the Re–Re–I angle is 104° 45′, quite close to the Re–Re–Cl angle of 103.7 ± 2.1° observed in $Re_2Cl_8^{2-}$. It is evident that the calculated minimum Re–Re bond length is extremely sensitive to the assumed limiting, nonbonded I–I contact. However, from the information presently available, it appears that the $Re_2I_8^{2-}$ ion may be sterically feasible. Further work on this question is presently under way in this laboratory.

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The Crystal and Molecular Structures of a Toluene-Containing Form of Di-μ-aquo-di-μ_3-hydroxo-deca(1,1,1-trifluoropentane-2,4-dionato)hexanickel(II)[1]

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The crystal and molecular structures of di-μ-aquo-di-μ_3-hydroxo-deca(1,1,1-trifluoropentane-2,4-dionato)hexanickel(II)–toluene (an enclosure compound) have been determined. The compound crystallizes in space group $P2_1/c$ with unit cell dimensions $a = 14.268 \pm 0.006$ Å, $b = 17.519 \pm 0.006$ Å, $c = 16.862 \pm 0.006$ Å, $\beta = 107.57 \pm 0.05°$, and $Z = 2$. Of 4215 reflections collected by counter methods 2559 above background were used to solve and refine the structure by least-squares methods to a conventional R factor of 8.4%. The molecule is composed of two trinuclear units joined by two bridging water molecules. Each nickel atom in the trinuclear unit is octahedrally coordinated by oxygen atoms of the ligands. The octahedra share a common vertex occupied by a hydroxide ion which bridges three nickel atoms. The toluene molecules lie on symmetry centers between the hexanickel units and are disordered about an axis perpendicular to the phenyl ring.

Introduction

In the course of attempts to prepare polymeric nickel and cobalt complexes with unsymmetrically substituted acetylacetones (*e.g.*, $RCOCH_2COCH_3$, with $R = C_6H_5$, $C(CH_3)_3$, and CF_3), which were suitable for single-crystal X-ray diffraction studies, a complex of nickel(II) with the anion 1,1,1-trifluoropentane-2,4-dione (TFA) was isolated. A preliminary investigation suggested that the complex was either a trimer or a centrosymmetric hexamer of $Ni(TFA)_2$ in the solid phase. The complete structural determination was therefore undertaken with the hope of finding a possible relationship with the structures of $Ni_3(DEPAM)_6$[3,4] and $Ni_3(AA)_6$.[5] However, the substance was found to be far more complicated, chemically and structurally, as the following report will explain.

Experimental Section

Preparation.—A solution of 11.9 g (0.0774 mol) of 1,1,1-trifluoropentane-2,4-dione (HTFA; Peninsular ChemResearch, Inc., Gainesville, Fla.) in 50 ml of benzene was refluxed in the presence of 4.0 g (0.0337 mol) of $NiCO_3$ (J. T. Baker Chemical Co., Phillipsburg, N. J.) for 20 hr. The resulting suspension, containing a light green solid (presumably $Ni(TFA)_2 \cdot 2H_2O$) which formed after 3 hr, was filtered; the solid was washed with four 40-ml portions of petroleum ether (bp 40–60°) and dried in air. In an attempt to remove the water of hydration, the compound was dried under vacuum at 108° (0.05 mm) for 24 hr. The intense, broad band at 3400 cm^{-1} in the ir spectrum of the original solid (in Nujol) disappeared after the compound was heated to 108° under vacuum. A weak, sharp absorption, not present in the original solid, appeared at 3560 cm^{-1}. This vacuum-dried material was then recrystallized from toluene and analyzed. *Anal.* Calcd for $Ni_6(TFA)_{10}(H_2O)_2(OH)_2 \cdot C_6H_5CH_3$ ($Ni_6C_{57}H_{54}O_{24}F_{30}$): C, 29.75; H, 2.37; F, 29.18; Ni, 18.04. Found: C, 30.6; H, 2.21; F, 28.4; Ni, 17.8. Calcd for $Ni(CF_3COCHCOCH_3)_2$: C, 32.92; H, 2.21; F, 31.24; Ni, 16.09.

X-Ray Crystallography.—Crystals of the complex suitable for X-ray crystallographic examination were grown by slow cooling in a nitrogen atmosphere of a hot toluene solution. Monoclinic prisms mounted on glass fibers and coated with a thin layer of shellac to prevent exposure to atmospheric moisture were used for reciprocal lattice photography and collection of data. Precession photographs with Cu Kα radiation of the $0kl$, $1kl$, $h0l$, $h1l$, and $hk0$ levels indicated the systematic extinctions $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, uniquely characteristic of the space group[6] $P2_1/c$ (no. 14, C_{2h}^5). Preliminary cell constants were measured from the precession films. The density calculated for two hexanuclear molecules with two toluene molecules of crystallization is 1.69 g/cm^3. Attempts to measure the density by flotation in a mixture of ethyl iodide and carbon tetrachloride gave an approximate value of 1.73 ± 0.05 g/cm^3. Two molecules per unit cell in space group $P2_1/c$ requires that each molecule lie at a center of symmetry. The two toluene molecules must occupy a different set of centers and must be disordered.

Accurate unit cell dimensions were measured on a General Electric XRD-5 manual diffractometer. The cell parameters are $a = 14.268 \pm 0.006$ Å, $b = 17.519 \pm 0.006$ Å, $c = 16.862 \pm$

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(1) Research supported by the National Science Foundation under Grant No. GP 7034X.

(2) NIH Predoctoral Fellow, 1965–1968.

(3) F. A. Cotton and B. H. C. Winquist, unpublished work. It has been found that $Ni_3(DEPAM)_6$ (where DEPAM is the anion $(C_2H_5O)_2P(O)CHC(O)CH_3^-$) is crystallographically isomorphous and apparently isostructural with $Co_3(DEPAM)_6$ which has been reported to have an unusual structure.[4]

(4) F. A. Cotton, R. Hugel, and R. Eiss, *Inorg. Chem.*, **7**, 18 (1968).

(5) G. J. Bullen, R. Mason, and P. Pauling, *ibid.*, **4**, 456 (1965).

(6) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

0.006 Å, and $\beta = 107.57 \pm 0.05°$ measured with Cu Kα radiation (λ Kα_1) 1.5405 Å; λ(Kα_2) 1.5443 Å) at 21°. The values of a, b, and c are those obtained after measuring d spacings at different values of 2θ, plotting[7] the measured spacing against the function $1/2\{[(\cos^2\theta)/(\sin\theta)] + [(\cos^2\theta)/\theta]\}$, and linearly extrapolating to $\theta = 90.0°$. The uncertainties of the cell constants represent the maximum estimated errors of the measurements based on the same procedure applied to crystals of known unit cell dimensions.[8]

Intensity data for the structure determination were collected on an XRD-5 manual diffractometer using the θ–2θ scan technique with nickel-filtered Cu Kα radiation at a takeoff angle of 2°. A 40-sec scan of 2.66° about the value of 2θ for each reflection was sufficient to include the entire peak. The intensities were monitored with a scintillation counter with the pulse height discriminator set to receive 95% of the Cu Kα radiation when set on the peak. Backgrounds were counted for 20 sec at the maximum and minimum values of 2θ. The distances from the crystal to the source and from the crystal to the circular screening aperture (2°) were 5.73 and 7.05 in., respectively.

It was necessary to use two monoclinic prisms, each mounted with the b axis coincident with the ϕ axis of the diffractometer, for the collection of the data, because of decomposition of the first crystal during data collection. The intensities of four standard reflections decreased about 5% from their original value after two-thirds of the data had been collected. The dimensions, in the [110], [1$\bar{1}$0], and [001] directions, of the first and second crystals were 0.021 × 0.019 × 0.011 and 0.012 × 0.013 × 0.007 cm, respectively. One quadrant of data was collected comprising 4215 independent reflections within the range $\theta \leq 50.5°$. Of these, 28 reflections exceeded the linear response range of the counter and were remeasured with the X-ray source current reduced. The data sets collected from the two crystals were put on the same scale by measurement of eight common reflections. The intensities of four standard reflections [$(\sin\theta)/\lambda = 0.30$–$0.85$] were monitored every 6 hr during the collection of data. Since only a 5% decrease in the intensities of the standard reflections was tolerated before the crystal was changed, no correction was made for decomposition.

Of the original 4215 reflections measured, 2559 were used in the structure solution and refinement. Only those reflections were accepted for which $(P - B_1 - B_2)/(P + B_1 + B_2)^{1/2} \geq 3.0$, where P represents the scan counts and B_1 and B_2 are the initial and final background counts. The measured intensities were corrected for Lorentz and polarization effects and were reduced to $|F|^2$ and $|F|$ for calculation of the Patterson function and least-squares refinement. Absorption corrections and weighting factors were applied later as described below.

Solution and Refinement of the Structure

A three-dimensional Patterson function was solved for the positions of the three independent nickel atoms. It became apparent that the molecule was not a linear trimer but a hexamer, formed from two triangular nickel units. A set of structure factors was calculated based on the positions of the nickel atoms derived from the Patterson function, for which the usual discrepancy index, $R_1 = [\Sigma(||F_o| - |F_c||)]/(\Sigma|F_o|)$, where F_o is the observed structure factor and F_c is the calculated structure factor, was 60.3% and the weighted discrepancy index, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, was 70.3%. A cycle of full-matrix least-squares refinement, using unit weights, minimizing $\Sigma w[|F_o| - |F_c|]^2$, reduced R_1 and R_2 to 55.6 and 65.9%, respectively. A Fourier electron density map phased on the nickel atom positions revealed the location of 12 oxygen atoms, 24 carbon atoms, and 15 fluorine atoms. Three more cycles of refinement varying a scale factor for each data set, all atom positional parameters, and isotropic thermal parameters resulted in agreement indices R_1 and R_2 of 15.6 and 22.5%, respectively. The atomic scattering factors used in the least-squares refinement for Ni^{2+}, C, O, and F are those given by Ibers.[9] The real and imaginary terms arising from anomalous dispersion by Ni^{2+} and F were included in the structure factor calculation.[10]

A difference Fourier map was then calculated, revealing the position of one more 1,1,1-trifluoroacetylacetonate methyl carbon atom, C55, and a disordered toluene molecule occupying a center of symmetry at $^1/_2$, $^1/_2$, 0.

Electron density (approximately 20% of that of a fluorine atom) was present near the methyl carbon atom of ligand 5. This is appreciably greater than that expected for methyl hydrogen atoms, suggesting partial occupation by fluorine atoms at these positions. The trifluoromethyl group of ligand 5 gave evidence of fluorine disorder, and individual fluorine atoms were not readily resolved. These two observations suggested that this ligand suffers a twofold disordering about an axis passing through the C53 carbon atom and bisecting a line connecting the oxygen atoms. Evidence for a similar type of disorder was also observed, to a lesser degree, for ligand 4. No attempt was made to provide for ligand disorder in the refinement.

Considerable electron density was observed near all of the fluorine atoms, suggesting librational motion of the trifluoromethyl groups, so the fluorine thermal parameters were allowed to vary anisotropically for the remainder of the refinement.

At this point in the refinement the unit weighting scheme was replaced by one similar to that of Doedens and Ibers,[11] and corrections for absorption ($\mu = 27.4$ cm^{-1}, Cu Kα radiation) were applied to the data. The ranges of the calculated transmission factors for the two crystals were 0.635–0.760 and 0.746–0.833. Four more cycles of full-matrix refinement of all parameters resulted in $R_1 = 9.6$ and $R_2 = 13.5\%$.

The refinement of the toluene carbon parameters was proceeding quite poorly. The benzene ring carbon–carbon bond distances were about 0.1 Å longer than the normal distance, and individual carbon thermal parameters were in the range 15–18 Å^2. Fourier electron density maps showed that the molecule was disordered about an axis perpendicular to the aromatic ring, since individual atoms could not be resolved. Attempts to refine the disordered toluene methyl carbon atom resulted in an extremely high thermal parameter and poor methyl carbon–ring carbon distances (1.8 Å). From two Fourier electron density maps, including an oblique Fourier section through the plane of the toluene ring, it was apparent that the methyl carbon atom was not randomly disordered but preferred two positions *para* to each other (to conform to the required centro-

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(7) A. Taylor and H. Sinclair, *Proc. Phys. Soc.* (London), **57**, 126 (1945); J. B. Nelson and D. P. Riley, *ibid.*, **5**, 160 (1945).

(8) See ref 6, Vol. III, p 122.

(9) See ref 6, Vol. III, p 202.

(10) See ref 6, Vol. III, p 214.

(11) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967). The factor "p" in the expression for σ has been changed to 0.045 in this work.

symmetric position occupied by the molecule). At each of these two positions the electron density was approximately four times that at each of the other four positions around the ring. It was then decided that the best solution to the problem of disorder of the toluene molecule was to treat it as a rigid body, omitting the methyl carbon atom, using the accurately known benzene ring geometry and allowing only the orientation of the ring to refine at its symmetry-fixed position. For this refinement the ring carbon–carbon distance was fixed at 1.397 Å. Four cycles of refinement of three toluene orientation angle parameters and ring carbon isotropic thermal parameters with all other atom parameters fixed resulted in $R_1 = 8.6\%$ and $R_2 = 11.6\%$. The toluene refinement was carried no further since no parameter changed more than 0.35 times its estimated standard deviation. Two methyl carbon positions were calculated assuming (1) a methyl carbon–ring carbon distance of 1.47 Å and (2) a twofold disorder conforming to the symmetry of the special position, $\bar{1}$, and the results of the electron density maps.

Two more cycles of least-squares refinement varying all parameters except the toluene positional parameters resulted in convergence at $R_1 = 8.4\%$ and $R_2 = 11.5\%$. During the last cycle of refinement, no parameter shift was greater than half its estimated standard deviation. An observation of unit weight had a standard deviation of 1.84 at the end of the refinement. This large value is probably due in part to the neglect of anisotropic thermal motion of the atoms refined isotropically, the inadequacy of the calculated scattering from the librational motion of the trifluoromethyl groups, the two disordered chelate rings, and the disordered toluene molecule. The largest peak on a final difference Fourier map had a maximum density of 0.79 $e^-/Å^3$ and was in the region of atoms F51, F52, and F53, the most disordered trifluoromethyl group. A search for electron density in the expected hydrogen atom positions revealed some peaks of approximately 0.6 $e^-/Å^3$, but since some of the hydrogen atoms could not be located, none was included in the final structure factor calculation. The largest remaining electron density peaks could be attributed to anisotropic motion of the nickel atoms. However, owing to computer size limits, anisotropic refinement of the nickel atoms was not undertaken.

Comparison of $|F_o|$ and $|F_c|$ for intense reflections at low angle ($(\sin \theta)/\lambda \leq 0.1$) indicated that no correction for extinction was necessary.

The following computer programs were used in the course of the structure analysis. All have been modified for use with the IBM 360/65 computer at the MIT Information Processing Center. (1) D. P. Shoemaker, "MIT X-Ray Goniometer Package, MIXG-2," 1962; calculation of diffractometer settings; (2) R. C. Elder, PDATA2; listing of diffractometer settings for data collection; (3) M. J. Bennett, PMMO; data reduction program producing F's and F^2's; (4) A. Zalkin, FORDAP; computation of Fourier summations; (5) W. C. Hamilton, GONO9, "Goniostat Polyhedral Absorption and Extinction Correction Program for the IBM 7094," Brookhaven National Laboratory 1960; (6) C. T. Prewitt, SFLS5, "Full-Matrix Crystallographic Least-Squares Program," 1966; with rigid-body refinement routine written by M. J. Bennett and B. M. Foxman; (7) J. S. Wood, MGEOM, "Molecular Geometry Program," MIT, 1964; (8) D. P. Shoemaker, DISTAN, "Crystallographic Bond Distance, Bond Angle, and Dihedral Angle Program," 1963; (9) D. P. Shoemaker and R. C. Srivastava, VIBELL, 1963; analysis of anisotropic thermal parameters; (10) R. C. Elder, PUBTAB, preparation of table F_o and F_c for publication.

Results

The observed and final calculated structure amplitudes listed as $10|F_o|$ and $10|F_c|$ are shown in Table I. The atomic positional and isotropic thermal parameters of all nonhydrogen atoms with corresponding estimated standard deviations derived from the diagonal elements of the inverse matrix of the final least-squares cycle are in Table II. In Table III the anisotropic thermal parameters of the fluorine atoms and their equivalent isotropic thermal parameters are listed. Nickel–oxygen bond distances and bond angles appear in Tables IV and V, respectively. The nickel atom which is bonded to the water of hydration is labeled Ni2, the hydroxyl oxygen atom is O1, and the oxygen atom of the water molecule is O2.

The trifluoroacetylacetonate oxygen atoms are labeled O*n*1 and O*n*2, where *n* is the number of the ligand, ranging from 1 to 5. The ligand carbon atoms are labeled C*n*1 through C*n*5, beginning with the trifluoromethyl carbon atom. Oxygen atom O*n*1 is bonded to C*n*2. Figure 1 shows the trinuclear asymmetric unit of $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$ viewed along a direction perpendicular to the plane of the nickel atoms. The oxygen atoms of both water molecules have been included to show more clearly where the halves of the molecule are joined. Figure 2 shows the nickel and oxygen atoms of the entire molecule projected onto the *ac* plane with the ligands represented by curved lines. The ligand bond distances and angles with their averages and weighted averages are given in Tables VI and VII. The direction cosines of the best least-squares ligand planes are in Table VIII; the distances of atoms from these planes are given in Table IX. The nickel–nickel distances and angles are listed in Table X. Intermolecular contacts less than 3.5 Å are given in Table XI.

Discussion

The crystal structure of di-μ-aquo-di-μ_3-hydroxo-deca(1,1,1-trifluoropentane-2,4-dionato)hexanickel(II), $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$, is composed of two discrete hexanuclear molecules located at the inversion centers at (0, 0, 0) and (0, $^1/_2$, $^1/_2$) in the monoclinic unit cell. The closest intermolecular contacts between these molecules are between carbon atoms of the trifluoroacetylacetonato methyl groups and fluorine atoms of neighboring trifluoromethyl moieties,

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES IN UNITS OF 0.1 ELECTRON FOR $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$

H	K	FOBS	FCAL
[illegible]	[illegible]	[illegible]	[illegible]

Table II

Final Atom Coordinates and Isotropic Thermal Parameters[a]

Atom	x	y	z	B, Å²
Ni1	0.22940 (13)	0.08538 (10)	0.16171 (11)	4.07 (5)
Ni2	0.00985 (12)	0.04865 (10)	0.07964 (10)	3.58 (4)
Ni3	0.12913 (13)	0.95244 (10)	0.23533 (10)	4.24 (5)
O1	0.13912 (46)	0.99489 (36)	0.12732 (39)	3.55 (15)
O2	0.95297 (45)	0.93838 (36)	0.03267 (37)	3.48 (14)
O11	0.87834 (50)	0.09367 (40)	0.02882 (41)	4.31 (16)
O12	0.98538 (52)	0.02226 (39)	0.18616 (42)	4.20 (16)
O21	0.11719 (58)	0.93061 (44)	0.34575 (49)	5.63 (19)
O22	0.20654 (50)	0.05093 (40)	0.27709 (44)	4.61 (16)
O31	0.30117 (54)	0.18552 (45)	0.18782 (44)	5.11 (18)
O32	0.09825 (48)	0.14121 (40)	0.13029 (41)	4.05 (16)
O41	0.04586 (49)	0.86520 (40)	0.17617 (41)	4.09 (16)
O42	0.25027 (58)	0.88781 (48)	0.25789 (48)	5.90 (19)
O51	0.23232 (53)	0.09412 (41)	0.04209 (43)	4.77 (17)
O52	0.36015 (57)	0.03308 (43)	0.19470 (45)	5.13 (18)
C1[b]	0.4839 (21)	0.5433 (17)	0.0643 (17)	18.02 (90)
C2	0.5356 (19)	0.4745 (20)	0.0822 (11)	15.60 (78)
C3	0.5517 (15)	0.4312 (7)	0.0179 (27)	21.45 (122)
C4[c]	0.4651	0.5898	0.1308	40.78 (377)
C11	0.7198 (12)	0.1340 (9)	0.0195 (10)	6.71 (33)
C12	0.8149 (8)	0.0929 (7)	0.0687 (7)	5.05 (27)
C13	0.8184 (9)	0.669 (7)	0.1457 (8)	5.60 (30)
C14	0.9049 (9)	0.0311 (7)	0.2006 (7)	5.10 (27)
C15	0.8963 (10)	0.9994 (8)	0.2817 (9)	7.21 (36)
C21	0.1510 (14)	0.9342 (11)	0.4925 (11)	7.89 (41)
C22	0.1586 (9)	0.9688 (7)	0.4100 (8)	5.70 (30)
C23	0.2161 (9)	0.0336 (7)	0.4190 (8)	5.76 (30)
C24	0.2376 (9)	0.0731 (7)	0.3546 (8)	5.55 (29)
C25	0.2920 (10)	0.1453 (8)	0.3716 (8)	6.70 (34)
C31	0.3321 (14)	0.3134 (11)	0.1870 (12)	8.29 (44)
C32	0.2579 (9)	0.2499 (7)	0.1750 (7)	5.16 (28)
C33	0.1607 (9)	0.2674 (6)	0.1515 (7)	5.02 (27)
C34	0.0839 (8)	0.2138 (7)	0.1320 (7)	4.59 (25)
C35	0.9808 (9)	0.2419 (7)	0.1143 (7)	5.99 (31)
C41	0.9977 (11)	0.7400 (9)	0.1411 (10)	6.53 (34)
C42	0.0781 (8)	0.7971 (7)	0.1782 (7)	4.55 (25)
C43	0.1703 (10)	0.7708 (7)	0.2081 (8)	6.05 (31)
C44	0.2513 (10)	0.8178 (8)	0.2441 (8)	5.90 (30)
C45	0.3580 (14)	0.7813 (12)	0.2690 (11)	11.99 (57)
C51	0.3091 (15)	0.1313 (12)	0.9441 (12)	7.93 (42)
C52	0.3153 (10)	0.0945 (8)	0.0272 (8)	5.86 (30)
C53	0.4062 (10)	0.0742 (8)	0.0776 (8)	6.48 (33)
C54	0.4203 (11)	0.0397 (8)	0.1546 (9)	6.71 (32)
C55	0.5267 (14)	0.0050 (11)	0.1998 (11)	11.34 (53)
F11	0.6944 (6)	0.1134 (6)	0.9408 (6)	...
F12	0.7298 (7)	0.2055 (5)	0.0177 (8)	...
F13	0.6437 (6)	0.1181 (7)	0.0418 (7)	...
F21	0.1855 (8)	0.8666 (6)	0.5049 (5)	...
F22	0.0551 (9)	0.9238 (6)	0.4829 (5)	...
F23	0.1838 (11)	0.9748 (6)	0.5571 (5)	...
F31	0.2980 (6)	0.3806 (5)	0.1870 (10)	...
F32	0.4046 (8)	0.3079 (6)	0.2558 (8)	...
F33	0.3761 (10)	0.3145 (7)	0.1322 (8)	...
F41	0.9437 (7)	0.7600 (5)	0.0669 (5)	...
F42	0.0274 (8)	0.6706 (5)	0.1352 (9)	...
F43	0.9332 (8)	0.7347 (6)	0.1813 (6)	...
F51	0.3725 (17)	0.0983 (17)	0.9111 (12)	...
F52	0.3240 (18)	0.1975 (9)	0.9482 (9)	...
F53	0.2315 (10)	0.1192 (8)	0.8895 (7)	...

[a] Numbers in parentheses are estimated standard deviations and occur in the last significant figure of each parameter. [b] Coordinates and estimated standard deviations of atoms C1–C3 were derived from the rigid-body refinement of the toluene ring. [c] The coordinates of the toluene methyl carbon were not refined.

and the shortest of these is 3.02 Å between C25 and F52. This number may be considerably in error, since atoms F51, F52, and F53 are disordered. Other short

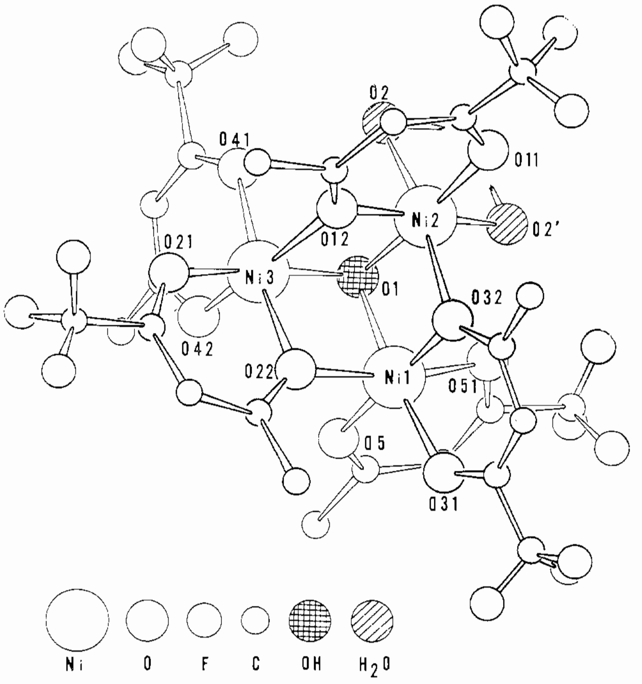

Figure 1.—The trinuclear unit of a molecule of $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$ viewed along an axis perpendicular to the plane of the nickel atoms. Both bridging water oxygens are included to show more clearly where the trinuclear halves are joined.

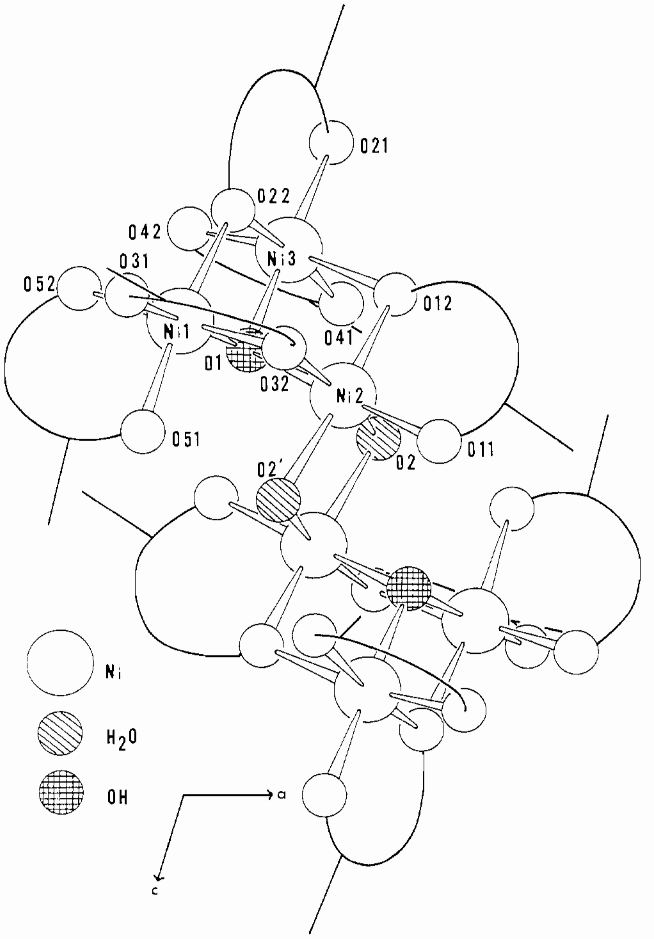

Figure 2.—A molecule of $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$ projected onto the *ac* plane. The origin of the unit cell is on the midpoint of a line joining O2 and O2′. The trifluoroacetylacetonate ligand is represented by a curved line with an appendage at the location of the trifluoromethyl group.

TABLE III

FLUORINE ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Equivalent isotropic B, Å^2
F11	109.0 (69)	114.5 (62)	85.2 (57)	43.6 (54)	2.1 (53)	1.4 (46)	10.8
F12	112.8 (73)	50.5 (42)	230 (11)	16.1 (46)	0.9 (72)	14.6 (53)	13.8
F13	66.2 (60)	173.5 (89)	163.2 (88)	33.9 (58)	62.0 (61)	60.8 (70)	13.8
F21	195 (11)	88.9 (55)	64.0 (47)	13.7 (62)	30.7 (58)	24.1 (40)	10.8
F22	209 (12)	108.5 (63)	73.6 (49)	11.0 (70)	81.8 (63)	14.7 (44)	11.3
F23	390 (19)	119.8 (65)	45.8 (43)	−108.7 (94)	76.3 (73)	−31.5 (45)	15.7
F31	90.5 (71)	46.8 (42)	335 (16)	−13.8 (44)	56.0 (88)	−20.6 (63)	16.0
F32	163.2 (96)	83.3 (56)	153.7 (89)	−64.6 (63)	7.8 (80)	−13.6 (54)	13.5
F33	240 (13)	110 6 (74)	167 (10)	−98.2 (86)	136 (10)	−33.7 (66)	14.8
F41	183.3 (92)	67.7 (43)	72.9 (48)	−39.2 (53)	−2.2 (58)	−5.5 (37)	10.6
F42	184 (10)	37.7 (38)	228 (11)	12.3 (52)	−4.4 (89)	−29.8 (51)	15.2
F43	168.7 (93)	121.1 (68)	95.3 (59)	−86.1 (70)	64.3 (64)	−17.5 (49)	11.9
F51	372 (26)	381 (27)	182 (14)	224 (23)	190 (17)	148 (16)	28.9
F52	552 (35)	85.8 (68)	134.4 (95)	−101 (14)	31 (14)	38.2 (67)	23.0
F53	196 (12)	173 (10)	74.8 (59)	−61.3 (94)	27.8 (74)	17.2 (59)	14.7

[a] Numbers in parentheses are estimated standard deviations occurring in the last significant figure listed.

TABLE IV

NICKEL–OXYGEN BOND DISTANCES

Atom A	Atom B	Bond A–B, Å
Ni1	O1	2.015 (7)
	O22	2.154 (7)
	O31	2.012 (8)
	O32	2.035 (7)
	O51	2.036 (7)
	O52	2.001 (8)
Ni2	O1	2.010 (6)
	O2	2.152 (6)
	O2′	2.127 (6)
	O11	1.977 (7)
	O12	1.985 (7)
	O32	2.074 (7)
Ni3	O1	2.011 (7)
	O12	2.316 (7)
	O21	1.958 (8)
	O22	2.055 (7)
	O41	2.008 (7)
	O42	2.005 (8)

TABLE V

NICKEL–OXYGEN BOND ANGLES (DEG)

Ni1–O1–Ni2	100.2 (3)	O2–Ni2–O11	89.7 (3)
Ni1–O1–Ni3	104.1 (3)	O2′–Ni2–O11	91.8 (3)
Ni1–O32–Ni2	97.4 (3)	O2–Ni2–O12	88.5 (3)
Ni1–O22–Ni3	97.9 (3)	O2′–Ni2–O12	171.7 (3)
Ni2–O1–Ni3	103.2 (3)	O2–Ni2–O32	165.6 (3)
Ni2–O12–Ni3	93.9 (3)	O2′–Ni2–O32	89.9 (3)
Ni2–O2–Ni2′ [a]	93.7 (3)	O11–Ni2–O32	104.3 (3)
O1–Ni1–O22	77.4 (3)	O12–Ni2–O11	94.7 (3)
O1–Ni1–O31	171.2 (3)	O12–Ni2–O32	93.5 (3)
O1–Ni1–O32	81.1 (3)	O1–Ni3–O12	77.2 (3)
O1–Ni1–O52	100.4 (3)	O1–Ni3–O21	169.6 (3)
O22–Ni1–O31	104.6 (3)	O1–Ni3–O22	79.8 (3)
O22–Ni1–O32	89.5 (3)	O1–Ni3–O41	91.4 (3)
O22–Ni1–O51	165.9 (3)	O1–Ni3–O42	95.0 (3)
O22–Ni1–O52	90.2 (3)	O12–Ni3–O21	97.0 (3)
O31–Ni1–O32	90.3 (3)	O12–Ni3–O22	90.3 (3)
O31–Ni1–O51	89.4 (3)	O12–Ni3–O41	84.1 (3)
O31–Ni1–O52	88.2 (3)	O12–Ni3–O42	170.4 (3)
O32–Ni1–O51	89.9 (3)	O21–Ni3–O42	170.4 (3)
O32–Ni1–O52	178.3 (3)	O21–Ni3–O22	91.7 (3)
O51–Ni1–O52	90.8 (3)	O21–Ni3–O42	91.5 (3)
O1–Ni2–O11	175.4 (3)	O22–Ni3–O42	93.8 (3)
O1–Ni2–O12	85.4 (3)	O41–Ni3–O22	170.5 (3)
O1–Ni2–O32	80.3 (3)	O41–Ni3–O42	90.6 (3)
O2–Ni2–O2′	86.3 (3)		

[a] Primed atoms are related to unprimed atoms by the center of symmetry at the origin.

carbon–fluorine intermolecular distances lie in the range 3.2–3.4 Å and are consistent with calculated van der Waals contact distances.[12]

At another pair of centers at ($^1/_2$, 0, $^1/_2$) and ($^1/_2$, $^1/_2$, 0) are two molecules of toluene of crystallization. To conform to the symmetry of the sites which they occupy, the toluene molecules are rotationally disordered about an axis perpendicular to the plane of the molecule. The methyl carbon atom is not quite randomly oriented around the ring but preferentially occupies two rather diffuse positions on the ring that are *para* to each other. The disorder of the toluene molecule probably results because it is somewhat loosely held in its position; the closest intermolecular approach to a phenyl carbon atom is 3.53 Å involving atoms C1 and C25.

The molecular structure of $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$ as shown in Figures 1 and 2 is composed of two trinuclear units, related by a center of symmetry and joined by two bridging water molecules. The three nickel atoms in the asymmetric unit are each octahedrally coordinated by oxygen atoms. The three octahedra are joined at edges so that they share a common vertex at the position of the hydroxyl oxygen atom. The same form of triangular grouping of octahedra is also found in the Mo_3 unit of $Zn_2Mo_3O_8$[13] and in the lower halides of niobium of phase composition Nb_3X_8.[14] The coordination octahedron of Ni2 shares a third edge with the symmetry-related octahedron of the other trinuclear unit. The set of nickel atoms approximates but is slightly distorted from an equilateral triangle. The nickel–nickel distances are 3.087 ± 0.002 Å, 3.151 ± 0.002 Å, and 3.176 ± 0.002

(12) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(13) W. H. McCarroll, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **79**, 5410 (1957).

(14) A. Simon and H. G. von Schnering, *J. Less-Common Metals*, **11**, 31 (1966).

TABLE VI

TRIFLUOROACETYLACETONATO LIGAND BOND DISTANCES (Å)

Ligand	C*n*1–C*n*2, C*n*4–C*n*5		C*n*2–C*n*3, C*n*3–C*n*4	
1	1.539 (20)	1.515 (18)	1.363 (17)	1.443 (17)
2	1.550 (22)	1.466 (18)	1.381 (18)	1.399 (18)
3	1.507 (23)	1.493 (17)	1.358 (17)	1.404 (16)
4	1.507 (19)	1.586 (24)	1.341 (18)	1.400 (19)
5	1.520 (24)	1.599 (24)	1.366 (19)	1.391 (19)
Av	1.525	1.532	1.362	1.407
Wtd av	1.525 (10)	1.518 (9)	1.362 (8)	1.409 (8)
Lit. av[a]	1.524 (3)		1.390 (3)	

Ligand	O*n*1–C*n*2, O*n*2–C*n*4		C*n*1–F*n*1	C*n*1–F*n*2	C*n*1–F*n*3
1	1.280 (14)	1.253 (14)	1.32 (2)	1.26 (2)	1.28 (2)
2	1.259 (15)	1.305 (14)	1.28 (2)	1.34 (2)	1.27 (2)
3	1.272 (15)	1.291 (14)	1.28 (2)	1.30 (2)	1.26 (2)
4	1.274 (14)	1.249 (16)	1.30 (2)	1.30 (2)	1.30 (2)
5	1.282 (15)	1.247 (16)	1.33 (3)	1.18 (3)	1.23 (2)
Av	1.273	1.269		1.29	
Wtd av	1.274 (7)	1.271 (7)		1.28 (1)	
Lit. av	1.274 (3)				

[a] The literature average given is that for acetylacetonate complexes by E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, **88,** 2951 (1966).

TABLE VII

TRIFLUOROACETYLACETONATO LIGAND BOND ANGLES (DEG)

Ligand	C*n*1–C*n*2–O*n*1, C*n*5–C*n*4–O*n*2		C*n*1–C*n*2–C*n*3, C*n*3–C*n*4–C*n*5	
1	111.1 (11)	117.3 (10)	116.3 (11)	116.9 (11)
2	114.9 (12)	117.0 (11)	115.0 (12)	120.1 (11)
3	110.3 (11)	118.3 (10)	119.2 (12)	118.7 (10)
4	112.7 (10)	114.3 (12)	117.8 (12)	118.6 (13)
5	112.5 (12)	114.6 (12)	117.6 (13)	117.3 (13)
Av	112.3	116.3	117.2	118.3
Wtd av	112.2 (5)	116.5 (5)	117.1 (5)	118.4 (5)
Lit av	114.9 (2)		119.8 (3)	

Ligand	O*n*1–C*n*2–C*n*3, O*n*2–C*n*4–C*n*3		C*n*2–C*n*3–C*n*4
1	132.5 (11)	125.8 (11)	122.3 (11)
2	129.8 (12)	122.8 (11)	125.7 (12)
3	130.6 (11)	123.1 (10)	125.1 (11)
4	129.6 (11)	127.2 (12)	123.3 (12)
5	129.6 (12)	128.1 (13)	122.4 (13)
Av	130.4	125.4	123.8
Wtd av	130.4 (5)	125.1 (5)	123.8 (5)
Ltd. av	125.3 (3)		124.0 (3)

Ligand	F*n*1–C*n*1–F*n*2	F*n*2–C*n*1–F*n*3	F*n*3–C*n*1–F*n*1
1	104.3 (13)	109.5 (13)	103.6 (13)
2	102.9 (14)	106.1 (14)	110.9 (16)
3	105.6 (15)	102.5 (16)	105.0 (16)
4	106.8 (13)	105.6 (13)	102.3 (12)
5	108.6 (20)	108.8 (19)	100.7 (19)
Av	105.5		
Wtd av	105.4 (4)		

TABLE VIII

DIRECTION COSINES OF BEST WEIGHTED LEAST-SQUARES PLANES OF CONJUGATED RING SYSTEMS[a]

Ring	*L*	*M*	*N*	*D*
1	0.2047	0.8985	0.3884	1.272
2	0.8179	−0.5580	0.1403	1.384
3	−0.3174	−0.0308	0.9478	1.686
4	−0.4348	−0.1572	0.8867	2.993
5	0.0656	0.9229	0.3795	1.983

[a] Direction cosines are with respect to a Cartesian coordinate system. The matrix for transforming from monoclinic fractional coordinates to Cartesian coordinates is

$$\begin{bmatrix} 14.27 & 0.0 & 0.0 \\ 0.0 & 17.52 & 0.0 \\ 5.090 & 0.0 & 16.07 \end{bmatrix}$$

Å, within the triangle, with 3.121 ± 0.003 Å as the shortest distance between two nickel atoms of different triangles. Thus, as in other polynuclear metal β-ketoenolates no metal–metal bond formation takes place.

The structure of only one other polymeric nickel β-diketonate has been determined in the solid state, that of bis(acetylacetonato)nickel(II),[5] which has a linear trinuclear structure and nickel–nickel distances of 2.882 and 2.896 Å (esd 0.018 Å). Since the present structure involves octahedra joined on edges and the other involves octahedra joined on faces, a direct comparison of these distances is not meaningful, but a longer nickel–nickel distance is not unexpected in the present structure.

Three ligand chelate rings (*n* = 1–3) lie on one side of the plane determined by the nickel atoms of the trinuclear unit; the other two ligands (*n* = 4, 5) and the two bridging water molecules lie on the opposite side. The behavior of ligands 4 and 5 during the refinement and the appearance of Fourier and difference Fourier maps indicated that each of these ligands is disordered in such a way that the CF_3 and CH_3 groups exchange positions in about 20% of the molecules according to Fourier electron density estimates. The disorder is most severe for ligand 5 and is demonstrated by the large equivalent isotropic temperature factors of the fluorine atoms, the long C*n*4–C*n*5 bond lengths (about 0.09 Å longer than similar bonds on rings 1–3), and large peaks (up to 0.79 e$^-$/Å^3) near the methyl carbon atoms of rings 4 and 5 on the final difference Fourier map.

Inspection of Figure 1 shows that the carbonyl oxygen atoms of chelate rings 1–3, those exhibiting no disorder, form both bridging and nonbridging bonds to metal atoms, whereas the two disordered ligands contain only nonbridging oxygens. In the former cases the nonbridging oxygen atom of each ligand is the one closer to the trifluoromethyl group. Thus, for ligands 1–3 an ordered arrangement of the unsymmetrical ligands is strongly favored by the great difference in the two types of coordination sites available. For the remaining two ligands, however, the available sites are similar and do not tend to discriminate strongly between the CH_3CO and the CF_3CO ends of the ligand. Whether steric or electronic factors or both play a major role in causing the bridging positions to prefer the CH_3CO end of the ligand is difficult to say with certainty.

The metal–oxygen bonds may be placed in three categories, as has been done in previous studies of polymeric β-diketone complexes. There are primary bonds that join the metal atom to an oxygen of a ligand chelated about that atom, and there are secondary bonds that join a metal to an oxygen atom of a ligand chelated about another metal atom. Primary bonds may be bridging or nonbridging, whereas secondary

TABLE IX

DISTANCES OF ATOMS FROM LIGAND PLANES

Ring	C*n*1	C*n*2	C*n*3	C*n*4	C*n*5	O*n*1	O*n*2	Ni1	Ni2	Ni3
1	0.120	0.007	0.008	−0.017	−0.119	−0.003	0.004	. . .	−0.063	−0.419
2	0.083	−0.010	0.010	−0.003	−0.104	0.002	0.000	0.150	. . .	0.139
3	−0.209	−0.040	−0.006	0.043	0.195	0.014	−0.012	−0.047	−0.415	. . .
4	0.060	0.016	0.009	−0.031	−0.182	−0.005	0.010	. . .	0.212	. . .
5	0.107	−0.003	0.044	−0.055	−0.257	−0.001	0.012	0.545	. . .	. . .

TABLE X

NICKEL–NICKEL INTERATOMIC DISTANCES AND ANGLES

Distance	Å	Angle	Deg
Ni1–Ni2	3.087 (2)	Ni1–Ni2–Ni3	61.19 (6)
Ni1–Ni3	3.176 (2)	Ni1–Ni3–Ni2	58.40 (5)
Ni2–Ni2′	3.121 (3)	Ni2–Ni1–Ni3	60.41 (5)
Ni2–Ni3	3.151 (2)	Ni2′–Ni2–Ni3	108.08 (7)
		Ni2′–Ni2–Ni1	108.38 (7)

TABLE XI

INTERMOLECULAR CONTACTS LESS THAN 3.5 Å

Atom A	Atom B	A–B, Å	Position of atom B with respect to coordinates in Table II
C4	O52	3.38	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
C4	C55	3.19	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
F21	C35	3.40	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
F21	F12	3.14	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
F22	F22	3.24	$\bar{x}, 2 - y, 1 - z$
F22	F42	3.18	$x, {}^1/_2 - y, {}^1/_2 + z$
F23	C15	3.28	$1 - x, 2 - y, \bar{z}$
F23	F31	3.42	$x, {}^3/_2 - y, {}^1/_2 + z$
F31	C55	3.43	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
F42	C15	3.35	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
F43	C25	3.44	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
F43	C34	3.25	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
F43	C35	3.29	$1 - x, {}^1/_2 + y, {}^1/_2 - z$
F51	C55	3.24	$1 - x, \bar{y}, 1 - z$
F52	C25	3.02	$x, {}^1/_2 - y, {}^1/_2 + y$
F51	F32	3.24	$x, {}^1/_2 - y, {}^1/_2 + z$

TABLE XII

PRIMARY AND SECONDARY METAL–OXYGEN DISTANCES (Å)

	Primary		
Metal	Nonbridging	Bridging	Secondary
Ni1	O31 2.012 (8) O51 2.036 (7) O52 2.001 (8)	O32 2.035 (7)	O22 2.154 (7)
Ni2	O11 1.977 (7)	O12 1.985 (7)	O32 2.074 (7)
Ni3	O21 1.958 (8) O41 2.008 (7) O42 2.005 (8)	O22 2.055 (7)	O12 2.316 (7)
Av	2.00 (3)	2.02 (4)	2.18 (12)

bonds are always bridging. Studies of $[Co(AA)_2]_4$,[15] $[Co(AA)_2H_2O]$,[16] $[Co(AA)_2]_3 \cdot H_2O$,[17] and $[Ni(AA)_2]_3$,[5] where AA represents the acetylacetonate anion, have indicated that there is not always a correlation between metal–oxygen bond lengths and metal–oxygen bond types, although secondary metal–oxygen bonds are usually longer than primary metal–oxygen bonds. This relationship is present in $Ni_6(TFA)_{10}(OH)_2(H_2O)_2$ as is shown in Table XII. That it does not hold for $[Zn(AA)_2]_3$[18] and $[Co(DEPAM)_2]_2$[4] suggests that the significance of such a comparison is not great in terms of the bonding in polymeric molecules of this kind.

A triply bridging hydroxyl group lies at the common vertex of the three coordination octahedra. Within experimental error the hydroxyl oxygen atom symmetrically bridges the three nickel atoms, since each independently determined metal–oxygen bond length is within one esd of the average value of 2.012 ± 0.004 Å. Triply bridging OH groups appear to be rare, although they presumably occur in some other compounds, such as $[(CH_3)_3PtOH]_4$[19] and $U_6O_4(OH)_4(SO_4)_6$.[20] This appears to be the first time that such a group has been characterized structurally with any precision.

A search for the hydroxyl hydrogen atom in the final difference Fourier map revealed a peak of maximum density 0.54 $e^-/Å^3$ at a distance of 0.99 Å from O1 (fractional coordinates: 0.140, −0.035, 0.092). A peak of this height is very probably significant, since it is considerably larger (about 4 times) than the random "noise" in the final difference Fourier map.[21,22] The hydroxyl hydrogen atom peak lies close to a line between O1 and O11′. However, the distance (3.00 Å) between the two oxygen atoms precludes the possibility of significant hydrogen bonding. Evidence for a hydroxyl group is present in the infrared spectrum of the compound in the form of a weak but sharp absorption at 3560 cm^{-1}.

Another novel feature of this molecule is that the two trinuclear halves are joined only by bridging water molecules. The bridging nickel–oxygen distances, 2.152 ± 0.006 and 2.127 ± 0.006 Å, are not significantly different.

The carbonyl oxygen atoms, O41 and O51′, approach the water oxygen atom at distances of 2.706 and 2.625 Å, respectively, shorter than the expected van der Waals contact distance of 2.8 Å. To confirm the suspected hydrogen bonding involving these atoms, a search of the final difference Fourier map was made for electron density along lines connecting O2 with O41 and O2 with O51′. Peaks of 0.34 and 0.43 $e^-/Å$, respectively, were located near these interatomic vectors at distances of

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(15) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **4**, 1145 (1965).

(16) F. A. Cotton and R. C. Elder, *ibid.*, **5**, 423 (1966).

(17) F. A. Cotton and R. Eiss, *J. Am. Chem. Soc.*, **90**, 38 (1968).

(18) F. A. Cotton and R. Eiss, *Acta Cryst.*, **B24**, 904 (1968).

(19) *Cf.* F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1966, p 1036.

(20) G. Lundgren, *Arkiv Kemi*, **5**, 349 (1953).

(21) The estimated standard deviation of the electron density, calculated employing Cruickshank's formula,[22] was 0.06 $e^-/Å^3$

$$\sigma(\rho) = \frac{1}{V}\left\{\sum_h \sum_k \sum_l (\Delta F_{hkl})^2\right\}^{1/2}$$

This estimate, like any based on the assumption of purely random error, is very likely to be too low.

(22) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 154 (1949).

0.79 and 1.33 Å from the water oxygen atom. Coordinates of hydrogen atoms that were calculated assuming the known geometry of the water molecule (H–O distance, 0.958 Å; H–O–H angle, 104.5°)[23] and the observed coordinates are shown in Table XIII with the calculated and observed geometries. It appears quite certain that the water molecules are hydrogen bonded to oxygen atoms of the adjacent ligands. The hydrogen bonding contributes to the strength of the linkage between the two trinuclear units, since the two oxygen atoms to which each water molecule is hydrogen bonded are not in the same trinuclear unit.

TABLE XIII

CALCULATED AND OBSERVED POSITIONS OF WATER HYDROGEN ATOMS

	X/a		Y/b		Z/c	
Atom	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
H2a	−0.016	−0.020	−0.104	−0.092	0.066	0.067
H2b	0.116	0.118	0.069	0.075	−0.025	−0.010

	Value, deg	
Angle	Obsd	Calcd
O2–H2a–O41	156.8	143.5
O2–H2b–O51	176.6	147.8

	Value, Å	
Distance	Obsd	Calcd
O2–H2a	0.79	0.958
O2–H2b	1.34	0.958
H2a–O41	1.95	1.87
H2b–O51	1.50	1.76

The geometry of the 1,1,1-trifluoroacetylacetonato ligands is quite close to that given as average for acetylacetonato ligands by Lingafelter and Braun.[24] A small but significant reduction of the C*n*1–C*n*2–O*n*1 angle near the CF_3 group is apparent with a concomitant opening of the O*n*1–C*n*2–C*n*3 angle to maintain the planarity of the chelate ring. The reason for this distortion is not clear, and, unfortunately, there have been no other crystal structure determinations of this ligand for comparison.

The structure of $Ni_6(CF_3COCHCOCH_3)_{10}(OH)_2(H_2O)_2$ is radically different from any other structure found for polymeric acetylacetonates, in that it contains closed triangles of metal atoms. The type of aggregation of octahedral units found in this structure is, of course, only possible in the presence of a moiety which may simultaneously bridge three metal atoms, a role played by the hydroxyl groups in the present case.

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[23] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968.

[24] E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, **88**, 2951 (1966).

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The Crystal and Molecular Structure of Bis(benzoylacetonato)zinc Monoethanolate and X-Ray Data on Related Crystals[1a]

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The crystal structure of bis(benzoylacetonato)zinc monoethanolate has been determined by three-dimensional Fourier methods with the positional and anisotropic thermal parameters refined by least-squares methods to a conventional R factor of 0.12 based on 2989 independent nonzero reflections. The data were collected on multiple films by the equiinclination Weissenberg technique. The crystals are monoclinic, space group $P2_1/c$ with $a = 12.28 \pm 0.01$ Å, $b = 8.39 \pm 0.01$ Å, $c = 20.52 \pm 0.02$ Å, and $\beta = 100° 58' \pm 10'$. The density, as measured by flotation, is 1.40 ± 0.01 g/cm³, in agreement with 1.39 ± 0.01 g/cm³ calculated for four molecules of $(CH_3COCHCOC_6H_5)_2Zn \cdot C_2H_5OH$ (FW = 433.80 g/mol) in the unit cell. The coordination around the zinc ion is close to square pyramidal with the four chelate oxygen atoms forming the base of the pyramid and being ∼1.99 Å from Zn and the ethanol oxygen atom being in the apical position at 2.06 Å from Zn. The benzene rings in each ligand are *cis* to one another, and the molecules are associated in loosely bound pairs in the lattice. Each zinc ion can be considered as forming a weak bond (3.34 Å) to the middle carbon atom of a chelate ring of the second molecule, and this carbon atom is slightly raised (0.078 Å) from the plane of its chelate ring toward the zinc atom to which it is coordinated. These pairs are linked by O–H---O hydrogen bonding to produce stacks of molecules along the b direction. The unit cell parameters and space groups of bis(benzoylacetonato)zinc monohydrate and of bis(3-phenylacetylacetonato)zinc monohydrate are also reported; a powder diffraction pattern of bis(benzoylacetonato)magnesium monohydrate suggests that it is isostructural with the corresponding zinc compound. It seems likely that these three complexes also contain five-coordinate metal ions.

Introduction

The metal complexes formed by the acetylacetonato (acac ≡ $CH_3COCHCOCH_3^-$) anion and its derivatives have often shown interesting variation in stereochemistry.

The crystal structures of the 2:1 complexes formed by the benzoylacetonato (benzac ≡ 1-phenyl-1,3-butanedionato ≡ $CH_3COCHCOC_6H_5^-$) anion with the transition metal ions copper,[2] palladium,[3] and vanadyl[4] show several features of special interest; in particular, the phenyl groups are *trans* in the copper and

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