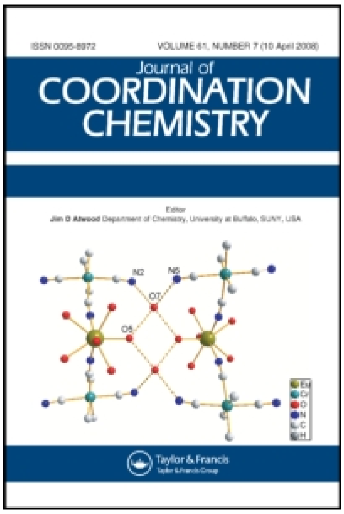

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THE CRYSTAL AND MOLECULAR STRUCTURE OF DIAQUOBIS(ACETYLACETONATO)NICKEL(II). MONOHYDRATE†

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The monoclinic form of diaquobis(acetylacetonato)nickel(II) is well known; however, the existence of the triclinic monohydrate form is not well recognized although preparations of the diaquo complex yield predominantly the monohydrated species when water is present in excess amounts. Diaquobis(acetylacetonato)nickel(II) monohydrate has a unit cell of dimensions $a = 9.083$ Å, $b = 11.012$ Å, $c = 7.578$ Å, $\alpha = 95.85°$, $\beta = 92.12°$ and $\gamma = 106.00°$ and contains two molecules related by a center of symmetry. 3,122 pieces of three-dimensional intensity data (CuKα) were collected using an automated diffractometer. The structure was solved by conventional Patterson and Fourier techniques and was refined by least squares methods to a conventional R of 0.09. The structure is that of the hydrate water molecule hydrogen bonded predominantly to the acetylacetone oxygens of the diaquobis(acetylacetonato)nickel(II) molecule. The structure of the diaquobis(acetylacetonato)nickel(II) molecule obtained in this study is compared to its structure in the non-hydrated monoclinic form. Observed changes in the axial water bond length and the oxygen square plane are interpreted to be the result of the stronger hydrogen bond interactions in the monohydrated species.

INTRODUCTION

The well-known and extensively investigated octahedral complex diaquo(acetylacetonato)nickel(II), hereafter referred to as $Ni(AcAc)_2 \cdot 2H_2O$, crystallizes in the monoclinic crystal class and its structure has been determined some time ago.[1] The existence of a hydrated form of $Ni(AcAc)_2 \cdot 2H_2O$ is, however, not generally recognized although the isolation of a triclinic and presumably hydrated species was first observed and partially characterized by Montgomery[2] and later reported by Morosin.[3] Which of the two species, the monoclinic diaquo complex or the triclinic diaquohydrated complex, or a mixture thereof, one obtains from a reaction or recrystallization solution is determined solely by the amount of water present and to some extent by the temperature. We have noted that the method of Charles and Pawlikowski,[4] which has been widely reported in the literature as the method used for the preparation of the diaquo complex, yields a mixture. Morosin[3] has also shown that the X-ray powder pattern reported by Holm and Cotton for the diaquo complex is that of a mixture of the monoclinic and triclinic forms. We undertook the determination of the complete crystal structure of the triclinic form in order to determine the exact composition of the triclinic species, which up to now had not been determined, and to determine the effect of the presumably hydrogen-bonded crystal water on the structure of the diaquo complex.

EXPERIMENTAL

Blue-green elongated plates of the triclinic hydrate were obtained by slow evaporation of a saturated 7:1 water-acetone solution of the mixed triclinic-monoclinic complex. The majority of crystals obtained were twinned and all slowly lost water in air of very low humidity. All of our measurements were made during the humid summer months and no instability was observed during the course of data collection. Lattice parameters determined from NaCl calibrated rotation, Weissenberg and precession photographs are: $a = 9.083 \pm 0.003$ Å, $b = 11.012 \pm 0.007$ Å, $c = 7.578 \pm 0.003$ Å, $\alpha = 95.85 \pm 0.08°$, $\beta = 92.12 \pm 0.08°$, and $\gamma = 106.00 \pm 0.08°$. A density of 1.433 g/cm^3 was measured by floatation which agreed well with a density of 1.426 g/cm^3 calculated for two molecules of diaquobis(acetylacetonato)nickel(II) · monohydrate per unit-cell.

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Integrated intensities ($\theta - 2\theta$ scan, 2°/min) for 3122 reflections were collected on a Canberra Industries automated Quarter-Circle General Electric XRD-6 single crystal diffractometer using Ni filtered CuKα radiation. Thirty second fixed backgrounds were taken at 0.5° 2θ to the appropriate side of Kα_1 and Kα_2 respectively. The crystal was mounted along c* and had the dimensions of $0.15 \times 0.25 \times 0.50$ mm. The intensities were corrected for background, counting chain nonlinearity, X-ray generator, etc., instabilities as reflected in small changes in the reference reflections, and Lorentz-polarization. Absorption corrections, other than experimentally determined phi corrections obtained by measuring 001 reflections *vs.* phi at chi = 90°, were not applied. μ for this compound is 20.8 cm^{-1} for CuKα radiation.

A calculation of the statistical distribution of the diffraction intensities indicated the space group to be the centro-symmetric P$\bar{1}$ which proved to be correct on the basis of the final structure solution. Weights were assigned as unity except for $\sqrt{I} > 80$ and $\sqrt{I} < 1$ (I = measured I/100) where a value of 0.5 was assigned.

A 3-D Patterson map was calculated from which the positions of all of the heavy atoms could be deduced and which indicated the compound to be a monohydrate. Several cycles of least-squares refinement on these atomic coordinates and isotropic thermal parameters using ORFLS^6 led to an agreement index, *R*, of 0.15. At this point a difference map was calculated which showed broad positive regions of electron density near each of the methyl carbons and water oxygens, however individual hydrogen atoms, except for the hydrogen attached to the central carbon of the acetylacetone ring, could not be located with certainty. After conversion to anisotropic thermal parameters, several cycles of continued least squares refinement reduced R to 0.096 for all 3122 reflections (0.088 omitting 324 unobserved reflections). Another difference map calculated at this point proved to be similar to the first; methyl carbon and water hydrogens could not be unambiguously determined. The difference map, except for regions of electron density in the vicinity of the methyl carbons, the central carbon and the water oxygens, was free of detail. No evidence for heavy atom disordering or incomplete occupation of the single hydrate water site could be found.

The refined atomic coordinates and anisotropic thermal parameters with their estimated standard deviations are listed in Table I. A listing of observed and calculated structure factors may be obtained from the authors upon request. All calculations were performed on an IBM 360/50 computer at the Syracuse University Computer Center using locally written programs or modified National Research Council of Canada programs.^{7}

TABLE I

Final atomic coordinates and anisotropic thermal motion parameters ($\times 10^4$) with e.s.d.'s

Anisotropic thermal parameters are of the form:

$$\exp[-(h^2\beta11 + k^2\beta22 + l^2\beta33 + 2hk\beta12 + 2hl\beta13 + 2kl\beta23)]$$

Atom	*x*	*y*	*z*
Ni	0.2055 1	0.0412 1	0.2550 1
O_1	0.0625 4	0.1515 4	0.2706 7
O_2	0.3912 5	0.1950 4	0.2688 7
O_3	0.0188 4	−0.1110 4	0.2380 7
O_4	0.3418 4	−0.0751 4	0.2418 6
O_5	0.2063 5	0.0411 5	−0.0210 6
O_6	0.2085 5	0.0444 5	0.5315 6
O_7	0.6308 5	0.0754 5	0.2611 8
C_1	−0.0294 8	0.3324 7	0.3013 12
C_2	0.1014 7	0.2700 6	0.2853 9
C_3	0.2525 8	0.3494 6	0.2904 11
C_4	0.3855 7	0.3078 6	0.2785 10
C_5	0.5400 9	0.4076 8	0.2804 14
C_6	−0.1384 8	−0.3225 7	0.2057 13
C_7	0.0190 7	−0.2260 6	0.2197 9
C_8	0.1497 8	−0.2703 6	0.2094 12
C_9	0.3014 7	−0.1948 6	0.2226 10
C_{10}	0.4321 9	−0.2571 8	0.2155 14

Atom	β11	β22	β33	β12	β13	β23
Ni	90 1	86 1	214 2	25 1	−0 1	14 1
O_1	63 5	67 4	245 11	25 4	−8 6	10 5
O_2	60 5	66 4	328 14	11 4	−6 7	5 6
O_3	59 5	59 4	291 12	13 4	−6 6	4 5
O_4	72 5	71 4	228 10	32 4	−4 6	13 5
O_5	104 6	146 7	166 10	44 5	9 6	37 6
O_6	110 7	140 6	157 9	47 5	7 6	15 6
O_7	79 6	116 6	282 13	40 5	−10 7	14 7
C_1	108 10	82 7	346 23	53 7	−6 12	17 10
C_2	94 8	69 6	179 13	36 6	−9 8	13 7
C_3	102 9	64 6	279 18	19 6	−8 10	13 8
C_4	76 8	67 6	213 15	4 5	−1 8	6 7
C_5	93 10	80 8	441 28	−14 7	2 13	−2 12
C_6	94 10	71 7	365 24	−11 6	−18 12	12 10
C_7	76 8	67 6	199 14	11 5	3 8	21 7
C_8	113 10	63 6	299 20	31 6	−5 11	24 9
C_9	92 8	78 6	201 14	40 6	13 8	30 8
C_{10}	124 11	97 8	413 27	73 8	6 14	30 12

DISCUSSION

Bond distances and angles for the molecule are summarized in Figure 1 with a complete listing being given in Table II. The numbering scheme being used can be obtained from Figure 1. Distances and angles for the acetylacetonate groups are those expected.[8] The coordination sphere about the nickel atom is basically a tetragonally distorted octahedron. The crystal lattice consists of discrete molecules of diaquobis(AcAc)Ni(II) and waters of crystallization held together in an extensive hydrogen bond network. Figure 2 is a stereo molecular packing diagram which indicates some of these possible hydrogen bond interactions. The possibilities, even if sometimes relatively weak, are numerous; thus the hydrogens involved may not be in single fixed positions, but may be randomly located in several possible locations. Other intermolecular contacts, with one exception, are of the order of van der Waals distances. The exception involves methyl carbon atoms C_5 and C_6' (C_6 in the adjacent sheet) which are only 3.66 Å apart, much less than the 3.9 to 4.0 Å expected. The carbon–carbon bonds of these methyl groups, C_4–C_5 and C_7'–C_6', are almost colinear, thus a

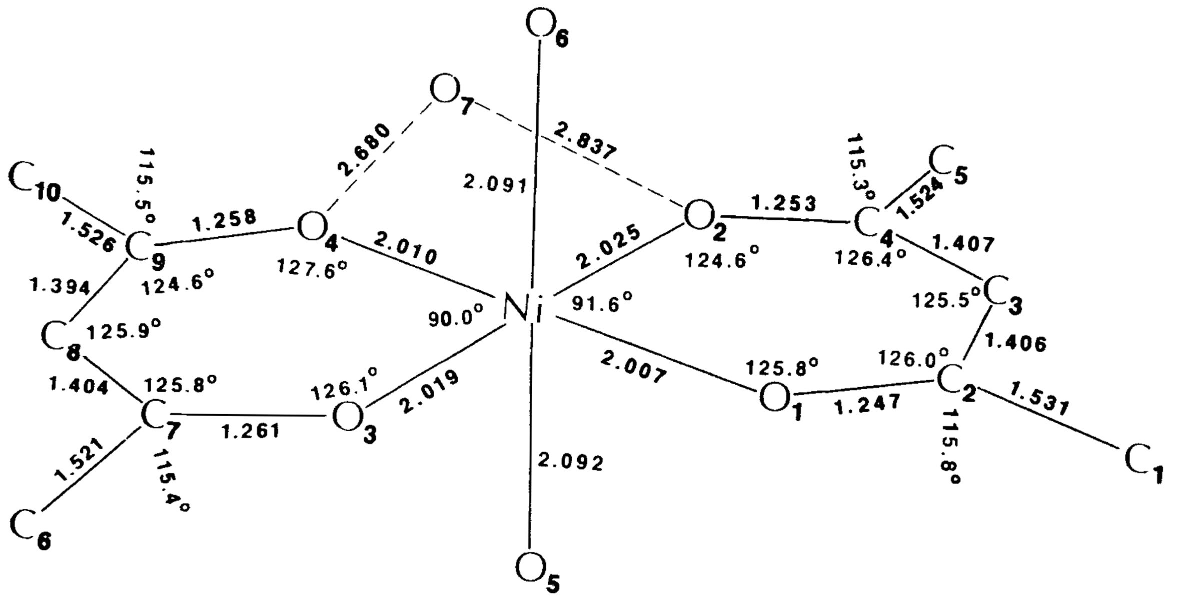

FIGURE 1 Bond distances and angles for diaquobis(acetylacetonato)nickel(II)·monohydrate.

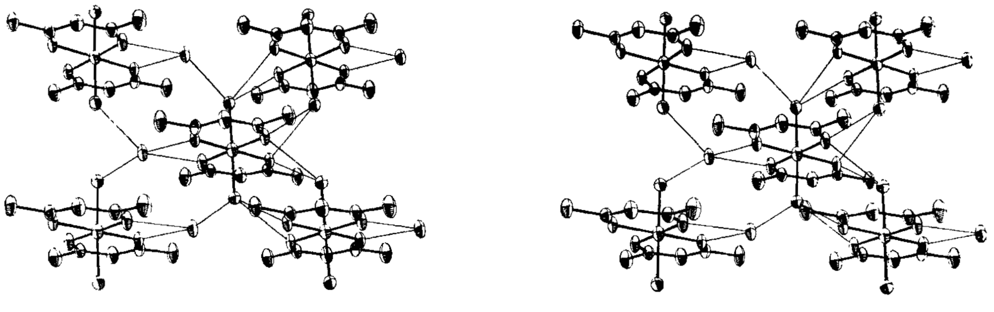

FIGURE 2 Stereographic Molecular packing diagram of diaquobis(acetylacetonato)nickel(II)monohydrate showing possible intermolecular hydrogen bonds.

staggering of the hydrogens must occur to allow this close contact. There appears to be no reason why random ordering of the hydrogens of the methyl groups as well as random distribution of the hydrogens of the water molecules could not occur, thus explaining the inability to unambiguously locate these hydrogens in the difference maps.

TABLE II

Bond distances and angles for the diaquobis(acetylacetonato)nickel(II)·monohydrate complex

Bond Distances (Å°)			Bond Angles (°)		
Ni—O$_1$	2.007	4	O$_1$—Ni—O$_2$	91.6	3
Ni—O$_2$	2.025	4	O$_3$—Ni—O$_4$	90.0	3
Ni—O$_3$	2.019	4	O$_1$—Ni—O$_3$	87.8	3
Ni—O$_4$	2.010	4	O$_2$—Ni—O$_4$	90.6	3
Ni—O$_5$	2.092	5	O$_1$—Ni—O$_5$	91.4	3
Ni—O$_6$	2.091	5	O$_2$—Ni—O$_5$	86.2	3
			O$_3$—Ni—O$_5$	93.1	3
O$_1$—C$_2$	1.247	8	O$_4$—Ni—O$_5$	89.4	3
O$_2$—C$_4$	1.253	8			
O$_3$—O$_7$	1.261	8	O$_1$—Ni—O$_6$	88.6	3
O$_4$—C$_9$	1.258	8	O$_2$—Ni—O$_6$	92.7	3
			O$_3$—Ni—O$_6$	88.0	3
C$_3$—C$_2$	1.406	10	O$_4$—Ni—O$_6$	90.6	3
C$_3$—C$_4$	1.407	10			
C$_8$—C$_7$	1.404	10	Ni—O$_1$—C$_2$	125.8	5
C$_8$—C$_9$	1.394	10	Ni—O$_2$—C$_4$	124.6	5
			Ni—O$_3$—C$_7$	126.1	5
C$_2$—C$_1$	1.531	10	Ni—O$_4$—C$_9$	127.6	5
C$_4$—C$_5$	1.524	10			
C$_7$—C$_6$	1.521	10	O$_1$—C$_2$—C$_3$	126.0	8
C$_9$—C$_{10}$	1.526	10	O$_2$—C$_4$—C$_3$	126.4	8
			O$_3$—C$_7$—C$_8$	125.8	8
"bite"			O$_4$—C$_9$—C$_8$	124.6	8
O$_1$—O$_2$	2.892	6			
O$_3$—O$_4$	2.849	6	O$_1$—C$_2$—C$_1$	115.8	8
			O$_2$—C$_4$—C$_5$	115.3	8
"between Acac Ligands"			O$_3$—C$_7$—C$_6$	115.4	8
O$_1$—O$_3$	2.790	6	O$_4$—C$_9$—C$_{10}$	115.5	9
O$_2$—O$_4$	2.868	6			
"oxygen-oxygen separations involving possible hydrogen bonds"			C$_1$—C$_2$—C$_3$	118.2	9
			C$_3$—C$_4$—C$_5$	118.3	9
			C$_6$—C$_7$—C$_8$	118.8	9
O$_5$—O$_1$	2.934	7	C$_8$—C$_9$—C$_{10}$	119.9	9
O$_5$—O$_2$	2.814	7			
O$_5$—O$_3$	2.984	7	C$_2$—C$_3$—C$_4$	125.5	9
O$_5$—O$_4$	2.886	7	C$_7$—C$_8$—C$_9$	125.9	9
O$_6$—O$_1$	2.865	7			
O$_6$—O$_2$	2.978	7			
O$_6$—O$_3$	2.856	7			
O$_6$—O$_4$	2.916	7			
O$_7$—O$_2$	2.837	7			
O$_7$—O$_4$	2.680	7			
O$_7$—O$_6$	2.767	7			
O$_7$—O$_5$	2.814	7			

Figure 3 is a stereo molecular packing diagram of the previously determined[1] unhydrated monoclinic diaquobis(AcAc)Ni(II). A comparison of the structure of the diaquobis(AcAc)Ni(II) part of the hydrated molecule with the unhydrated diaquobis(AcAc)Ni(II) is given in Table III. It can be seen from a comparison of Figures 2 and 3 that the monohydrate structure is much more extensively hydrogen bonded than the unhydrated diaquo complex. Hydrogen bond distances, that is oxygen-oxygen separations, vary from a relatively short 2.680 Å to a long 2.948 Å for the monohydrate as compared to the two long interactions of 2.970 Å for the unhydrated diaquo complex. The hydrate water molecule lies almost in the same plane as the acetylacetone ligands (approx. 0.11 Å deviation) as can be seen from Figure 2 and from the results of the mean plane calculation shown in Figure 4. Davis and Fackler[9] in their infrared study have shown that hydrogen bonding occurs in solution with planar bis, many tris- and many tetrakis-acetylacetonates. The logical assumption that this interaction was with the acetylacetone oxygens is herewith shown to be correct. Considering Table III, several changes in the structure of the diaquo

TABLE III

A comparison of structural dimensions of diaquobis(acetylacetonato)nickel(II) and diaquobis(acetylacetonato)nickel(II)monohydrate

(All distances are in Angstroms, all angles in degrees.)

Values given are averages unless more than one value is listed

	Ni(AcAc)$_2$·2H$_2$O	Ni(AcAc)$_2$·3H$_2$O
C—O	1.271	1.255
C—C (ring)	1.412	1.403
CH$_3$—	1.510	1.525
Ni—O (AcAc)	2.014 2.021	2.007 2.025 2.019 2.010
Ni—O (axial)	2.139	2.092
O—Ni—O ("bite" angle)	92.4	90.0
O—Ni—O (interligand angle)	87.6	90.6 87.8
Ni atom displacement	0.32	0.020

complex are noted. (1) the molecule has become considerably more planar. It no longer exhibits the "chair" configuration typical of these diaquo (acetylacetonato)metal(II) complexes;[10, 11] (2) angular distortion in the acetylacetone oxygen square plane has changed (also see Figure 5); and (3) what is most interesting, the bond length of the axially coordinated water ligand has decreased by almost 0.05 Å. This of course ignores the probable error in this distance. The observed shortening is however clearly significant as the value of one estimated standard deviation is 0.004 Å for the hydrate and 0.010 Å for the unhydrated complex.

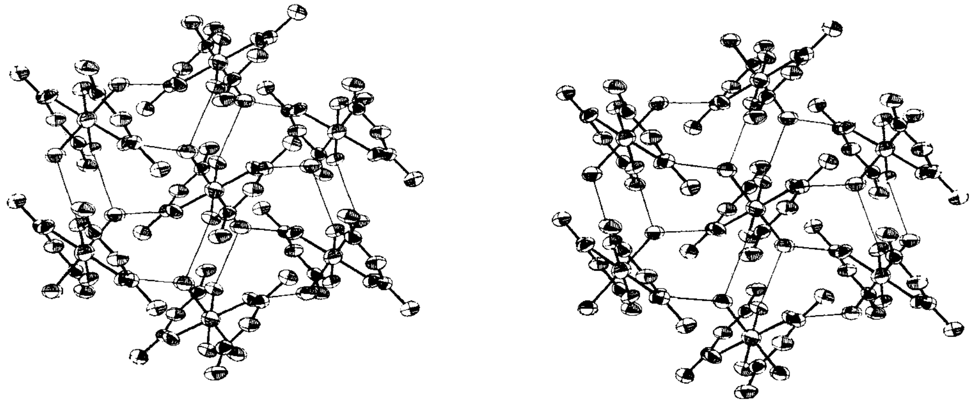

FIGURE 3 Stereographic molecular packing diagram of diaquobis(acetylacetonato)nickel(II) including hydrogen bonds.

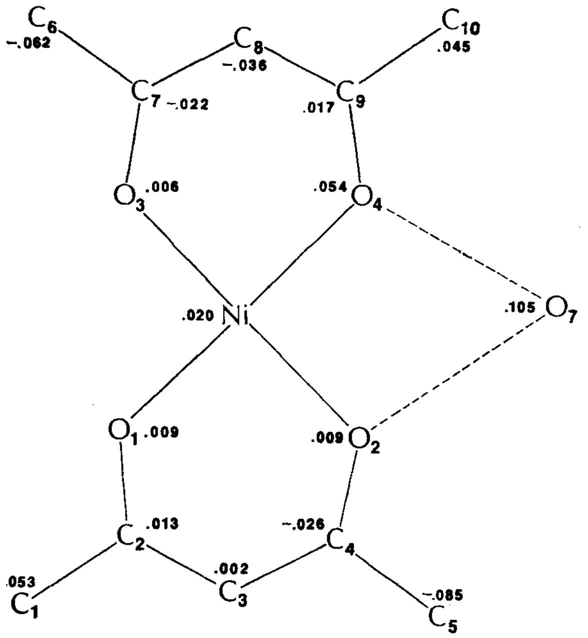

FIGURE 4 Deviations (Å) from the mean plane calculated for all atoms in the bis(acetylacetonato)nickel(II) part of the molecule. Equation of the plane:

$$0.018X - 0.087Y + 0.997Z = 1.901$$

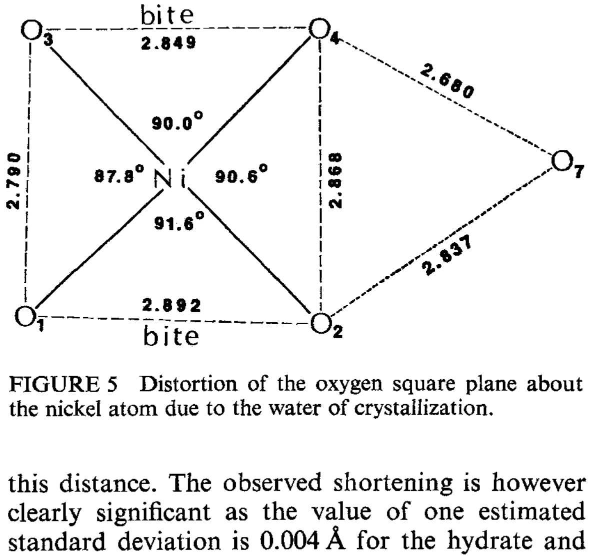

FIGURE 5 Distortion of the oxygen square plane about the nickel atom due to the water of crystallization.

An examination of Figure 5 reveals the interligand angle (between the AcAc's) closest to the hydrate water (90.6°) is greater than the same angle on the opposite side of the complex (87.8°). The "bite" and "bite angle" (2.849 Å and 90.0°) for the AcAc ligand nearest the hydrated water is also less than their counterparts in the second AcAc ligand (2.892 and 91.6°). The interligand angle in the non-hydrated molecule is 87.6°, whereas the "bite" distance and "bite angle" is 2.913 Å and 92.4° respectively. These values agree well with the values for the AcAc ligand fartherest from the water of crystallization in the hydrate molecule. It thus appears that the relatively close approach of the water molecule (O_7) has caused O_4 to move away from O_2 of the second acetylacetone and towards O_3 of the same ligand, increasing the O_4—Ni—O_2 interligand angle and decreasing the O_3—O_4 "bite" distance.

The increased planarity of the entire bis(acetylacetonato)nickel(II) part of the molecule may be solely the result of van der Waals interactions; however, it is also possible that the short hydrogen bond interaction to one of the acetylacetone oxygens has perturbed the electronic symmetry of the chelate ring giving rise to a change in the ring conformation as well as possible small changes in ring bond distances. Although one does find the ring bond distances to be shorter for the hydrate structure, the magnitude of the errors in the structure determinations of the two complexes unfortunately prevents one from making any meaningful comparison of these distances. Fackler, Davis and Chawla[12] have also shown that hydrogen bonding to tris(acetylacetonato)Mn(III) complexes *in* solution influences their visible and near IR absorption spectrum. Likewise we have observed a blue-shift when going from the unhydrated to the hydrated solid-state species.

Whereas the change in planarity may be rationalized on the basis of crystal packing forces (not including hydrogen bond interactions under this heading) as Morosin has contended,[3] the significant change in the axial bond length and the distortion to the oxygen square plane are clearly the result of the relatively speaking much stronger hydrogen bond interactions in the monohydrate complex. It is thus obvious that caution must be exercised in any discussion of the significance of X-ray diffraction determined bond lengths in coordination compounds of this type, for example, those arguments relating ligand coordinate bond lengths to electron pair donor strengths.

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