

- (20) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 2056 (1974).
 (21) R. G. Meisenheimer and J. D. Swalen, *Phys. Rev.*, **123**, 831 (1961).
 (22) T. J. Przystas and N. Sutin, *J. Am. Chem. Soc.*, **95**, 5545 (1973).
 (23) R. A. Marcus, *J. Chem. Phys.*, **24**, 979 (1956); **26**, 867 (1957); *Discuss. Faraday Soc.*, **29**, 129 (1960).
 (24) R. D. Cannon and J. Gardiner, *J. Am. Chem. Soc.*, **92**, 3800 (1970); *Inorg. Chem.*, **13**, 390 (1974).
 (25) J. K. Hurst and R. H. Lane, *J. Am. Chem. Soc.*, **95**, 1703 (1973).
 (26) S. S. Isied and H. Taube, *J. Am. Chem. Soc.*, **95**, 8198 (1973).
 (27) D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, **96**, 7845 (1974).
 (28) J. K. Farr, L. G. Hulet, R. H. Lane, and J. K. Hurst, *J. Am. Chem. Soc.*, **97**, 2654 (1975).
 (29) D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, **93**, 7347 (1971).
 (30) A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, **5**, 45 (1971).
 (31) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities", Oxford University Press, London, 1932, Chapter XII.

Contribution from the Department of Chemistry,
 University of Michigan, Ann Arbor, Michigan 48104

Crystal and Molecular Structure of 2,2'-Bis[1-thia-closo-decaborane(8)], 2,2'-(1-B₉H₈S)₂

W. R. PRETZER, TERRENCE K. HILTY, and R. W. RUDOLPH*

Received January 7, 1975

AIC50017K

The crystal and molecular structure of 2,2'-bis[1-thia-closo-decaborane(8)] was determined by single-crystal X-ray diffraction techniques. The crystals form in the monoclinic space group $P2_1/n$ with $a = 12.184$ (4), $b = 9.777$ (3), and $c = 6.601$ (1) Å with $\beta = 95.72$ (2)°, and $Z = 2$. The conventional R index converged at 0.0437 with full-matrix least-squares refinement including the overall scale factor, all positional parameters and all anisotropic temperature factors for nonhydrogen atoms, and isotropic temperature factors for the hydrogen atoms. The molecule has $C_i(1)$ space group imposed point symmetry; the center of inversion of the molecule is at the midpoint of a B-B bond [1.678 (5) Å] joining the two bicapped square antiprism frameworks of the B₉H₈S moieties. The sulfur atom is in an "axial" position and the equatorial belt of four boron atoms closest to the sulfur atom contains the boron through which the B₉H₈S units are connected. The average B-S distance is 1.923 (3) Å. The B-B distances of the cage range from 1.940 (3) to 1.689 (4) Å.

Introduction

The vacuum pyrolysis of thiadecaborane(11) produces three isomers of (B₉H₈S)₂ in about 5% yield.^{1,2} As described previously, ¹¹B NMR cannot distinguish between two of the possible isomers, 2,2'-(1-B₉H₈S)₂ and 6,6'-(1-B₉H₈S)₂.¹ An X-ray structural study was initiated to elucidate the structure of one of these isomers. It was also realized that a definitive location of the B-B bond linking the two B₉H₈S moieties would allow assignment of the NMR for (B₉H₈S)₂ molecules and extrapolation of these results to the parent molecule, 1-B₉H₉S, and many of its derivatives. Subsequent to completion of the crystallographic study certain structural features of the molecule were found to correlate with known reaction chemistry of 1-B₉H₉S.

Experimental Section

Collection and Reduction of the X-Ray Diffraction Data. The synthesis, separation, and spectral properties of (1-B₉H₈S)₂ thiaboranes have been described previously.¹ Single crystals (mp 159.5–161.0° uncor, sealed capillary) of 2,2'-(1-B₉H₈S)₂ were obtained by gradual evaporation of solvent from a CH₂Cl₂ solution of pure 2,2'-(1-B₉H₈S)₂.

The crystal used for the X-ray diffraction work was a rather irregular trapezoidal plate with parallel sides, altitude, and thickness of ca. 0.18, 0.27, 0.20, and 0.11 mm, respectively. The crystal was mounted with the a axis (direct space) approximately parallel to the glass fiber (spindle axis).

Precession photographs gave approximate cell dimensions, indicated $2/m$ (C_{2h}) Laue symmetry, and exhibited the systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$, consistent only with the centrosymmetric space group $P2_1/n$.

The density of another crystal was determined to be 1.66 g cm⁻³ using the flotation method in aqueous KCl; the calculated value is 1.167 g cm⁻³ for two (B₉H₈S)₂ molecules per unit cell. In this space group this requires that the center of symmetry of each molecule resides at a special position.

The crystal from which the precession photographs were obtained was transferred to an arcless goniometer head on a Syntex PI autodiffractometer equipped with graphite-monochromatized Cu K α radiation. After centering and orientation, 2θ , ω , and χ settings for 15 different reflections were accurately determined. The Syntex

Table I. Experimental Data for the X-Ray Diffraction Study of 2,2'-(1-B₉H₈S)₂

(a) Crystal Parameters	
$a = 12.184$ (4) Å	Space group $P2_1/n$
$b = 9.777$ (3) Å	Mol wt 275.02
$c = 6.601$ (1) Å	$\rho(\text{obsd}) = 1.166$ g cm ⁻³
$\beta = 95.72$ (2)°	$\rho(\text{calcd}) = 1.167$ g cm ⁻³
$V = 782.4$ (4) Å ³	2 molecules/unit cell
(b) Intensity Measurements	
Reflections measd: hkl for $h, k > 0$; $0kl$ for $l > 0$	
Maximum 2θ : 118.6°	
Radiation: Cu K α	
Scan speed: 2.0–24.0°/min	
Standard background counts were taken at the beginning and end of each 2θ scan	
Scan mode: $\theta(\text{crystal}) - 2\theta(\text{counter})$	
Three standard reflections measured after every 36 reflections, no decay observed, no unusual deviation in intensity	
1140 reflections collected, plus 82 systematically extinct	

least-squares routine gave the unit cell dimensions listed in Table I. Intensity data were then collected on magnetic tape. Specifics of the intensity measurements are given in Table I. No absorption corrections were made. The linear absorption coefficient for Cu K α radiation was estimated to be 26.25 cm⁻¹.

Solution and Refinement of the Structure. Programs used in determining the structure included DATRDN, NORMSF, FC, FOURR, LOADAT, BONDLA, and LISTFC from ref 3. The least-squares structure refinement program used was CLS written by Schilling.⁴ The thermal ellipsoid drawing was obtained by use of ORTEP, by Johnson,⁵ and ORFFE, by Busing, Martin, and Levy,⁵ was used for bond distances, angles, and errors.

Scattering factors for neutral boron and sulfur were taken from ref 6, and the values of Stewart, Davidson, and Simpson were used for hydrogen.⁷ The function minimized during least-squares refinement was $\sum w||F_o| - |F_c||^2$ where $w = \sigma^{-2}$ for the appropriate F_o . The residual discrepancy term used was defined in the usual manner, i.e., $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$.

Following data reduction in which Lorentz and polarization corrections were made, an origin-removed Patterson map was determined. The position of the sulfur atom was easily determined and using only this atom a structure factor calculation was made using

Table IV. Anisotropic Temperature Factors^a for Nonhydrogen Atoms

Atom	10 ⁴ B ₁₁	10 ⁴ B ₂₂	10 ⁴ B ₃₃	10 ⁴ B ₁₂	10 ⁴ B ₁₃	10 ⁴ B ₂₃
S	400 (3)	353 (3)	670 (4)	77 (2)	70 (2)	67 (3)
B(2)	349 (12)	316 (12)	451 (14)	3 (10)	2 (10)	-7 (11)
B(3)	512 (15)	376 (14)	427 (15)	-40 (12)	-7 (12)	-20 (11)
B(4)	744 (19)	309 (13)	539 (17)	-59 (13)	117 (15)	18 (12)
B(5)	661 (17)	344 (13)	465 (15)	-57 (12)	123 (13)	-50 (11)
B(6)	412 (14)	426 (14)	518 (16)	-24 (12)	8 (12)	-65 (12)
B(7)	642 (18)	481 (15)	471 (15)	-180 (13)	147 (14)	31 (12)
B(8)	722 (19)	457 (16)	492 (16)	-252 (14)	72 (14)	-54 (13)
B(9)	446 (14)	463 (14)	464 (15)	-107 (12)	-39 (12)	1 (13)
B(10)	452 (15)	676 (20)	701 (19)	-171 (15)	89 (14)	-57 (16)

^a The form of the anisotropic thermal factor is $\exp[-1/4(h^2B_{11}a^{*2} + k^2B_{22}b^{*2} + l^2B_{33}c^{*2} + 2hkB_{12}a^*b^* + 2hlB_{13}a^*c^* + 2klB_{23}b^*c^*)]$; units are Å².

Table V. Final Atom Parameters

Atom	x	y	z	B _{iso} , Å ²
S	0.41918 (4)	0.21309 (6)	0.38783 (9)	3.76
B(2)	0.52721 (18)	0.07326 (23)	0.46163 (36)	2.96
B(3)	0.51957 (22)	0.15970 (25)	0.19609 (39)	3.49
B(4)	0.53347 (25)	0.33683 (27)	0.32021 (42)	4.22
B(5)	0.54131 (25)	0.25325 (26)	0.58513 (42)	3.91
B(6)	0.64048 (20)	0.07776 (27)	0.31058 (39)	3.61
B(7)	0.64474 (25)	0.25470 (28)	0.21492 (42)	4.23
B(8)	0.65947 (26)	0.31827 (29)	0.47884 (42)	4.44
B(9)	0.65550 (21)	0.14115 (28)	0.57421 (40)	3.64
B(10)	0.73879 (24)	0.19181 (32)	0.39753 (47)	4.86
H(3)	0.4760 (16)	0.1274 (20)	0.0515 (30)	3.92 (45)
H(4)	0.4991 (17)	0.4343 (22)	0.2701 (31)	4.58 (50)
H(5)	0.5172 (18)	0.2910 (21)	0.7280 (34)	4.66 (51)
H(6)	0.3356 (18)	0.0188 (22)	0.7523 (32)	4.39 (50)
H(7)	0.6650 (18)	0.2993 (22)	0.0722 (35)	5.27 (56)
H(8)	0.6944 (16)	0.4131 (23)	0.5473 (31)	4.78 (51)
H(9)	0.6903 (15)	0.0973 (21)	0.7180 (31)	3.91 (46)
H(10)	0.8309 (21)	0.1829 (26)	0.4021 (36)	6.87 (68)

in Table IV, and final atom coordinates are in Table V.

A bicapped square antiprism has two positions coincident with the principal symmetry axis (axial positions) and two square sets of four positions around and normal to that symmetry axis (equatorial belts). The structure can be described as two bicapped square antiprisms joined through an equatorial B-B bond. Such a framework is typical of ten vertex closo polyhedra¹⁰ and this structure strongly supports the suggested structure of the parent 1-B₉H₉S,² i.e., a bicapped square antiprism with axial sulfur placement.

The four boron-sulfur distances range from 1.918 (3) to 1.930 (3) Å and do not vary significantly. The average bond distance¹¹ of 1.923 (3) Å is somewhat shorter than the average boron-sulfur distance of 2.02 (5) Å given for the metallo-thiaborane [(C₂H₅)₃P]₂Pt(H)B₉H₁₀S¹² but longer than the average B-S distance for B₉H₁₂S⁻, 1.89 (3) Å.¹³ An expolyhedral B-S distance of 1.92 (1) Å was observed in B₁₀H₁₂[S(CH₃)₂]₂.¹⁴ The boron-boron bond coupling the two B₉H₈S units is 1.678 (5) Å, slightly shorter than the 1.74 (6) Å boron-boron distance joining the two pyramids of 1,1'-(B₅H₈)₂.¹⁵ The boron-boron distances within the cage framework range from a high of 1.940 (3) Å for the borons occupying the square belt adjacent to the sulfur to a low of 1.689 (4) Å for the distance between the lower belt boron, B(8), and the unique axial boron, B(10).

Typically, boron-boron near neighbors range from 1.70 to 1.86 Å apart. However, observed B-B distances range from 2.01 Å in B₁₀H₁₄¹⁴ to a minimum of 1.60 Å for the distance between two borons in the base of B₆H₁₀.¹⁷ This latter short distance has been attributed to a two-electron, two-center bond predicted by topological considerations.¹⁸ We feel that the B-B bond of 1.678 (5) Å joining the two B₉H₈S moieties, the shortest B-B distance observed in the molecule, is a two-electron, two-center bond. Even though the B-B distances associated with the axial belts of boron atoms are not significantly longer, they are considered to be multicentered in

nature. The latter distances compare favorably with the apex-base distances reported for pentaborane(9),¹⁹ 1.69 Å, bonds possessing considerable three-center character.

The length of the boron-boron bond joining the two cages may be longer than expected due to the bulky nature of the two units which it joins. A more important reason, however, may be the withdrawal of electrons from this bond by the more electronegative sulfur atom in the cage. The average B-B distance in the belt of four boron atoms adjacent to the sulfur (upper belt) is 1.930 (4) Å, while the corresponding distance for the belt adjacent to the axial boron (lower belt) is 1.842 (4) Å. This significant difference,²⁰ is most readily attributed to a combination of electron withdrawal by the sulfur atom and size. For comparison, the Cu(I) salt of the isoelectronic B₁₀H₁₀²⁻ polyhedron has a boron-boron length of 1.86 Å for similar bonds.²¹

One more point directs itself to the nature of the upper belt boron-boron distances. If the sulfur atom were drawing electron density toward itself, the boron atoms in the upper belt would be more positive relative to those of the lower belt. The "parent" 1-B₉H₉S, whose bond lengths should not vary significantly from those in 2,2'-(1-B₉H₉S), is in fact subject to facile nucleophilic attack by methoxide ion and amines.² Such reactions do not readily occur for the isoelectronic species B₁₀H₁₀²⁻²² and 1,10-B₈C₂H₁₀²³ nothing is reported regarding B₉CH₁₀²⁴ but degradation is reported for 1,6-B₈C₂H₁₀ in which case the placement of the carbon atoms also renders certain boron sites positive and susceptible to nucleophilic attack.²³ Oxidation of the degradation product from 1-B₉H₉S leads to B₈H₁₀S, the framework structure of which from spectroscopic evidence is consistent with removal of an upper belt boron atom from the B₉H₉S framework.²⁵

Acknowledgment. We thank the National Science Foundation for support (Grant MPS74-00047 A01) and Marianna Strumpel for assistance with the X-ray analysis.

Registry No. 2,2'-(1-B₉H₈S)₂, 54748-44-6.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC50017K-10-75.

References and Notes

- W. R. Pretzer and R. W. Rudolph, *J. Chem. Soc., Chem. Commun.*, 629 (1974).
- W. R. Pretzer and R. W. Rudolph, *J. Am. Chem. Soc.*, **95**, 931 (1973).
- J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, Ed., "The X-Ray System of Crystallographic Programs", Technical Report TR-192, University of Maryland Computer Science Center, June 1972 version.
- J. W. Schilling, "Crystallographic Computing", F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, pp 201-204.

- (5) ORTEP: C. K. Johnson, "A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-3974, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965. ORFFE: W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Function and Error Program", Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
- (6) C. H. Macgillivray and G. D. Rieck, Eds., "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, p. 202.
- (7) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (8) W. H. Zachariassen, *Acta Crystallogr., Sect. A*, **24**, 212 (1968).
- (9) It should be noted that the preliminary account of this structure¹ reported errors for the bond lengths which did not include contributions from coordinate covariance.
- (10) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11**, 1974 (1972).
- (11) The estimated standard deviations of average values were calculated by the expression $\sigma = [\sum_m(l_m - \bar{l})^2/m(m-1)]^{1/2}$, where l_m is the m th value and \bar{l} is the mean of m measurements.
- (12) A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Am. Chem. Soc.*, **92**, 2571 (1970).
- (13) L. J. Guggenberger, *J. Organomet. Chem.*, **81**, 271 (1974).
- (14) D. E. Sands and A. Zalkin, *Acta Crystallogr.*, **15**, 410 (1962).
- (15) R. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.A.*, **46**, 996 (1961).
- (16) J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Crystallogr.*, **3**, 436 (1950).
- (17) F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **28**, 56 (1958).
- (18) See W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, N.Y., 1963.
- (19) W. J. Dulmage and W. N. Lipscomb, *Acta Crystallogr.*, **5**, 260 (1952).
- (20) The normally accepted criterion of a meaningful difference is 3σ ; $\sigma(\text{difference}) = [\sigma_1^2 + \sigma_2^2]^{1/2}$.
- (21) R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962).
- (22) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).
- (23) P. M. Garrett, J. C. Smart, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **91**, 4707 (1969).
- (24) W. H. Knoth, *Inorg. Chem.*, **10**, 598 (1971).
- (25) W. R. Pretzer and R. W. Rudolph, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973, No. INOR 90.

Contribution from the Department of Chemistry,
University of Hawaii, Honolulu, Hawaii 96822

Crystal and Molecular Structure and Isotropic Hydrogen-1 Nuclear Magnetic Resonance Shifts of Hexa(acetic acid)nickel(II) Tetrafluoroborate, $[\text{Ni}(\text{AcOH})_6](\text{BF}_4)_2$ ¹

ROGER E. CRAMER,* WILLIAM VAN DOORNE, and RONALD DUBOIS

Received January 16, 1975

AIC50036U

The crystal structure of hexa(acetic acid)nickel(II) tetrafluoroborate has been determined and the structure of the coordinated acetic acid is compared with the structure of free acetic acid and with the coordinated acetate ion of bis(acetato)tetraaquonickel(II). The crystals of $[\text{Ni}(\text{AcOH})_6](\text{BF}_4)_2$ are triclinic belonging to space group $P\bar{1}$ with $a = 10.092$ (2) Å, $b = 8.706$ (2) Å, $c = 9.147$ (2) Å, $\alpha = 112.29$ (2)°, $\beta = 97.81$ (2)°, and $\gamma = 115.34$ (2)° at 20°, with one molecule per unit cell. All unique reflections for which $2\theta < 50^\circ$ were measured using graphite-monochromatized Mo $K\alpha$ radiation with a pulse height analyzer. The structure was refined by large block diagonal least-squares methods using 1764 reflections to a final R index of 0.058. The acetic acid is coordinated to the Ni(II) ion through the carbonyl oxygen with an average bond length of 2.055 (4) Å, which is slightly shorter than the Ni-O bond length of 2.068 (1) Å found for $\text{Ni}(\text{H}_2\text{O})_4(\text{AcO})_2$. Other changes in geometry of the acetic acid upon coordination are barely significant. The hydroxyl hydrogen of the acetic acid is involved in a bifurcated hydrogen bond to the carbonyl group of the same acid and to a fluorine of the BF_4^- anion. The isotropic ¹H NMR shifts determined from magnetic dilution experiments for the methyl and hydroxyl protons are -4.33 and -2.49 ppm, respectively. When compared to the contact shifts determined from a neat solution of $[\text{Ni}(\text{AcOH})_6](\text{BF}_4)_2$, these results indicate some dissociation of the complex in solution.

Introduction

Recently Van Leeuwen² reported both the synthesis and spectral properties of a new series of compounds which contained six acetic acid groups coordinated to the divalent cations of Mg, Mn, Co, Ni, Cu, and Zn and with the tetrafluoroborate, perchlorate, and nitrate counteranions. In an effort to continue our investigations into both the structural and bonding characteristics of similar complexes of protonated ligands,^{3,4} we have determined the structure of hexa(acetic acid)nickel(II) tetrafluoroborate, $[\text{Ni}(\text{AcOH})_6](\text{BF}_4)_2$, by crystallographic techniques.

In order to compare accurately the structural differences of a coordinated carboxylic acid with that of the corresponding conjugate base, a coordinated carboxyl anion, we repeated independently the structure of bis(acetato)tetraaquonickel(II) $[\text{Ni}(\text{H}_2\text{O})_4(\text{AcO})_2]$ first reported by Van Niekerk and Schoening⁵ in 1953 and again by Raper⁶ et al. in 1971. In order to compare reliably the two structures the intensity data for both compounds were collected and analyzed under identical conditions using the same statistical and least-squares methods.

In an effort to determine whether the structure of the molecule was maintained in solution we have determined the ¹H NMR isotropic shifts.

Experimental Section

Synthesis of $[\text{Ni}(\text{AcOH})_6](\text{BF}_4)_2$ was accomplished by the method of Van Leeuwen.² $\text{Ni}(\text{H}_2\text{O})_4(\text{AcO})_2$ was obtained commercially and

purified by recrystallization from a 50:50 v/v solution of water and ethanol.

Collection and Reduction of Intensity Data

Light green crystals of $[\text{Ni}(\text{AcOH})_6](\text{BF}_4)_2$ were grown by slow cooling over a 4-day period from a solution of the salt in dried glacial acetic acid, nearly saturated at 60°. A single crystal, of space group $P\bar{1}$, irregularly shaped with maximum dimensions of $0.030 \times 0.040 \times 0.060$ cm, was selected and was lodged and sealed in a thin-walled capillary tube. A volume of mother liquor approximately equal to that of the crystal was included in such a way that the crystal was entirely bathed in liquid throughout data collection. The crystal of $\text{Ni}(\text{H}_2\text{O})_4(\text{AcO})_2$ was monoclinic, space group $P2_1/c$, with maximum dimensions of $0.034 \times 0.016 \times 0.016$ cm.

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($K\alpha_1$, λ 0.70926 Å; $K\alpha_2$, λ 0.71354 Å) and with a pulse height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants were determined by least-squares methods from the centered angular coordinates of 15 intense reflections. The cell constants at 20° for $[\text{Ni}(\text{AcOH})_6](\text{BF}_4)_2$ are $a = 10.092$ (2) Å, $b = 8.706$ (2) Å, $c = 9.147$ (a) Å, $\alpha = 112.29$ (2)°, $\beta = 97.81$ (2)°, and $\gamma = 115.34$ (2)°; $V = 627.9$ (2) Å³ and $\rho_{\text{calcd}} = 1.567$ g/cm³. The density was not successfully measured by flotation because of the instability of the complex. The cell constants for $\text{Ni}(\text{H}_2\text{O})_4(\text{AcO})_2$ were obtained similarly and at 20° were found to be $a = 4.760$ (1) Å, $b = 11.761$ (4) Å, $c = 8.419$ (4) Å, and $\beta = 93.82$ (3)° with $V = 470.3$ (3) Å³. The calculated density $\rho_{\text{calcd}} = 1.75$ g/cm³ agrees with the measured density of $\rho_{\text{measd}} = 1.78$ g/cm³.

Diffraction intensities were collected by the θ - 2θ scan technique at a minimum scan rate of 3°/min in 2θ to 24°/min in such a way