227 (24)	0.0024 (2)	0.0002 (11)	0.0007 (3)	0.0025 (12)
C(25)	0.0019 (2)	0.0226 (23)	0.0023 (2)	0.0008 (11)	0.0011 (3)	0.0017 (11)
C(26)	0.0011 (1)	0.0165 (19)	0.0020 (2)	0.0008 (9)	0.0008 (3)	0.0010 (10)
C(27)	0.0020 (2)	0.0189 (20)	0.0013 (1)	0.0021 (10)	0.0004 (3)	−0.0005 (10)
C(28)	0.0025 (2)	0.0175 (22)	0.0021 (2)	0.0009 (12)	0.0004 (3)	−0.0012 (11)
C(29)	0.0019 (2)	0.0216 (23)	0.0022 (2)	0.0021 (12)	−0.0004 (3)	−0.0020 (12)
C(30)	0.0019 (2)	0.0192 (22)	0.0022 (2)	−0.0005 (11)	0.0001 (3)	−0.0016 (11)
C(31)	0.0015 (2)	0.0179 (20)	0.0017 (2)	−0.0004 (9)	0.0001 (3)	−0.0002 (9)
SC(1)	0.0024 (2)	0.0245 (28)	0.0028 (2)	−0.0017 (14)	0.0008 (4)	0.0010 (14)
SC(2)	0.0020 (2)	0.0319 (26)	0.0020 (2)	−0.0014 (13)	0.0002 (3)	0.0012 (13)
SC(3)	0.0023 (2)	0.0201 (27)	0.0031 (2)	−0.0004 (13)	0.0004 (4)	−0.0006 (14)
SC(4)	0.0033 (3)	0.0345 (34)	0.0022 (2)	−0.0043 (16)	0.0007 (4)	−0.0038 (14)
SC(5)	0.0030 (3)	0.0381 (33)	0.0015 (2)	−0.0027 (15)	0.0004 (4)	0.0010 (14)
SC(6)	0.0024 (2)	0.0212 (25)	0.0020 (2)	0.0000 (13)	0.0006 (3)	0.0022 (12)
SC(7)	0.0030 (3)	0.0087 (21)	0.0015 (2)	0.0 (0)	0.0016 (5)	0.0 (0)
SC(8)	0.0032 (3)	0.0147 (22)	0.0035 (3)	−0.0011 (13)	0.0014 (4)	−0.0004 (13)
SC(9)	0.0026 (2)	0.0231 (27)	0.0031 (2)	−0.0008 (14)	0.0006 (4)	0.0010 (14)
SC(10)	0.0027 (4)	0.0212 (34)	0.0027 (4)	0.0 (0)	0.0000 (6)	0.0 (0)

[a] The form of the anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Atoms C(27)–C(31) are from the coordinated pyridine group; C(15)–C(26), the phenyl groups; and SC(1)–SC(10), the pyridine groups of crystallization.

Table II. Positional and Thermal Parameters for NiVO(BAA)$_2$en with the Estimated Standard Deviations of the Last Digit in Parentheses

	x	y	z		x	y	z
Ni	0.320 64 (6)	0.102 22 (4)	−0.088 28 (6)	C10	0.1287 (5)	0.0781 (4)	−0.2526 (5)
V	0.295 81 (8)	0.024 78 (5)	0.114 49 (7)	C11	0.0858 (5)	0.0148 (4)	−0.1948 (4)
O1	0.424 1 (3)	−0.016 9 (2)	0.218 3 (3)	C12	0.1302 (5)	−0.0096 (3)	−0.0936 (4)
O2	0.408 4 (3)	0.080 5 (2)	0.044 7 (3)	C13	0.0805 (4)	−0.0741 (3)	−0.0425 (4)
O3	0.227 2 (3)	0.026 4 (2)	−0.038 3 (3)	C14	0.1217 (4)	−0.1054 (3)	0.0556 (4)
O4	0.217 3 (3)	−0.079 6 (2)	0.120 4 (3)	C15	0.0633 (5)	−0.1760 (3)	0.0985 (4)
O5	0.233 3 (3)	0.095 1 (2)	0.168 4 (3)	C16	−0.0443 (5)	−0.2073 (3)	0.0460 (5)
N1	0.420 7 (5)	0.176 0 (3)	−0.127 4 (4)	C17	−0.0958 (5)	−0.2714 (4)	0.0897 (5)
N2	0.223 9 (4)	0.119 1 (3)	−0.215 6 (3)	C18	−0.0422 (6)	−0.3068 (4)	0.1837 (6)
C1	0.526 4 (5)	0.017 9 (3)	0.245 9 (5)	C19	0.0635 (6)	−0.2774 (4)	0.2361 (6)
C2	0.573 1 (4)	0.069 9 (4)	0.184 2 (5)	C20	0.1158 (5)	−0.2118 (4)	0.1938 (5)
C3	0.519 2 (5)	0.100 7 (4)	0.081 7 (5)	C21	0.5899 (5)	−0.0073 (4)	0.3539 (5)
C4	0.574 7 (5)	0.150 0 (4)	0.021 9 (6)	C22	0.5445 (5)	−0.0706 (4)	0.4066 (5)
C5	0.526 6 (6)	0.187 4 (4)	−0.076 2 (6)	C23	0.5991 (7)	−0.0924 (5)	0.5086 (6)
C6	0.606 9 (5)	0.244 1 (4)	−0.121 2 (6)	C24	0.6954 (8)	−0.0513 (7)	0.5588 (6)
C7	0.372 9 (7)	0.219 9 (4)	−0.227 4 (5)	C25	0.7414 (6)	0.0109 (6)	0.5087 (7)
C8	0.261 4 (6)	0.185 6 (4)	−0.281 0 (5)	C26	0.6901 (6)	0.0329 (4)	0.4060 (6)
C9	0.058 2 (6)	0.095 8 (5)	−0.361 8 (5)				

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.007 91 (7)	0.002 46 (3)	0.005 46 (5)	0.000 03 (4)	0.002 59 (5)	0.000 69 (4)
V	0.006 35 (8)	0.002 78 (4)	0.004 39 (6)	−0.000 34 (5)	0.001 15 (6)	0.000 12 (4)
O1	0.007 0 (3)	0.003 9 (2)	0.006 3 (3)	−0.000 7 (2)	−0.000 1 (3)	0.000 5 (2)
O2	0.007 4 (4)	0.003 5 (2)	0.006 4 (3)	−0.001 6 (2)	0.001 9 (3)	0.000 4 (2)
O3	0.007 8 (3)	0.003 0 (2)	0.004 4 (2)	−0.000 4 (2)	0.001 6 (2)	0.000 4 (2)
O4	0.006 6 (3)	0.003 5 (2)	0.005 9 (3)	−0.001 0 (2)	0.000 3 (3)	0.000 7 (2)
O5	0.008 8 (4)	0.004 3 (2)	0.006 2 (3)	0.000 4 (2)	0.001 6 (3)	−0.000 8 (2)
N1	0.010 2 (5)	0.002 7 (2)	0.008 3 (4)	0.000 7 (3)	0.004 2 (4)	0.001 0 (3)
N2	0.010 3 (5)	0.002 9 (2)	0.005 5 (4)	0.000 7 (3)	0.003 8 (3)	0.001 0 (2)
C1	0.006 6 (5)	0.003 0 (3)	0.006 9 (5)	0.001 5 (3)	0.000 7 (4)	−0.000 1 (3)
C2	0.005 9 (5)	0.003 5 (3)	0.009 1 (6)	0.000 1 (3)	0.001 0 (4)	0.000 0 (3)
C3	0.006 9 (5)	0.003 0 (2)	0.009 2 (5)	0.000 1 (3)	0.002 2 (4)	0.000 4 (3)
C4	0.006 0 (5)	0.004 4 (3)	0.012 1 (7)	0.000 1 (3)	0.002 9 (5)	0.002 2 (4)
C5	0.008 8 (7)	0.003 0 (3)	0.012 1 (7)	0.000 5 (3)	0.005 4 (6)	0.001 8 (4)
C6	0.010 5 (7)	0.004 4 (3)	0.016 7 (8)	0.000 2 (4)	0.006 3 (6)	0.002 9 (4)
C7	0.019 7 (10)	0.003 7 (3)	0.006 6 (5)	−0.002 1 (4)	0.003 1 (6)	0.001 3 (3)
C8	0.010 1 (6)	0.005 1 (3)	0.008 5 (6)	0.001 2 (4)	0.003 6 (5)	0.002 1 (4)
C9	0.012 9 (7)	0.007 6 (4)	0.005 8 (5)	0.000 7 (5)	0.000 6 (5)	0.002 9 (4)
C10	0.010 0 (6)	0.003 7 (3)	0.005 9 (5)	0.001 2 (3)	0.002 5 (5)	0.000 7 (3)
C11	0.009 4 (6)	0.003 6 (3)	0.005 0 (4)	−0.000 8 (3)	0.001 1 (4)	−0.000 1 (3)
C12	0.007 9 (5)	0.002 8 (2)	0.004 7 (4)	0.000 2 (3)	0.001 6 (4)	−0.000 6 (3)
C13	0.007 5 (5)	0.003 1 (2)	0.004 5 (4)	−0.000 4 (3)	0.001 3 (4)	−0.000 0 (3)
C14	0.006 9 (5)	0.002 8 (2)	0.005 6 (4)	0.000 4 (3)	0.002 1 (4)	−0.000 1 (3)
C15	0.007 0 (5)	0.002 8 (2)	0.006 1 (4)	−0.000 1 (3)	0.002 5 (4)	0.000 3 (3)
C16	0.008 2 (6)	0.003 4 (3)	0.006 9 (5)	−0.001 0 (3)	0.002 8 (4)	−0.000 8 (3)
C17	0.009 0 (6)	0.003 8 (3)	0.008 9 (6)	−0.001 8 (3)	0.003 6 (5)	−0.000 5 (3)
C18	0.011 2 (7)	0.004 0 (3)	0.012 1 (7)	−0.000 7 (4)	0.005 1 (6)	0.001 9 (4)
C19	0.008 1 (6)	0.006 8 (4)	0.011 6 (7)	−0.000 9 (4)	0.001 8 (5)	0.004 7 (4)
C20	0.006 8 (5)	0.005 8 (3)	0.008 7 (6)	−0.000 6 (3)	0.001 3 (4)	0.002 4 (4)
C21	0.006 4 (5)	0.004 0 (3)	0.006 9 (5)	0.002 4 (3)	0.000 2 (4)	−0.001 2 (3)
C22	0.009 4 (6)	0.006 0 (4)	0.006 3 (5)	0.002 4 (4)	0.002 0 (5)	0.000 6 (4)
C23	0.012 3 (8)	0.008 1 (5)	0.007 8 (6)	0.004 7 (6)	0.003 2 (6)	0.001 8 (5)
C24	0.012 3 (10)	0.010 6 (7)	0.008 4 (7)	0.006 4 (6)	−0.000 1 (7)	−0.000 8 (5)
C25	0.008 7 (8)	0.010 0 (6)	0.011 7 (8)	0.002 7 (6)	−0.002 7 (7)	−0.003 4 (6)
C26	0.008 6 (7)	0.005 7 (4)	0.011 2 (7)	0.001 5 (4)	−0.001 3 (6)	−0.001 1 (4)

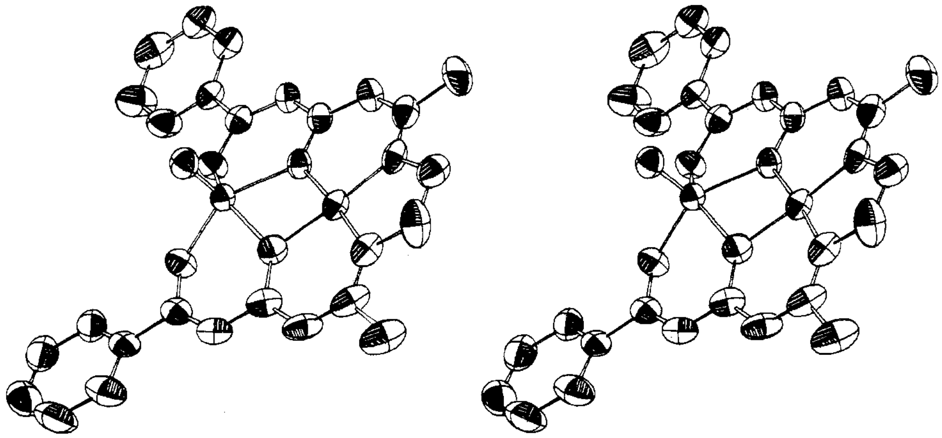


Figure 5. Stereoscopic view of NiVO(BAA)$_2$en.

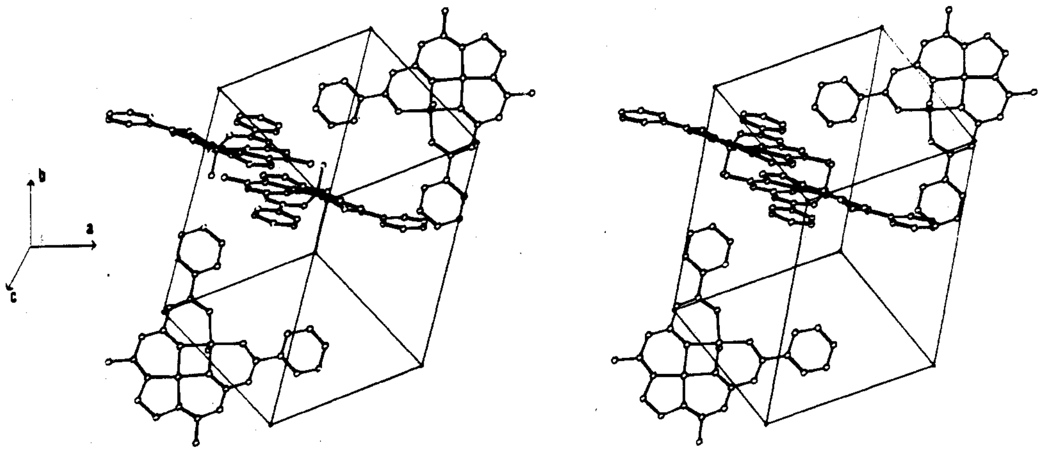


Figure 6. Stereoscopic view of the NiVO(BAA)$_2$en unit cell.

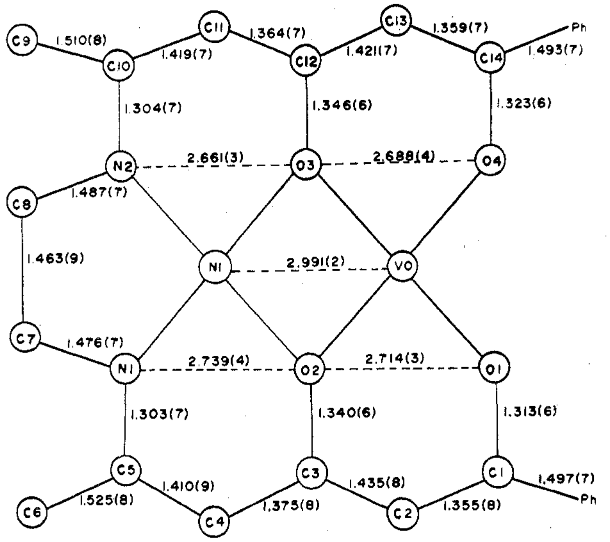


Figure 7. Distances in NiVO(BAA)$_2$en.

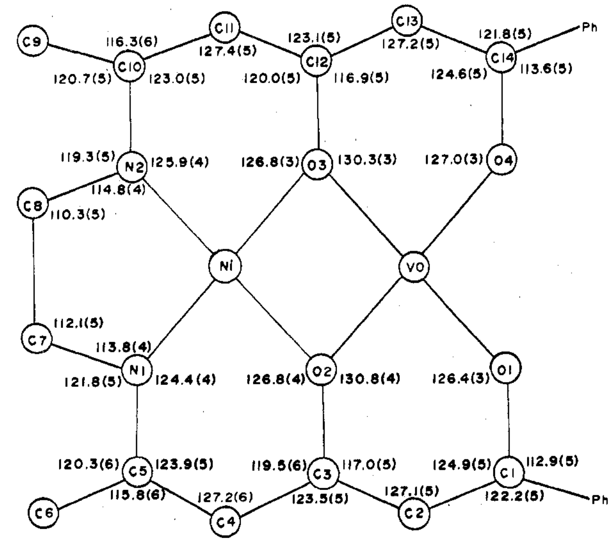


Figure 8. Angles within the ligand framework in NiVO(BAA)$_2$en.

ring N–Ni–O angle is about 96.5°, the five-membered ring N–Ni–N angle is about 88°, and the four-membered O–Ni–O angle is about 79°. We conclude that the nickel atom in NiZn(py)(BAA)$_2$en and NiVO(BAA)$_2$en is in a four-coordinate, square-planar geometry which is quite typically found in other square-planar Ni(II) complexes regardless of whether the ligands are oxygen donors, nitrogen donors, or mixtures of the two.

Table III. Comparison between Some Ni–O and Ni–N Distances in Square-Planar and Octahedral Ni(II) Complexes

	Ni–O, Å	Ni–N, Å	Ni(II) coord sphere geometry	Ref
Ni(DPM)$_2$^{a}	1.836		Square planar	8
Ni(acac)$_2$(H$_2$O)$_2$^{b}	2.015		Distorted octahedral	9
Ni(OEPME$_2$)^c		1.904	Square planar	10
[Ni$_2$(C$_{14}$H$_{32}$N$_4$)$_2$(N$_3$)$_3$]$^{+\,d}$		2.15	Octahedral	11
H$_2$EDTA(OAcH$_2$O)Ni	2.03	2.11	Octahedral	12
Ni(sim)$_2$^{e}	1.82	1.87	Square planar	13
NiZn(py)(BAA)$_2$en	1.845	1.851	Square planar	This work
NiVO(BAA)$_2$en	1.851	1.821	Square planar	This work

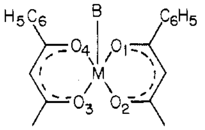
^{a} DPM$^-$ is the anion of 2,2,6,6-tetramethyl-3,5-heptanedione. ^{b} acac$^-$ is the anion of 2,4-pentanedione. ^{c} OEPMe$_2$$^{2-}$ is the dianion of α,γ-dihydrooctaethylporphyrin. ^{d} C$_{14}$H$_{32}$N$_4$ is tetramethylcyclam. ^{e} sim$^-$ is the anion of *N*-methylsalicylaldimine.

The coordination geometries of the V^{IV}O and Zn^{II} in the two heterobinuclear chelates should be comparable to the geometries in VO(1,3-dik)$_2$ and Zn(1,3-dik)$_2$(base) if there are no unusual structural features due to the presence of two metals per molecule. The comparison is even more straightforward when one realizes that the single-crystal x-ray structural data have been reported for *cis*-bis(1-phenyl-1,3-butanedionato)oxovanadium(IV)^{14} and *cis*-bis(1-phenyl-1,3-butanedionato)(ethanol)zinc(II).^{15} The comparative data presented in Table IV show that the metal ions in the 1,3-diketonate chelates and in the heterobinuclear complexes have very similar environments. The only significant difference between the binuclear and mononuclear analogues is that the four-membered M$_2$O$_2$ ring in NiVO(BAA)$_2$en and NiZn(py)(BAA)$_2$en causes the internal O$_2$–M–O$_3$ angle to be unusually small. This is compensated for by an increase in the O$_1$–M–O$_4$ angle. However, this distortion does not seem to affect other angles or distances to any significant extent.

It may thus be seen that it is structurally possible to prepare a very large number of heterobinuclear complexes of H$_4$(BAA)$_2$en and related ligands since these ligands will accommodate two metal ions in much the same manner as 1,3-diketonates and their Schiff base derivatives. We are currently investigating several other systems in which the Ni(II) is replaced by a different metal ion.

Some other aspects of these structures are of sufficient interest to mention at this point. One of these concerns the effect of the ethylenediamine bridge on the bridging angle

Table IV. Comparison of the Coordination Geometries of $V^{IV}O$ and Zn^{II} in Mononuclear and Heterobinuclear Complexes



	Distances, Å						Angles, deg					Distortion of M from O_4 plane, Å	Ref
	M-O_1	M-O_2	M-B	O_1-O_2	O_2-O_3	O_1-O_4	O_1-M-O_2	O_2-M-O_3	O_3-M-O_4	O_1-M-O_4	B-M-O_1		
$VO(BA)_2$[a]	1.95	1.98	1.61	2.71	2.70	2.56	87.3	85.8	87.5	82.2	106.9	0.564	14
$NiVO(BAA)_2en$	1.92	1.99	1.59	2.71	2.36	2.70	87.9	72.7	87.5	89.6	107.9	0.616	This work
$Zn(BA)_2(CH_3OH)$[a]	2.00	1.98	2.07				89.2	88.5	89.8	86.7	100.3	0.32	15
$NiZn(py)(BAA)_2en$	1.95	2.09	2.09	2.82	2.37	3.06	88.7	69.0	89.1	103.7	104.1	0.382	This work

[a] BA^- is the anion of 1-phenyl-1,3-butanedione (benzoylacetone).

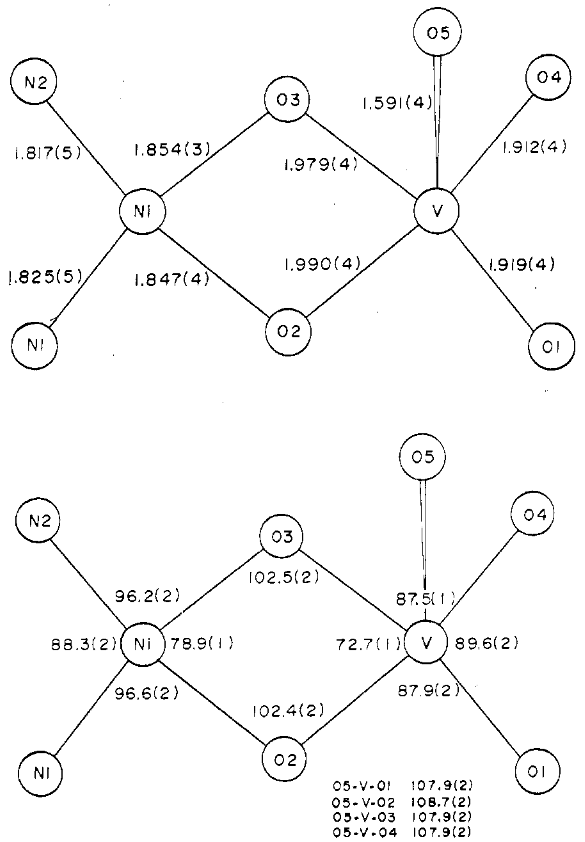


Figure 9. Coordination sphere parameters for the metal atoms in $NiVO(BAA)_2en$.

M–O–M. In the five reported structures of binuclear 1,3,5-triketonates[1-4] this angle is always close to 103°. It was originally assumed that the ethylenediamine group would cause sufficient strain to bring about a decrease in the M–O–M angle and, thereby, some interesting changes in magnetic exchange properties. The $NiVO(BAA)_2en$ and $NiZn(py)(BAA)_2en$ structures show, however, that any strain that may be caused by the ethylenediamine is absorbed in other parts of these molecules leaving the M–O–M angle apparently unaffected. The square-pyramidal geometry of V and Zn make it a bit difficult to compare these values with those of the more planar Co(II), Ni(II), and Cu(II) molecules.[1-4] A subsequent paper which reports the structure of $NiNi(py)_2(BAA)_2en$ deals with this point in more detail.[16]

Another point of interest is the decrease in the C–C bond distance in the ethylenediamine moiety upon coordination. In the mononuclear chelates of Cu(II)[3] and $V^{IV}O$[5] in which the N_2O_2 site is vacant the C_7–C_8 distance is 1.53 Å. When Ni(II) is coordinated in the N_2O_2 site, the C_7–C_8 distance decreases to 1.46 Å. Day and co-workers[17] reported a similar trend toward double-bond character in a manganese(III)–ethylenediamine Schiff base complex. The bond shortening would seem to favor a dehydrogenation which we have observed to take place in the mass spectrometer.[5] The products of such a dehydrogenation would be complexes containing a completely conjugated ligand. We are currently in the process of attempting to isolate such complexes by chemical dehydrogenations.

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Registry No. $NiZn(py)(BAA)_2en{\cdot}2py$, 59091-66-6; $NiVO(BAA)_2en$, 56027-77-1.

Supplementary Material Available: Listings of structure factor amplitudes and analyses of mean planes (26 pages). Ordering information is given on any current masthead page.

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(7) (a) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsees' program for data reduction; (2) FORDAP, A. Zalkin's Fourier program; (3) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; (4) ORTEP, C. K. Johnson's program for drawing crystal models; (5) HFINDR, A. Zalkin's program for calculating idealized hydrogen positions; (6) REFINE, J. J. Park's block-diagonal least-squares program. (b) Scattering factors for Ni(II), V(IV), O, N, C, and H, including anomalous scattering for the metal atoms, were taken from "International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., Kynoch Press, Birmingham, England 1974.
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