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Redetermination of the Crystal and Molecular Structure of *trans*-Diaquobis(2,4-pentanedione)nickel(II) Perchlorate, Including Location and Refinement of Hydrogen Atoms

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The crystal and molecular structure of *trans*-diaquobis(2,4-pentanedione)nickel(II) perchlorate $[Ni(C_5H_8O_2)_2(H_2O)_2](ClO_4)_2$ has been redetermined by single-crystal x-ray diffraction techniques using counter methods and has been refined by full-matrix least-squares procedures to a final conventional R index of 0.045. The turquoise crystals belong to the space group $P\bar{1}$ with $a = 10.504$ (4), $b = 13.019$ (9), $c = 7.965$ (3) Å; $\alpha = 93.22$ (7), $\beta = 109.26$ (2), and $\gamma = 101.31$ (9)°. There are two nonequivalent, centrosymmetric cations per unit cell. All hydrogen atoms were located, and their positional and thermal parameters refined. This, together with the detailed structure of the complex cations, establishes that the 2,4-pentanedione ligand is coordinated in the keto form in both molecules. The major difference in the two independent molecules is the conformation of the six-membered rings formed by the Ni(II) ion and the chelate. In one molecule, this ring system is nearly planar, but in the other it is folded in the boat conformation. The ring strain in these chelate rings produces large C–C–C angles (117.0 (5)° in the folded ring and 122.1 (5)° in the flatter ring) at the four-coordinate methylene carbon. A positive correlation is noted between these angles and the acidity of the methylene protons.

Introduction

In the recently reported[1] crystal structure of $[Ni(acHac)_2(H_2O)_2](ClO_4)_2$[2] two nonequivalent centrosymmetric molecules were found in each unit cell. In one of these molecules, the keto form of the acetylacetone chelate ring is clearly present with the chelate ring being quite puckered, as is also found for $Ni(acHac)_2Br_2$.[3] However, in the other molecule, the acHac ring is nearly flat and the average ring C–C bond length is 1.45 (3) Å; these observations suggest that the chelate ring should be formulated as an enolate anion. Yet the C–O bond lengths, 1.25 (2) Å, are consistent with a keto formulation for this chelate ring. Since the hydrogen atoms were not located, the authors were unable to conclude whether the flat chelate ring is in the keto form with the proton attached to the methylene carbon, whether it is in the enol form with the proton attached to an oxygen of the chelate ring, or whether the ring is in the enolate form with the proton ionized and residing elsewhere, perhaps associated with a perchlorate ion.

Since we were interested in mechanisms which establish the keto–enol tautomerism,[4] the spin-delocalization mechanisms,[5] and the conformations of chelate rings in such complexes, we decided to redetermine the structure of $[Ni(acHac)_2(H_2O)_2](ClO_4)_2$ in order to learn the correct formulation of this unusual diketone ring.

Data Collection and Reduction

Crystals of $[Ni(acHac)_2(H_2O)_2](ClO_4)_2$ grew slowly from a CH_3NO_2 solution of $[Ni(acHac)_3](ClO_4)_2$ in a capped NMR tube. Presumably the slow diffusion of H_2O into the solution displaced one of the chelate rings, causing the title compound to form. A crystal of dimensions 0.57 × 0.70 × 0.75 mm was sealed in a glass capillary inside a drybox and mounted for data collection.

The intensities of all reflections for which $3.0° < 2\theta < 50.0°$ were measured with a Syntex computer-controlled $P\bar{1}$ diffractometer in the manner previously described.[6] Of the 3546 reflections examined, 2352 had intensities greater than 3 times their standard deviations and only these were used in structure solution and refinement. Two check reflections, $\bar{2}04$ and 044, were measured after each 100 reflections throughout data collection and showed no decrease in intensity. Eight determinations of the cell parameters by the previously described method[7] yielded the average values $a = 10.504$ (4), $b = 13.019$ (9), $c = 7.965$ (3) Å; $\alpha = 93.22$ (7), $\beta = 109.26$ (2), $\gamma = 101.31$ (9)°. As shown by successful refinement, and in agreement with the earlier work,[1] the correct space group is $P\bar{1}$.

The net counts were corrected for Lorentz and polarization effects, and standard deviations were assigned according to the published formula[8] with $p = 0.0$. The computer programs used in this study were those previously described.[7] Atomic scattering factors[9] for Ni^+, O^0, C^0, Cl^0, and H (bonded)[10] were used.

Solution and Refinement of Structure

One solution to the Patterson function, that with Ni^{2+} ions at the origin and at ($^1/_2$, $^1/_2$, 0), proved to be correct. The remaining nonhydrogen atoms were located by successive Fourier syntheses. Full-matrix least-squares refinement of these atomic positions with anisotropic thermal parameters led to $R_1 = 0.056$ and $R_2 = 0.054$ where R_1 and R_2 are the usual error indices as previously defined.[7] At this point, a difference Fourier function revealed the positions of all 20 hydrogens. Including these in refinement with isotropic thermal parameters lowered the error indexes to $R_1 = 0.045$ and $R_2 = 0.042$. Application of Hamilton's significance test[11] shows that including the hydrogen atoms is justified at the 99.5% confidence level. The final goodness of fit, as defined previously,[7] is 1.37. The overdetermination ratio, 2353/333 = 7.1, is comfortably high. The largest peak remaining in the final difference Fourier function, whose esd was 0.080 e Å^{-3}, had a density of 0.3 e Å^{-3}.

Table I. Final Positional and Anisotropic Thermal Parameters with Standard Deviations[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	0	0	0	61 (1)	42 (1)	115 (2)	−2 (1)	14 (2)	14 (2)
Ni(2)	5000	5000	0	56 (1)	36 (1)	118 (2)	22 (1)	27 (2)	8 (2)
Cl(1)	6457 (2)	1987 (1)	7579 (2)	116 (2)	74 (1)	204 (3)	87 (2)	27 (4)	−29 (3)
Cl(2)	1990 (2)	3687 (1)	3578 (2)	113 (2)	73 (1)	130 (3)	16 (2)	87 (3)	−15 (3)
C(A1)	2099 (8)	69 (8)	5702 (10)	136 (9)	167 (9)	137 (13)	66 (14)	60 (18)	30 (17)
C(A2)	1863 (5)	222 (4)	3788 (7)	92 (6)	73 (4)	119 (10)	65 (8)	32 (13)	3 (10)
C(A3)	3038 (5)	881 (4)	3415 (8)	80 (6)	62 (4)	169 (13)	27 (7)	−8 (13)	−19 (11)
C(A4)	2961 (6)	1072 (4)	1579 (9)	77 (6)	40 (4)	204 (14)	15 (8)	42 (15)	15 (11)
C(A5)	4275 (7)	1616 (6)	1354 (13)	80 (6)	106 (6)	368 (23)	−33 (10)	87 (20)	103 (19)
O(A1)	740 (4)	−172 (3)	2646 (5)	85 (4)	75 (3)	136 (8)	12 (5)	37 (9)	38 (7)
O(A2)	1900 (4)	833 (3)	263 (5)	67 (4)	60 (3)	161 (8)	−10 (5)	26 (9)	34 (7)
O(HA)	−550 (4)	1309 (3)	714 (7)	105 (5)	60 (3)	263 (11)	46 (6)	−13 (12)	−31 (9)
C(B1)	880 (6)	2991 (4)	−2127 (8)	92 (6)	61 (4)	168 (12)	−11 (8)	61 (14)	34 (10)
C(B2)	2064 (6)	3919 (4)	−1473 (7)	75 (6)	51 (4)	95 (10)	2 (8)	42 (12)	15 (10)
C(B3)	1710 (5)	4995 (4)	−1550 (8)	72 (5)	65 (4)	185 (12)	35 (7)	83 (13)	28 (10)
C(B4)	2655 (5)	5852 (4)	−2031 (7)	73 (5)	41 (3)	132 (9)	39 (6)	20 (11)	9 (8)
C(B5)	2030 (6)	6617 (5)	−3171 (11)	98 (6)	62 (4)	286 (18)	50 (8)	18 (17)	109 (14)
O(B1)	3244 (3)	3825 (3)	−904 (5)	73 (4)	42 (2)	136 (7)	18 (4)	42 (8)	11 (6)
O(B2)	3900 (3)	5948 (2)	−1513 (5)	73 (4)	42 (2)	170 (8)	27 (4)	48 (9)	37 (6)
O(HB)	5547 (4)	4547 (3)	−2083 (6)	121 (5)	59 (3)	178 (9)	28 (5)	109 (11)	−15 (7)
O(1)	6454 (12)	1147 (7)	8625 (16)	493 (23)	184 (8)	795 (41)	391 (24)	832 (54)	463 (32)
O(2)	6617 (9)	1619 (6)	5992 (10)	302 (13)	167 (7)	279 (17)	191 (16)	242 (25)	25 (17)
O(3)	5222 (5)	2334 (4)	7268 (9)	120 (6)	91 (4)	408 (18)	93 (8)	−51 (16)	−130 (13)
O(4)	7606 (7)	2778 (7)	8615 (13)	137 (7)	194 (8)	591 (28)	101 (12)	−73 (23)	−339 (24)
O(5)	3403 (6)	3789 (5)	3804 (10)	147 (7)	161 (6)	442 (20)	109 (11)	246 (20)	254 (18)
O(6)	1401 (7)	2634 (4)	3854 (10)	263 (11)	74 (4)	463 (21)	16 (10)	366 (26)	30 (14)
O(7)	1231 (7)	3858 (8)	1845 (8)	197 (9)	289 (11)	165 (12)	82 (16)	96 (18)	142 (19)
O(8)	1784 (7)	4377 (4)	4818 (9)	291 (12)	94 (4)	282 (15)	43 (11)	245 (22)	−78 (13)

[a] Values are given ×10^4. The esd in parentheses is in units of the least significant digit given for the corresponding parameter. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

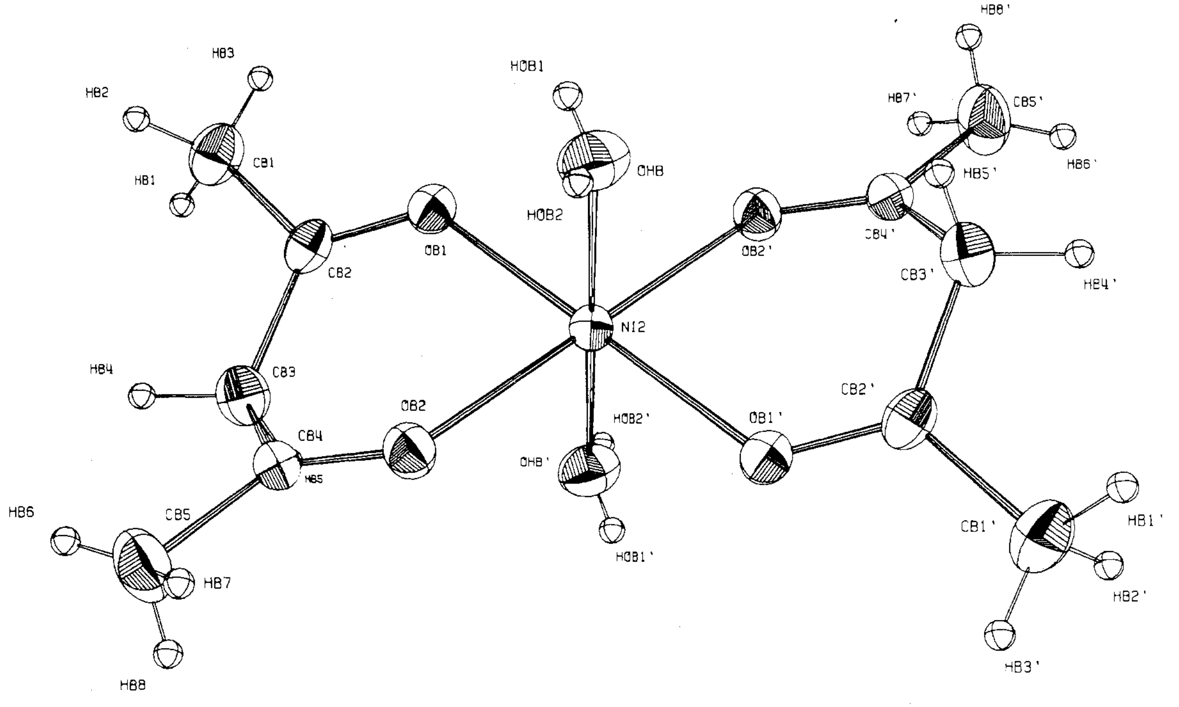


Figure 1. ORTEP drawing of the nearly flat cation, A. Ellipsoids of 30% probability are used.

The final parameters for the nonhydrogen atoms are presented in Table I while those for the hydrogens are listed in Table II. The bond distances and angles involving the nonhydrogen atoms are presented in Table III along with their standard deviations. Similar data involving hydrogen atoms are presented in Table IV. An ORTEP drawing of cation A is presented in Figure 1, and molecule B is shown in Figure 2.

Discussion

The conventional reduced triclinic unit cell used in this report is different from the cell selected by Anzenhofer and Hewitt.[1] Multiplication of the unit cell vectors, or Miller indices, of the earlier report by the matrix

$$\begin{bmatrix} 0 & 1 & \bar{1} \\ \bar{1} & \bar{1} & \bar{1} \\ 0 & 0 & 1 \end{bmatrix}$$

transforms them into those used here. Similarly, multiplication of the fractional coordinates of Anzenhofer and Hewitt by

$$\begin{bmatrix} \bar{1} & 1 & 0 \\ \bar{1} & 0 & 0 \\ \bar{2} & 1 & 1 \end{bmatrix}$$

followed, perhaps, by a suitable translation and/or an inversion,

Table II. Hydrogen Atom Positions and Thermal Parameters[a]

Atom	z	y	z	B, Å²
H(A6)	0.489 (7)	0.130 (5)	0.163 (11)	5.4 (1.6)
H(A7)	0.419 (13)	0.165 (9)	0.009 (20)	12.7 (3.5)
H(A8)	0.461 (12)	0.213 (9)	0.204 (17)	10.9 (3.0)
H(A4)	0.375 (6)	0.062 (4)	0.376 (8)	3.5 (1.1)
H(A5)	0.326 (9)	0.150 (6)	0.414 (12)	7.6 (2.0)
H(A1)	0.298 (9)	0.010 (7)	0.661 (13)	8.1 (2.1)
H(A2)	0.180 (6)	0.050 (5)	0.598 (9)	4.5 (1.3)
H(A3)	0.149 (8)	−0.052 (6)	0.590 (11)	6.9 (1.9)
H(OA1)	−0.110 (7)	0.149 (4)	0.029 (9)	4.3 (1.3)
H(OA2)	−0.012 (7)	0.166 (5)	0.125 (9)	4.5 (1.3)
H(B1)	0.016 (8)	0.303 (5)	−0.157 (11)	6.1 (1.7)
H(B2)	0.044 (9)	0.292 (6)	−0.329 (12)	7.5 (2.0)
H(B3)	0.113 (5)	0.239 (4)	−0.197 (7)	2.8 (1.0)
H(B4)	0.080 (6)	0.493 (4)	−0.227 (8)	3.4 (1.1)
H(B5)	0.182 (5)	0.526 (4)	−0.036 (7)	2.4 (.9)
H(B6)	0.127 (8)	0.637 (6)	−0.359 (11)	6.4 (1.8)
H(B7)	0.281 (11)	0.698 (8)	−0.361 (16)	10.2 (2.7)
H(B8)	0.214 (13)	0.711 (9)	−0.248 (18)	11.7 (3.2)
H(OB1)	0.525 (7)	0.407 (5)	−0.233 (9)	4.8 (1.4)
H(OB2)	0.563 (11)	0.487 (8)	−0.256 (15)	10.3 (2.8)

[a] The esd in parentheses is in the units of the least significant digit for the corresponding parameter.

Table III. Molecular Dimensions and Estimated Standard Deviations

Nickel Octahedra

Distances, Å

Ni(1)–O(A1)	2.034 (4)	Ni(2)–O(B1)	2.038 (3)
Ni(1)–O(A2)	2.013 (3)	Ni(2)–O(B2)	2.029 (3)
Ni(1)–O(HA)	2.014 (4)	Ni(2)–O(HB)	2.021 (4)

Angles, Deg

O(A1)-Ni(1)-O(A2)	88.6 (1)	O(B1)-Ni(2)–O(B2)	87.9 (1)
O(A1)-Ni(1)-O(HA)	88.0 (2)	O(B1)-Ni(2)–O(HB)	90.6 (1)
O(A2)-Ni(1)-O(HA)	91.7 (2)	O(B2)-Ni(2)–O(HB)	89.9 (1)

Acetylacetone

Distances, Å

C(A2)–O(A1)	1.218 (7)	C(B2)–O(B1)	1.205 (6)
C(A4)–O(A2)	1.222 (7)	C(B4)–O(B2)	1.212 (6)
C(A4)–C(A3)	1.475 (9)	C(B4)–C(B3)	1.498 (7)
C(A2)–C(A3)	1.484 (8)	C(B2)–C(B3)	1.518 (7)
C(A4)–C(A5)	1.495 (9)	C(B4)–C(B5)	1.487 (8)
C(A2)–C(A1)	1.493 (9)	C(B2)–C(B1)	1.480 (8)

Angles, Deg

Ni(1)–O(A1)–C(A2)	129.9 (4)	Ni(2)–O(B1)–C(B2)	127.4 (3)
Ni(1)–O(A2)–C(A4)	130.2 (4)	Ni(2)–O(B2)–C(B4)	127.2 (3)
O(A1)–C(A2)–C(A1)	119.5 (5)	O(B1)–C(B2)–C(B1)	121.8 (5)
O(A1)–C(A2)–C(A3)	124.1 (5)	O(B1)–C(B2)–C(B3)	121.9 (5)
C(A1)–C(A2)–C(A3)	116.4 (5)	C(B1)–C(B2)–C(B3)	116.4 (5)
C(A2)–C(A3)–C(A4)	122.1 (5)	C(B2)–C(B3)–C(B4)	117.0 (5)
O(A2)–C(A4)–C(A3)	124.4 (5)	O(B2)–C(B4)–C(B3)	122.5 (5)
O(A2)–C(A4)–C(A5)	118.8 (6)	O(B2)–C(B4)–C(B5)	119.4 (4)
C(A5)–C(A4)–C(A3)	116.8 (5)	C(B5)–C(B4)–C(B3)	118.1 (5)

Perchlorate Ions

Distances, Å

Cl(1)–O(1)	1.412 (8)	Cl(2)–O(5)	1.414 (6)
Cl(1)–O(2)	1.400 (8)	Cl(2)–O(6)	1.451 (6)
Cl(1)–O(3)	1.407 (5)	Cl(2)–O(7)	1.403 (7)
Cl(1)–O(4)	1.399 (8)	Cl(2)–O(8)	1.395 (6)

Angles, Deg

O(4)–Cl(1)–O(2)	111.0 (4)	O(8)–Cl(2)–O(7)	108.6 (4)
O(4)–Cl(1)–O(1)	105.0 (6)	O(8)–Cl(2)–O(5)	113.0 (4)
O(4)–Cl(1)–O(3)	110.9 (4)	O(8)–Cl(2)–O(6)	105.7 (3)
O(2)–Cl(1)–O(1)	107.6 (6)	O(7)–Cl(2)–O(5)	111.1 (5)
O(2)–Cl(1)–O(3)	112.8 (4)	O(7)–Cl(2)–O(6)	108.2 (5)
O(1)–Cl(1)–O(3)	109.2 (5)	O(5)–Cl(2)–O(6)	110.0 (4)

transforms these parameters into values in good agreement with those reported here. We have used an atom-numbering scheme which is in accord with the earlier report.[1]

The major differences between the two studies result from the larger data set available to us, 2352 vs. 1142 reflections, which allows us to refine all nonhydrogen atoms anisotropically and to determine and refine the hydrogen atom parameters. As a result, our standard deviations are about one-third those of the original study, and many of the detailed features of the molecular geometry which appeared in their study are altered in this one.

In the report by Anzenhofer and Hewitt, there are two structural features which suggested that ligand A might be present in the enol form. These were the near planarity of ligand A and the presence of two different Ni–O bond lengths (2.07 (1) and 2.02 (1) Å). Our results affirm that the two Ni–O lengths are significantly different (see Table III) but show that they are also in agreement with those found for ligand B, which is clearly a keto ligand. Furthermore, the location and refinement of all hydrogen atoms, including both of those located on the methylene carbons of each ligand, leave little doubt that the acetylacetone molecules are present in the keto form in both molecules.

The only other parameters which differ significantly between the two studies are those involving angles in the Ni^{2+} octahedra. It is interesting to note that the chelate bite angles, such as O(A1)–Ni(1)–O(A2), are all found to be slightly less than 90° in this study; some were reported to be greater than 90° in the earlier work. The parameters reported for the ClO_4^- ions agree particularly well.

There are no significant differences between the bond lengths of ligand A and ligand B. One is tempted to point out that the average ring C–C bond length in ligand A is shorter than the corresponding length in ligand B and to ascribe this difference to incipient delocalization in the flatter ring, but the difference at three to four standard deviations is barely significant.

It is more fruitful to compare the bond angles in the two ligands. Six-membered rings of this type (vide infra) are usually puckered, presumably because this relieves ring strain. If we compare the internal ring angles of ring A to those in ring B, we find that those in the flatter ring A are all larger than those of ring B, by four to ten esd's. Thus, the ring strain in the flatter ring does not result in puckering but rather in the opening the bond angles within the ring.

In the previous report,[1] it was inferred that cation A was planar because it represented the enol form of the ligand. We have, however, shown that in both cations, the keto form of the ligand is present, so one must look elsewhere for the source of the planarity of this chelate. The crystal packing and hydrogen-bonding forces in the neighborhood of cation A are apparently of sufficient energy to have caused its chelate rings, which must be quite flexible, to become planar. We note that the location and orientation of the perchlorate ions are different with respect to the two complex cations. There are two mechanisms by which these ions could influence the ring conformations of the complex. First are the interionic contacts, listed and illustrated earlier,[1] which show four interactions less than 3.4 Å between C(3) of cation A and the perchlorate oxygens but only three for cation B. Second, hydrogen bonding between the waters and perchlorate oxygens requires that the water molecule be rotated approximately 90° in comparing cation A to cation B. (See Figures 1 and 2.) Thus the closest approaches of water and methylene protons in molcule A are H(A5)–H(OA2), 3.6 Å, and H(A4)′–H(OA1), 3.9 Å, while in molecule B the shortest contacts between these types of atoms are H(B5)′–H(OB1), 3.1 Å, and H(B5)′–H(OB2), 3.0 Å. However, if we rotate the water molecule in complex B by 90° to approximate the orientation found in molecule A, the H(B5)′–H(OB2) distance decreases to 2.3 Å. Since these distances are calculated using the hydrogen positions from our x-ray data, it is likely that the true distance between hydrogens would be even less. Thus there would be some steric problems

Table IV. Bond Distances and Bond Angles Involving Hydrogen

	Distances, Å		
C(A1)-H(A1)	0.96 (9)	C(B1)-H(B1)	1.00 (8)
C(A1)-H(A2)	0.76 (6)	C(B1)-H(B2)	0.88 (9)
C(A1)-H(A3)	0.95 (8)	C(B1)-H(B3)	0.88 (5)
C(A3)-H(A4)	0.85 (5)	C(B3)-H(B4)	0.92 (5)
C(A3)-H(A5)	0.91 (8)	C(B3)-H(B5)	0.95 (5)
C(A5)-H(A6)	0.81 (7)	C(B5)-H(B6)	0.75 (8)
C(A5)-H(A7)	0.99 (15)	C(B5)-H(B7)	1.03 (11)
C(A5)-H(A8)	0.78 (12)	C(B5)-H(B8)	0.78 (12)
O(HA)-H(OA1)	0.66 (6)	O(HB)-H(OB1)	0.63 (7)
O(HA)-H(OA2)	0.60 (6)	O(HB)-H(OB2)	0.59 (11)
	Angles, Deg		
C(A2)-C(A1)-H(A1)	126 (6)	C(B2)-C(B1)-H(B1)	113 (4)
C(A2)-C(A1)-H(A2)	100 (5)	C(B2)-C(B1)-H(B2)	113 (5)
C(A2)-C(A1)-H(A3)	116 (5)	C(B2)-C(B1)-H(B3)	113 (3)
H(A1)-C(A1)-H(A2)	108 (7)	H(B1)-C(B1)-H(B2)	106 (7)
H(A1)-C(A1)-H(A3)	105 (7)	H(B1)-C(B1)-H(B3)	109 (6)
H(A2)-C(A1)-H(A3)	99 (7)	H(B2)-C(B1)-H(B3)	103 (6)
C(A2)-C(A3)-H(A4)	111 (4)	C(B2)-C(B3)-H(B4)	110 (3)
C(A2)-C(A3)-H(A5)	105 (5)	C(B2)-C(B3)-H(B5)	107 (3)
H(A4)-C(A3)-H(A5)	106 (7)	H(B4)-C(B3)-H(B5)	108 (4)
C(A4)-C(A3)-H(A4)	101 (4)	C(B4)-C(B3)-H(B4)	111 (3)
C(A4)-C(A3)-H(A5)	111 (5)	C(B4)-C(B3)-H(B5)	102 (3)
C(A4)-C(A5)-H(A6)	115 (6)	C(B4)-C(B5)-H(B6)	106 (6)
C(A4)-C(A5)-H(A7)	113 (7)	C(B4)-C(B5)-H(B7)	104 (5)
C(A4)-C(A5)-H(A8)	109 (8)	C(B4)-C(B5)-H(B8)	104 (8)
H(A6)-C(A5)-H(A7)	98 (9)	H(B6)-C(B5)-H(B7)	136 (8)
H(A6)-C(A5)-H(A8)	102 (10)	H(B6)-C(B6)-H(B8)	110 (11)
H(A7)-C(A5)-H(A8)	119 (12)	H(B7)-C(B5)-H(B8)	93 (11)
Ni(1)-O(HA)-H(OA1)	128 (6)	Ni(2)-O(HB)-H(OB1)	106 (6)
Ni(1)-O(HA)-H(OA2)	120 (6)	Ni(2)-O(HB)-H(OB2)	116 (10)
H(OA1)-O(HA)-H(OA2)	109 (8)	H(OB1)-O(HB)-H(OB2)	126 (12)

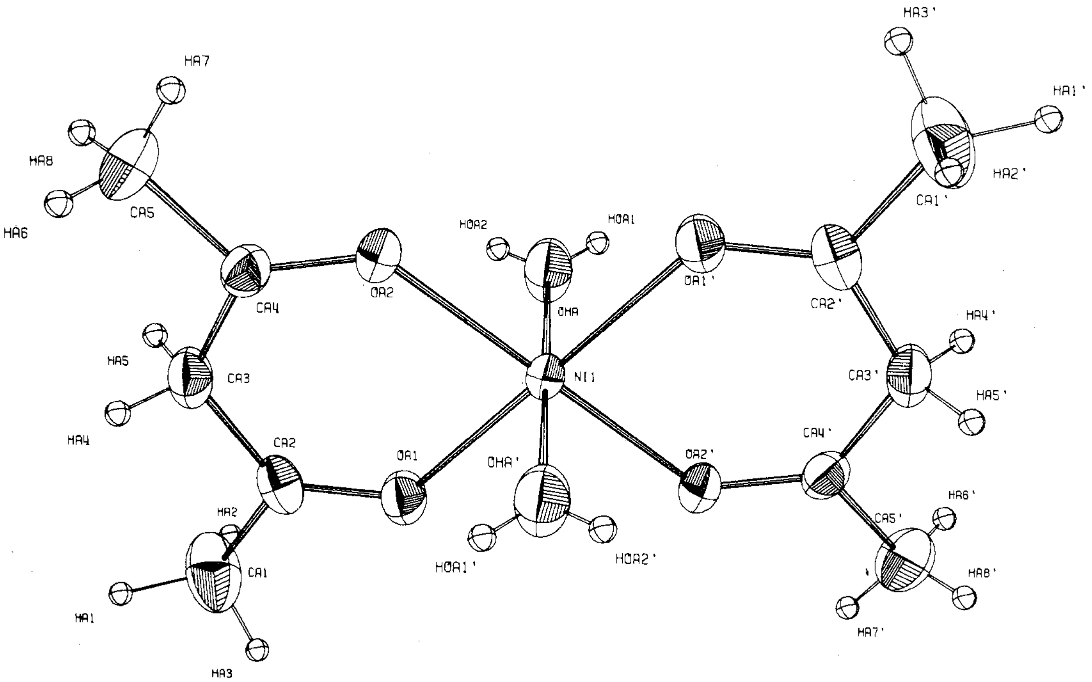


Figure 2. ORTEP drawing of the folded cation, B. Ellipsoids of 30% probability are used.

between a folded chelate ring and a water molecule oriented in the fashion found in the flatter chelate ring, A.

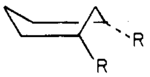
The conformations of the six-membered rings in this structure are of interest since few structures with this type of ring system have been reported. In this compound, the double-bond character of the carbonyl group restricts torsional motion about the C–O bond so that the four atoms of the $R_2C{=}O$ group must be planar. The ring system consists of a metal ion and two planar ketone groups separated by a flexible methylene group. The only torsional freedom available to the ring resides in the M–O bonds and the C–C bonds to the methylene group. One can think of many donor groups which would produce chelate rings of this type, including imines, aromatic heterocyclic rings, amides, ketones, aldehydes, and carboxylic acids. In spite of numerous potential examples of such chelate rings, the structures of only two, Ni(acHac)$_2$Br$_2$[3] and [*N,N'*-bis(2-aminoethyl)malondiamidato]nickel(II),[12] have been reported. Due to the double-bond character of the bond between the donor atom and the adjacent carbon, all of these six-membered rings adopt a "rowing" boat

Table V. Some Dihedral Angles in Six-Membered Rings of the Type $\overline{\mathrm{MD{=}C(R)CH_2C(R')}{=}\mathrm{D}}^a$

Species	Conformn	Dihedral angle,[b] deg			C–C–C, deg	Ref
		DMD–DCCD[c]	DCCR–DCCR′	DCCD[c]–CCC		
trans-$[Ni(acHac)_2(H_2O)_2]^{2+}$, molecule B	Boat	18.5	36.8	31.4	117.0 (5)	This work
trans-$[Ni(acHac)_2Br_2]$	Boat	19	29	29	114 (2)	3
[*N,N′*-Bis(2-aminoethyl)malondiamidato]nickel(II)	Boat	10.5	5.9	6.3	123.6 (2)	12
trans-$[Ni(acHac)_2(H_2O)_2]^{2+}$, molecule A	Skew boat	6.4, 6.0[d]	7.8		122.1 (5)	This work

[a] D indicates donor atom, either O or N in all compounds in this table. [b] The largest deviation of any atom from the indicated planes is 0.007 Å. [c] The DCCD plane is that which forms the bottom of the boat. [d] Dihedral angles between acetone planes (DCCR and DCCR′) and the O–Ni–O (DMD) plane. The atoms of the DCCD plane deviate from it by up to 0.040 Å.

conformation



where the R groups represent the oars. Various dihedral angles found in these ring systems are summarized in Table V.[13]

Examination of these dihedral angles indicates that the rings can be either quite puckered or relatively flat. This is best illustrated by the two nonequivalent molecules in this study, one of which is sharply folded while the other is nearly planar. The two previous reports (vide supra) furnish an additional example of such a pair; one ring is quite puckered[3] while the other[12] is only moderately folded.

The data presented in Table V reveal that as the ring becomes flatter, the C–C–C angle becomes larger. The central atom of this angle is bound to two carbons and two hydrogens, so that a near-tetrahedral C–C–C angle would be expected. However, the values for the last two entries in Table V, which are the two flatter rings, are significantly larger. As a consequence, the protons associated with the methylene carbon should be especially acidic. Ring strain, then, may be one of the driving forces responsible for the facile deprotonation reaction which transforms the keto form of β diketone ligands into the more commonly found enolate form.

The K_a of the methylene carbon of the same type of ring system in the macrocycle ATH and related compounds has been reported.[14] There is little difference in the acidity of 13- and 14-membered macrocycles, but the acidity of the 15-membered macrocycle is too small to be measured. The authors[14] attributed the decrease in acidity in the 15-membered ring system to ring strain resulting from the presence of an adjacent 6-membered ring. They suggested that the increased ring strain destabilized the planar, anionic form of the ligand, thus decreasing the tendency for the deprotonation reaction to take place. The K_a of Cu(II) complexes of the 13- and 14-membered macrocycles has also been reported.[14] For Cu(II) $K_a \approx 10^{-9}$ while for Ni(II) $K_a \approx 10^{-6}$. The lesser acidity of the Cu(II) complexes was attributed to the larger size of the Cu(II) ion, which would also increase ring strain, again destabilizing the conjugate base.

While this explanation of the trend in acidities is consistent with the available data, others have suggested that there is little strain in the conjugate base form of these macrocycles.[15] We wish to suggest another explanation of the acidity trend based upon strain in the uncharged, acidic form of the ligand. We suggest that the opening of the C–C–C angle in the neutral form of these ligands, from the expected 109.5° to values as great as 123.6 (2)°, is more important than the corresponding opening from 120 to 128 (2)° of this angle in the basic, planar form of the ligand. In the unstrained molecules, i.e., 13- and 14-membered macrocycles with Ni(II), the six-membered chelate ring can be quite flat, as observed in molecule A of the structure reported here. As a result the C–C–C angle is forced open to a value greater than 120° and the proton is easily lost from the central carbon. As ring strain is increased, e.g., in the Cu(II) complexes or the 15-membered Ni(II) macrocycles, the six-membered ring becomes less planar, resulting in a decrease in the C–C–C angle to a more normal value, with a cocomitant decrease in the acidity of the methylene protons.

Registry No. *trans*-$[Ni(acHac)_2(H_2O)_2](ClO_4)_2$, 35277-46-4.

Supplementary Material Available: Listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

References and Notes

(1) K. Anzenhofer and T. G. Hewitt, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **134**, 54 (1971).

(2) acHac is the keto form of 2,4-pentanedione.

(3) S. Koda, S. Ooi, H. Kuroya, K. Isobe, Y. Nakamura, and S. Kawaguichi, *Chem. Commun.*, 1321 (1971).

(4) R. E. Cramer and M. A. Chudyk, *Inorg. Chem.*, **12**, 1193 (1973).

(5) R. E. Cramer and M. A. Chudyk, *J. Magn. Reson.*, **12**, 168 (1973).

(6) R. E. Cramer and K. Seff, *Acta Crystallogr., Sect. B*, **28**, 3281 (1972).

(7) L. G. Warner, M. M. Kadooka, and K. Seff, *Inorg. Chem.*, **14**, 1773 (1975).

(8) R. E. Cramer, W. Van Doorne, and R. Dubois, *Inorg. Chem.*, **14**, 2462 (1975).

(9) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, p 201.

(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3178 (1965).

(11) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(12) R. M. Lewis, G. H. Nancollas, and P. Coppens, *Inorg. Chem.*, **11**, 1371 (1972).

(13) The *z* coordinate of atom N(2) in the structure of [*N,N′*-bis(2-aminoethyl)malondiamidato]nickel(II) was reported[12] incorrectly to be 0.1014. The correct value is 0.010 14: P. Coppens, private communication, Feb 10, 1976.

(14) J. G. Martin and S. C. Cummings, *Inorg. Chem.*, **12**, 1477 (1973).

(15) M. F. Richardson and R. E. Sievers, *J. Am. Chem. Soc.*, **94**, 4134 (1972).