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The Crystal Structures of High- and Low-Spin Nickel(II) Complexes Containing the Macrocyclic Ligand Tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine[1]

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The crystal structures of $Ni(TAAB)I_2 \cdot H_2O$ and $Ni(TAAB)(BF_4)_2$, where TAAB is the tetradentate macrocyclic ligand tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine, have been determined from three-dimensional single-crystal X-ray diffraction data collected by automatic counter methods. The structure of $Ni(TAAB)I_2 \cdot H_2O$ has been refined by least-squares techniques to a conventional R factor of 10.9% for 1368 reflections, and the structure of $Ni(TAAB)(BF_4)_2$ has been refined to an R factor of 14.1% for 1709 observed reflections. The compound $Ni(TAAB)I_2 \cdot H_2O$ crystallizes in the monoclinic space group C2/c with cell dimensions $a = 13.48 \pm 0.03$ Å, $b = 16.03 \pm 0.03$ Å, $c = 13.51 \pm 0.03$ Å, and $\beta = 90.9 \pm 0.1°$. The calculated density for $Z = 4$ is 1.69 g/cm³ as compared to an experimental density of 1.76 g/cm³. The compound $Ni(TAAB)(BF_4)_2$ crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions of $a = 11.55 \pm 0.02$ Å, $b = 13.76 \pm 0.03$ Å, $c = 19.59 \pm 0.04$ Å, and $\beta = 123.0 \pm 0.01°$. The calculated density for $Z = 4$ is 1.64 g/cm³ as compared to a measured density of 1.61 ± 0.05 g/cm³. The structure consists of discrete molecules with the macrocyclic ligands having approximately $S_4(\bar{4})$ symmetry. In the compound $Ni(TAAB)I_2 \cdot H_2O$, the nickel(II) ion has tetragonal coordination with in-plane Ni–N distances of 2.09 ± 0.03 Å corresponding to nickel(II) in the high-spin form. The apical positions are occupied by an iodide ion (the Ni–I distance is 2.903 ± 0.007 Å) and by a water molecule (the Ni–O distance is 2.20 ± 0.03 Å). The nickel(II) ion has planar coordination in the compound $Ni(TAAB)(BF_4)_2$ with average Ni–N distances of 1.90 + 0.02 Å corresponding to nickel(II) in the low-spin form. In both cases, disorder due to alternative orientations of packing of the molecules in the crystal has limited the accuracy of the macrocyclic ligand bond parameters.

Introduction

The tetradentate macrocyclic ligand tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine, $C_{28}H_{20}N_4$, hereafter referred to as TAAB, is formed as the self-condensation product of *o*-aminobenzaldehyde in the presence of nickel(II), copper(II), and cobalt(II) ions.[3] Another product formed in the presence of nickel(II) is the tridentate macrocyclic ligand tribenzo[*b,f,j*][1,5,9]triazacycloduodecine,[4] $C_{21}H_{15}N_3$, hereafter referred to as TRI, whose structure has previously been determined.[5]

In Melson and Busch's study of the spectral and magnetic properties of compounds of the formula $Ni(TAAB)X_2$ it was found[6,7] that when X^- is ClO_4^-, BF_4^-, or $B(C_6H_5)_4^-$, the compounds are uniformly diamagnetic, consistent with planar nickel(II) in its usual singlet state; whereas, when X^- is I^-, NO_3^-, or NCS^-, the compounds exhibit a magnetic moment of 3.2 BM, consistent with tetragonal nickel(II) in its triplet state. The *monohydrated* chloride and bromide exhibit intermediate magnetic moments at room temperature which has been interpreted as arising from a singlet–triplet equilibrium.[6] In order to establish more fully the molecular geometry of the TAAB ligand and to attempt an explanation of the curious role which water plays in these compounds, a series of structural investigations was performed in these laboratories. After examination of crystals of all of the above-mentioned TAAB complexes, the fluoroborate, iodide, and bromide were selected for further study.[8] This paper reports the structure determination of $Ni(TAAB)I_2 \cdot H_2O$ and $Ni(TAAB)(BF_4)_2$ by single-crystal X-ray diffraction methods.

Experimental Section

Crystals of $Ni(TAAB)I_2$ and $Ni(TAAB)(BF_4)_2$ were kindly supplied by Dr. D. H. Busch of The Ohio State University.

Unit Cell and Space Group of $Ni(TAAB)I_2 \cdot H_2O$.—The material as received was dark violet and had a brown powdered surface, presumably as a result of drying under vacuum over P_4O_{10}.[7] The material was recrystallized from a 50:50 mixture of ethanol and water. Slow evaporation yielded shiny violet crystals in the form of rectangular platelets. The infrared spectrum of the crystals in a Nujol mull indicated the presence of water through the existence of a broad band at 3200–3400 cm⁻¹, in contrast to Busch's anhydrous material.

A crystal of approximate dimensions of 0.2 × 0.1 × 0.2 mm was mounted along the short direction (b^*) and examined on a precession camera, equipped with a polaroid film cassett, using Cu Kα radiation (nickel filtered, λ 1.5418 Å; CaF_2 calibration, $a_0 = 5.4629$ Å); from these photographs taken at room temperature (~23°) the lattice parameters obtained are $a = 13.48 \pm 0.03$ Å, $b = 16.03 \pm 0.03$ Å, $c = 13.51 \pm 0.03$ Å, and $\beta = 90.9 \pm 0.1°$ (where the errors are estimated from the precision of film measurement). Systematic absences for hkl with $h + k$ odd and for $h0l$ with l odd indicated the possible monoclinic space groups Cc and C2/c. The density of 1.76 ± 0.05 g/cm³ measured by flotation in a mixture of carbon tetrachloride and iodomethane may be compared to a calculated density of 1.69 g/cm³ based on

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[2] (a) National Science Foundation predoctoral trainee, 1965–1968. (b) Alfred P. Sloan Foundation fellow.

[3] G. A. Melson and D. H. Busch, *Proc. Chem. Soc.*, 223 (1963).

[4] G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 1706 (1965).

[5] E. B. Fleischer and E. Klem, *Inorg. Chem.*, **4**, 637 (1965).

[6] G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 4830 (1964).

[7] G. A. Melson and D. H. Busch, *ibid.*, **86**, 4834 (1964).

[8] Unfortunately, the compound $Ni(TAAB)Br_2 \cdot H_2O$ crystallizes in a twinned monoclinic habit (as does the nitrate and chloride) and this has, for the time being, halted progress on its determination. The approximate cell constants of $Ni(TAAB)Br_2 \cdot H_2O$ are $a = 23.7$ Å, $b = 5.2$ Å, $c = 17.2$ Å, and $\beta = 136.5°$. The probable space groups are C2, Cm, or C2/m with $Z = 2$.

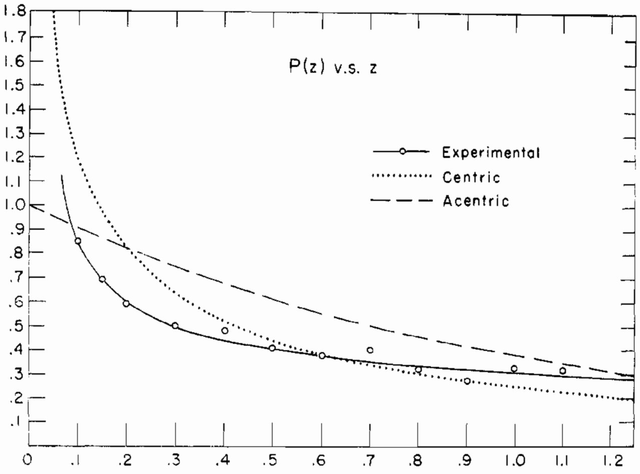

Figure 1.—$P(z)$ *vs.* z for $Ni(TAAB)I_2 \cdot H_2O$.

four molecules in the unit cell. The selection of the space group C2/c was based on the frequency distribution obtained by plotting $P(z)$ *vs.* z,[9] which indicated a centrosymmetric distribution (Figure 1), and by subsequent successful refinement of the structure. The space group C2/c requires the nickel ions and water molecules to be located on twofold axes corresponding to sets of fourfold positions (4e)[10] and the macrocyclic ligand thus to have at least $C_2(2)$ symmetry.

Unit Cell and Space Group of $Ni(TAAB)(BF_4)_2$.—The crystals supplied were ruby red prisms and were used without further recrystallization. The crystals are elongated prisms and a crystal of approximate dimensions 0.2 × 0.3 × 0.15 mm was mounted along the elongated direction (b^*). The experimental conditions used in determining the space group and unit cell dimensions for $Ni(TAAB)(BF_4)_2$ were identical with those above. The systematic absences for $h0l$ with l odd and $0k0$ with k odd are uniquely characteristic of space group $P2_1/c$ of the monoclinic system. The lattice parameters are $a = 11.55 \pm 0.02$ Å, $b = 13.76 \pm 0.03$ Å, $c = 19.59 \pm 0.04$ Å, and $\beta = 123.0 \pm 0.1°$. The calculated density for $Z = 4$ is 1.64 g/cm^3 as compared to a measured density of 1.61 ± 0.05 g/cm^3. The molecules therefore may lie in the fourfold general positions of the space group.

Single-Crystal Data Collection

The three-dimensional X-ray intensity data were collected on a Philips automated linear diffractometer, PAILRED, employing monochromatized Kα radiations obtained using a silicon crystal reflecting from the (111) plane. In the case of $Ni(TAAB)I_2 \cdot H_2O$, molybdenum radiation was employed, while copper radiation was employed for $Ni(TAAB)(BF_4)_2$ data collection. The data for both crystals were obtained by the ω-scan method for layers $h0l$ through $h,12,l$. The range of scan varied from ±1.0 to ±2.0° from the calculated peak.

In the case of $Ni(TAAB)I_2 \cdot H_2O$, background was counted for 20 sec on each end of the scan, while for $Ni(TAAB)(BF_4)_2$ the time was 12 sec. A reflection was monitored at the end of each layer of data collection and only random fluctuations were observed. For $Ni(TAAB)I_2 \cdot H_2O$ a total of 2328 reflections was examined within $2\theta \leq 50°$ ($(\sin\theta)/\lambda \leq 0.60$) and for $Ni(TAAB)(BF_4)_2$ a total of 2969 reflections was examined within $2\theta \leq 105°$ ($(\sin\theta)/\lambda \leq 0.51$). No attenuators were employed since all counting rates were less than 5×10^3 sec^{-1}. Only those reflections which had net positive intensities and which obeyed the condition $\sigma(I_o)/I_o < {}^2/_3$ for $Ni(TAAB)I_2 \cdot H_2O$ and $\sigma(I_o)/I_o < {}^3/_4$ for $Ni(TAAB)(BF_4)_2$ were accepted as observed reflections in the structure determination (the unobserved reflections were omitted from any further calculations). The statistical counting error $\sigma(I_o)$ was defined as $\sigma(I_o) = (T + t^2B)^{1/2}$, where T = total counts in time t_T, B = total background counts in time t_B, and $t = t_T/t_B$.[11] This procedure yielded (after symmetry averaging of $hk0$'s) a total of 1368 observed reflections for $Ni(TAAB)I_2 \cdot H_2O$ and 1709 reflections for $Ni(TAAB)(BF_4)_2$. The intensities were corrected for Lorentz and polarization effects (including monochromator polarization effects[12]) and placed on approximately absolute scales by Wilson's method. No corrections for absorption effects were made. The linear absorption coefficient for $Ni(TAAB)I_2 \cdot H_2O$ using Mo Kα radiation is 28.3 cm^{-1}; μR varies from 0.28 to 0.40 which would result in a maximum variation in intensity over the range of observed data ±11% for any reciprocal level of data. This was confirmed by a 360° ω scan for the 020 reflection. The same observation for the $Ni(TAAB)(BF_4)_2$ crystal yielded a variation of ±5%.

Determination of the Structures

The determination of the structure of $Ni(TAAB)I_2 \cdot H_2O$ proceeded from the location of iodine and nickel atoms in a three-dimensional Patterson function.[13] A three-dimensional Fourier synthesis based on the phases produced by these atoms yielded positions for the remaining atoms in the molecule. Several cycles of full-matrix least-squares refinement using isotropic temperature parameters were then performed and a difference Fourier function was calculated. From this map, it was evident that there were peaks at the positions of the nitrogen atoms obtained by reflecting the atoms through a mirror plane passing through the middle of opposite benzene rings (see Figure 2). This indicated a disorder produced by packing the molecules in two different orientations which left the outer parts of the molecule (the benzene rings) unchanged, but which substantially altered the appearance of the averaged structure in the region of the nitrogen and bridging carbon atom positions.

At this point, the determination of the structure of $Ni(TAAB)(BF_4)_2$ was begun in hopes that it would provide a clearer picture of the TAAB ligand. A trial structure was obtained through the use of MAGIC[14] (a

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[9] D. Rogers in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, London, 1965, p 122.

[10] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 101.

[11] M. Mack, *Norelco Reptr.*, **12**, 40 (June 1965).

[12] W. L. Bond, *Acta Cryst.*, **12**, 375 (1959).

[13] In addition to the Sly–Shoemaker–VandenHende ERFR2 Patterson and Fourier synthesis program, the main programs used in this work were Dewar's SORFLS least-squares program and SORFFE function and error program (substantially modified versions of ORFLS and ORFFE by Busing, Martin, and Levy), the symbolic addition program MAGIC written by Stone, Dewar, and Fleischer, and C. K. Johnson's ORTEP thermal ellipsoid plotting program. Various other data-handling programs of local origin were used; all calculations were performed on the University of Chicago IBM 7094 computer.

[14] E. B. Fleischer, *Trans. Am. Cryst. Assoc.*, **2**, 75 (1965).

Table I

Positional[a] and Thermal Parameters for $Ni(TAAB)I_2 \cdot H_2O$

	x	*y*	*z*	*B*, Å^2
I(1)	5000[b]	598 (2)	2500[b]	. . .
I(2)	5000[b]	6850 (2)	2500[b]	. . .
Ni	5000[b]	2409 (3)	2500[b]	. . .
O	500[b]	378 (2)	250[b]	4.6 (6)
N(1)[d]	487 (2)	231 (1)	403 (2)	2.3 (5)
N(9)[d]	346 (2)	255 (1)	236 (1)	2.1 (5)
DN(1)[d]	362 (3)	235 (3)	303 (3)	1.7 (9)
DN(9)[d]	447 (4)	252 (4)	102 (4)	2.6 (1.1)
C(2)	409 (1)	188 (1)	409 (1)	3.1 (4)
C(3)	412 (2)	143 (2)	531 (2)	4.1 (6)
C(4)	328 (2)	100 (2)	567 (2)	4.8 (7)
C(5)	238 (2)	102 (2)	515 (2)	4.6 (7)
C(6)	235 (2)	149 (2)	430 (2)	5.4 (7)
C(7)	320 (1)	186 (1)	392 (1)	2.8 (4)
C(8)	285 (2)	236 (2)	289 (2)	4.8 (6)
C(10)	303 (1)	306 (2)	160 (1)	3.3 (5)
C(11)	221 (2)	350 (2)	163 (2)	4.1 (6)
C(12)	185 (2)	400 (2)	77 (2)	5.4 (8)
C(13)	235 (2)	393 (2)	−7 (2)	4.3 (6)
C(14)	318 (2)	349 (2)	16 (2)	4.9 (7)
C(15)	361 (2)	302 (2)	70 (1)	4.0 (5)
C(16)	460 (2)	254 (2)	30 (2)	4.4 (6)

Anisotropic Temperature Factors[c] (×10^4)

	β_{11}	β_{22}	β_{33}	β_{12}[b]	β_{13}	β_{23}[b]
I(1)	93 (2)	27 (1)	46 (1)	0	56 (1)	0
I(2)	43 (1)	53 (1)	35 (1)	0	47 (1)	0
Ni	27 (2)	20 (2)	17 (2)	0	55 (1)	0

Root-Mean-Square Displacements (Å) of Thermal Ellipsoids Along Principal Axes

	1	2	3
Ni	0.116 (9)	0.164 (11)	0.166 (7)
I(1)	0.191 (6)	0.206 (4)	0.294 (4)
I(2)	0.176 (4)	0.203 (4)	0.264 (4)

[a] Multiplied by 10^4 for I and Ni and by 10^3 for the rest of the table. The numbers in parentheses, which correspond to the least significant digits of the parameters, are the standard deviations from the least-squares refinement. This convention will be used throughout the paper. [b] Fixed by twofold axis. [c] Anisotropic temperature factors, in the form of exp $\{(-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$. [d] Occupancy of N compared to DN is in the ratio of 2:1.

computer program which automates the symbolic addition method). Approximately 70% of the atoms were located in the *E* map and these atoms were used to calculate phases for a three-dimensional Fourier synthesis. The remaining atoms in the molecule were then located, and their positions were refined using block-diagonal least-squares methods. Again a difference Fourier was calculated which indicated essentially the same disordered appearance of the averaged structure as in the case of $Ni(TAAB)I_2 \cdot H_2O$.

Refinement of both structures was then begun by assuming that the pseudomirror planes passing through opposite benzene rings generated the nitrogen positions which appeared on the difference map. Positions for the bridging carbon atoms were obtained by using bond lengths $C_{benzene}—C$ = 1.48 Å and C=N = 1.27 Å, which were found in the chemically analogous structure of TRI.[5] These atoms were put into the refinement with an occupancy of 0.5 and this was then modified on

Table II

Positional[a] and Thermal Parameters for $Ni(TAAB)(BF_4)_2$

	x	*y*	*z*	*B*, Å^2
Ni	3528 (3)	1637 (2)	1315 (2)	. . .
F(1)	668 (1)	469 (1)	361	5.4 (3)
F(2)	540 (1)	348 (1)	283 (1)	8.8 (5)
F(3)	714 (2)	321 (1)	411 (1)	10.8 (6)
F(4)	522 (1)	392 (1)	385 (1)	8.0 (4)
B(1)	612 (2)	382 (1)	363 (1)	3.0 (5)
F(5)	3 (1)	181 (1)	370 (1)	9.3 (5)
F(6)	101 (2)	117 (1)	311 (1)	9.7 (5)
F(7)	217 (2)	164 (1)	438 (1)	14.0 (9)
F(8)	147 (2)	262 (1)	349 (1)	11.0 (6)
B(2)	112 (2)	179 (1)	363 (1)	2.7 (5)
N(1)[b]	545 (2)	167 (1)	188 (1)	2.8 (5)
N(9)[b]	360 (2)	167 (1)	231 (1)	2.6 (5)
N(17)[b]	162 (2)	202 (1)	74 (1)	2.7 (5)
N(25)[b]	334 (2)	132 (1)	32 (1)	2.5 (5)
C(2)[b]	627 (2)	124 (2)	258 (1)	3.0 (6)
C(3)	565 (2)	81 (1)	301 (1)	3.6 (5)
C(4)	663 (3)	19 (2)	359 (1)	6.7 (7)
C(5)	628 (2)	−23 (1)	409 (1)	4.8 (5)
C(6)	510 (2)	−8 (1)	404 (1)	4.2 (5)
C(7)	409 (2)	51 (2)	344 (1)	5.5 (6)
C(8)	443 (2)	100 (1)	294 (1)	3.1 (4)
C(10)[b]	293 (3)	227 (2)	247 (1)	2.5 (6)
C(11)	190 (2)	295 (1)	181 (1)	3.3 (4)
C(12)	163 (2)	369 (1)	215 (1)	4.7 (5)
C(13)	66 (2)	439 (1)	164 (1)	3.2 (4)
C(14)	3 (2)	430 (1)	82 (1)	2.8 (4)
C(15)	23 (2)	352 (1)	47 (1)	3.6 (5)
C(16)	124 (2)	282 (1)	99 (1)	3.6 (5)
C(18)	70 (2)	159 (2)	8 (1)	3.1 (6)
C(19)	104 (2)	87 (1)	33 (1)	4.1 (5)
C(20)	−8 (2)	35 (2)	−91 (1)	4.0 (5)
C(21)	2 (2)	35 (1)	139 (1)	4.5 (5)
C(22)	133 (2)	54 (2)	127 (1)	5.6 (6)
C(23)	242 (2)	6 (1)	73 (1)	4.9 (6)
C(24)	230 (2)	70 (1)	271 (1)	3.7 (5)
C(26)[b]	428 (2)	162 (2)	14 (1)	3.0 (6)
C(27)	548 (2)	216 (1)	77 (1)	3.0 (4)
C(28)	608 (2)	267 (1)	40 (1)	4.9 (6)
C(29)	724 (2)	317 (1)	82 (1)	5.2 (6)
C(30)	787 (2)	326 (2)	166 (1)	5.9 (6)
C(31)	736 (2)	279 (1)	205 (1)	4.8 (6)
C(32)	613 (2)	218 (1)	157 (1)	3.9 (5)
DN(1)[b]	273 (5)	202 (4)	190 (3)	2.8 (1.2)
DN(9)[b]	518 (5)	149 (4)	221 (3)	3.1 (1.1)
DN(17)[b]	422 (5)	154 (4)	63 (3)	3.3 (1.1)
DN(25)[b]	172 (5)	154 (4)	29 (3)	3.4 (1.1)
DC(2)[b]	314 (6)	170 (5)	263 (3)	2.9 (1.4)
DC(10)	635 (6)	178 (5)	239 (4)	3.5 (1.4)
DC(18)[b]	385 (6)	105 (5)	3 (4)	3.1 (1.4)
DC(26)[b]	597 (6)	195 (5)	3 (4)	3.2 (1.5)

Nickel Anisotropic Temperature Factors[c] (×10^5)

β_{11} = 717 (28), β_{22} = 513 (17), β_{33} = 272 (11), β_{12} = 43 (25), β_{13} = 242 (15), β_{23} = 24 (15)

Root-Mean-Square Displacements (Å) of Thermal Ellipsoids Along Principal Axes

1	2	3
0.182 (9)	0.192 (7)	0.223 (9)

[a] Multiplied by 10^3 except for N(1) which is multiplied by 10^4. [b] Those atoms prefixed by "D" have an occupancy of 0.3; those atoms with corresponding unprefixed labels have an occupancy of 0.7. [c] Anisotropic temperature factor in the form of exp $\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{.3}kl)\}$.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES FOR Ni(TAAB)$I_2 \cdot H_2O$

H	L	FOBS	FCAL
****K = 0****			
0	2	4886	4188
0	4	7999	7353
0	6	7259	6106
0	8	4897	4490
0	10	3759	3723
0	12	3016	3262
0	14	2181	2265
0	16	1299	1535
0	18	674	1137
0	20	908	927
-2	0	4149	4165
2	2	6890	6961
-2	2	7684	7001
2	4	6359	6411
-2	4	5577	5720
2	6	6257	5891
-2	6	6924	6395
2	8	5039	4802
-2	8	4430	4512
2	10	3637	3785
-2	10	3563	3807
2	12	1790	2179
-2	12	2710	2802
2	14	2347	2263
-2	14	2521	2699
-2	16	1209	1544
2	16	1467	1485
2	18	677	1149
-2	18	1353	1374
2	20	717	836
-4	0	6967	7136
4	2	4859	5413
-4	2	6467	6332
4	4	5527	5823
-4	4	5889	5743
4	6	4277	4178
-4	6	4705	4512
4	8	4404	4472
-4	8	4669	4617
4	10	2475	2484
-4	10	3337	3547
4	12	3347	3321
-4	12	2028	2358
-4	14	2007	2079
4	14	1937	1841
4	16	1196	1367
-4	16	1046	1331
4	18	910	1076
-4	18	747	1025
4	20	868	812
-4	20	761	801
-6	0	5613	5691
-6	2	5566	5609
6	2	5457	6090
6	4	3740	4082
-6	4	4150	4202
6	6	4800	4942
-6	6	5338	5117
6	8	3927	3904
-6	8	3347	3298
6	10	2561	2632
-6	10	2561	2808
6	12	2271	2414
-6	12	2374	2493
6	14	1798	1811
-6	14	1424	1735
6	16	1097	1236
-6	16	904	1343
6	18	927	983
-6	20	871	739
-8	0	3687	3906
8	2	3360	3866
-8	2	4247	4432
8	4	3754	4026
-8	4	4125	4198
-8	6	3934	3885
8	6	2775	2839
8	8	2446	2759
-8	8	2803	2898
8	10	2128	2132
-8	10	2217	2351
8	12	1639	1580
-8	12	2170	2275
8	14	1340	1277
-8	14	1265	1379
8	16	1007	1058
-8	16	1197	1314
8	18	747	798
-8	18	807	963
-8	20	714	629
-10	0	2879	3137
10	2	2964	3102
-10	2	2978	3126
10	4	2820	2940
-10	4	2157	2081
-10	6	2605	2465
10	6	2046	2416
-10	8	2154	2151
10	8	2067	1962
10	10	1687	1781
-10	10	1927	2000
10	12	1427	1362
-10	12	1327	1464
10	14	1037	1197
-10	14	1105	1200
-10	16	740	829
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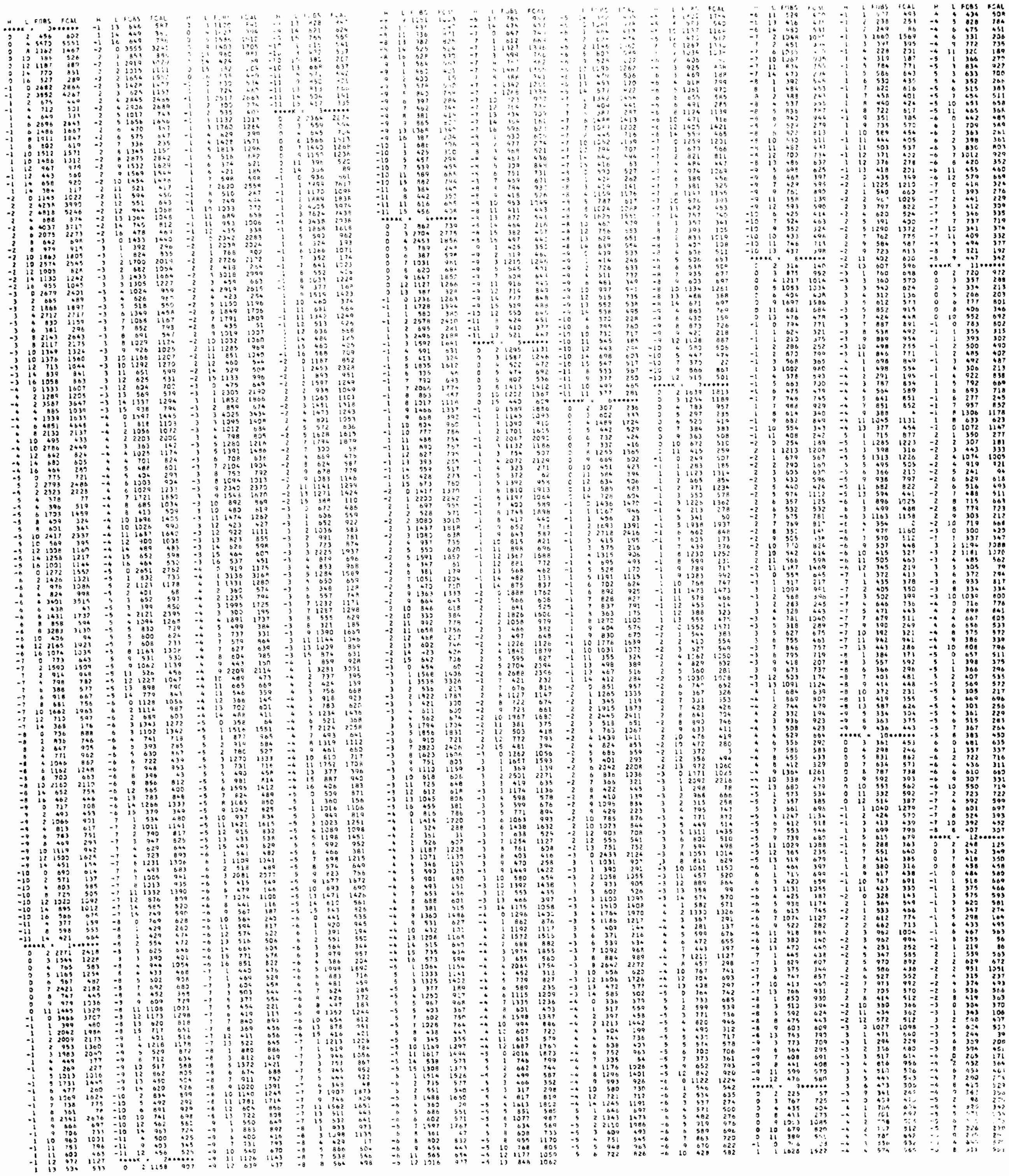
8	9	1467	1495
-8	9	1699	1369
8	11	983	915
-8	11	1172	1087
8	13	938	765
-8	13	1016	1032
10	1	1819	1987
-10	1	1447	1347
10	3	1036	1034
-10	3	1330	1423
10	5	1815	1811
-10	5	1516	1505
10	7	1432	1181
-10	7	1513	1303
10	9	1149	867
-10	9	904	1005
10	11	954	676
-10	11	1183	918
12	1	885	1076
-12	1	1325	1267
12	3	769	915
12	5	982	828
-12	5	1359	1312
12	7	785	770
-12	7	865	848
12	9	870	686
-12	9	987	798
14	1	793	803
-14	1	860	690
14	3	827	722
-14	3	889	946
14	5	842	584
-14	5	946	623
-14	6	900	179
****K = 7****			
1	2	2166	2284
1	3	3040	2829
-1	3	2425	2074
1	4	1376	1499
-1	4	1970	1700
1	5	2340	2341
-1	5	1195	1340
1	6	2138	2011
-1	6	1526	1464
1	7	1862	1673
-1	7	1757	1756
1	8	1485	1274
-1	8	1253	1210
1	9	1308	1188
-1	9	1798	1776
1	10	1116	981
-1	10	771	548
1	11	916	824
-1	11	891	881
1	13	1031	1154
-1	13	1036	1035
-1	14	925	519
-3	0	1734	1814
3	1	1912	1946
-3	1	2702	2748
3	2	2480	2666
-3	2	1381	1360
3	4	524	694
-3	4	1600	1778
3	5	1456	1522
-3	5	2108	2169
3	6	1963	1744
-3	6	1277	1118
3	7	1846	1679
-3	7	1661	1647
3	8	1169	867
-3	8	1172	1322
3	9	1427	1184
-3	9	436	924
3	10	848	764
-3	10	1123	1134
3	11	871	965
-3	11	1316	1390
3	13	965	1027
-5	0	2046	2011
5	1	1270	1376
-5	1	2271	2346
5	2	734	533
-5	2	1177	1258
5	3	2215	2325
-5	3	1563	1517
-5	4	1599	1532
5	4	1713	1569
5	5	1895	1998
-5	5	1788	2046
5	6	1354	1412
-5	6	1539	1587
5	7	1408	1201
-5	7	1166	1247
5	8	1027	989
-5	8	958	1043
5	9	1739	1614
-5	9	766	1085
5	11	887	965
-5	11	979	840
5	13	877	860
-7	0	1452	1281
7	1	1445	1738
-7	1	1555	1859
7	2	1391	1429
-7	2	1012	835
7	3	1533	1647
-7	3	1676	1771
7	4	928	793
-7	4	790	863
7	5	1426	1539
-7	5	1104	1311
7	6	790	425
-7	6	940	646
7	7	1058	1373
-7	7	1078	1393
-7	8	1063	776
7	8	833	759
7	9	1082	897
-7	9	1335	1405
-7	10	868	530
7	11	1002	1055
-7	11	1012	988
-7	12	823	560
7	13	1127	891
9	1	1743	1713
-9	1	737	1347
-9	2	834	922
9	3	1298	1080
-9	3	923	1157
-9	4	925	645
9	5	939	920
-9	5	1451	1524
-9	6	950	951
9	7	1347	1359
-9	7	1052	920
9	10	734	280
-11	1	915	777
11	3	1356	1538
-11	3	1334	1128
-11	5	947	851
-11	6	891	473
11	7	767	1040
11	9	884	883
13	1	857	1028
-13	1	1244	1209
13	2	739	367
13	3	948	861
-13	3	957	1011
13	7	787	773
-13	7	1356	908
****K = 8****			
0	3	584	696
0	4	1361	1360
0	5	989	662
0	6	1975	2099
0	8	1328	1376
0	10	1493	1555
2	0	2069	2486
2	2	2509	2615
-2	3	1696	1421
2	4	2489	2295
-2	4	3551	3342
2	5	777	422
2	6	1825	1872
-2	6	1549	1769
2	7	694	442
2	8	1475	1455
-2	8	1446	1534
2	10	1661	1545
-2	10	980	1023
2	12	917	847
-2	12	1227	1033
-4	0	1240	1439
4	1	510	314
4	2	3231	3142
-4	2	2417	2434
4	3	767	429
4	4	2027	1862
-4	4	2267	2105
4	6	1750	1953
-4	6	1236	1241
4	8	1054	977
-4	8	2067	2038
-4	10	997	1320
4	10	1217	1050
4	12	808	749
-6	0	1736	1862
6	2	1333	1473
-6	2	1507	1521
6	3	818	515
6	4	797	862
-6	4	1760	1850
6	5	746	199
6	6	867	980
-6	6	1318	1228
6	8	1469	1222
-6	8	1114	1279
-6	10	717	928
6	10	821	622
-8	0	1175	1057
-8	2	1200	1145
8	2	1174	1149
8	4	1481	1546
-8	5	668	15
8	6	1286	961
-8	6	1457	1339
8	9	797	690
8	10	945	745
-8	10	1200	751
8	11	781	58
-8	11	821	39
-10	0	1258	1274
10	2	775	550
-10	2	1147	1226
-10	4	917	896
10	4	1057	897
10	6	829	517
-10	6	951	787
-10	8	1001	945
10	9	828	77
10	10	798	476
-10	10	1130	699
-12	0	916	604
12	1	767	44
12	2	787	550
12	4	807	331
-12	4	847	641
****K = 9****			
1	2	957	862
-1	2	467	518
1	3	2291	2278
-1	3	2021	1920
-1	4	871	1025
1	5	1397	1641
-1	5	1670	1512
1	6	810	239
1	7	1939	1967
-1	7	1770	1498
-1	9	1461	1358
-1	11	1056	972
1	13	1058	970
1	14	1098	102
-3	0	780	813
3	1	1887	1848
-3	1	2291	2126
3	3	1057	908
-3	3	826	945
3	5	1586	1449
-3	5	1145	1287
3	7	1156	999
-3	7	1633	1452
3	9	1148	1315
-3	9	998	1211
3	10	891	114
3	11	946	781
-3	12	837	45
-3	13	1190	972
-5	1	1471	1699
5	1	1341	1462
-5	2	747	675
5	2	818	737
-5	3	1015	1404
5	3	1223	1392
-5	5	2031	2092
5	5	2155	2055
-5	7	1117	1138
5	7	1361	1285
-5	9	1244	806
5	9	1284	1261
5	11	833	933
-5	11	989	811
7	1	1053	1402
-7	1	2065	2082
-7	3	1158	1111
7	3	1648	1604
7	5	1359	1307
-7	5	1328	1263
-7	7	1129	989
7	9	894	922
-7	9	1074	1378
-7	11	1320	872
9	1	1148	1170
9	3	1210	1182
-9	3	1106	1307
9	5	803	677
-9	5	1245	1164
9	7	1240	1266
-9	7	865	889
9	9	1111	736
9	10	877	43
11	3	1364	1089
-11	3	784	802
-11	7	983	813
13	1	1058	739
13	3	1212	897
-13	3	719	831
13	5	708	574
-13	5	925	615
****K = 10****			
0	3	1265	1431
0	4	1646	1633
0	5	1888	1667
0	6	821	1006
0	7	1279	1143
0	8	1069	1098
0	9	943	1220
0	11	905	737
-2	0	1657	1814
2	1	1657	1512
2	2	787	648
-2	2	537	549
2	3	1540	1695
-2	3	1724	1930
2	4	1585	1516
-2	4	1110	934
2	5	1213	1209
-2	5	1643	1727
2	6	928	967
-2	6	993	1031
2	7	892	767
-2	7	885	941
2	8	966	1033
-2	8	1408	1159
2	9	948	707
-2	9	906	1146
-2	11	974	767
2	12	1033	708
2	13	705	391
-2	13	1057	447
-4	0	1301	1400
4	1	861	1044
-4	1	1608	1502
4	2	834	565
-4	2	1500	1454
4	3	1569	1501
-4	3	1619	1573
4	5	1229	1234
-4	5	1031	943
4	6	948	757
-4	6	1602	1695
4	7	1165	1038
-4	9	810	953
-4	10	843	775
4	11	1019	707
-6	0	808	808
6	1	1186	1118
-6	1	1192	1197
6	2	850	879
-6	2	745	765
6	3	1128	1147
-6	3	1259	1279
6	4	1821	1858
-6	4	1019	927
6	5	942	911
-6	5	1038	922
-6	6	732	527
6	7	827	921
-6	7	1065	1177
6	8	804	784
-6	8	1068	1117
6	11	834	407
6	12	911	528
-8	1	1083	941
8	2	941	757
-8	2	1162	947
8	3	1236	1062
-8	3	1132	1042
8	5	775	661
-8	5	944	768
8	6	909	926
-8	6	755	628
8	7	875	461
-8	7	1090	632
-10	3	1001	710
10	4	765	603
10	9	870	251
-10	9	949	511
-12	2	868	443
12	3	878	473
12	5	888	397
****K = 11****			
1	2	2330	2384
1	3	2153	2212
-1	3	1913	2063
1	4	2309	2384
-1	4	1550	1838
1	5	1604	1876
-1	5	1800	1986
1	6	2071	2069
-1	6	1615	1670
1	7	1650	1915
-1	7	1716	1637
1	8	1836	1736
-1	9	1791	1676
1	9	994	1231
-1	9	1343	1450
1	10	983	1262
-1	10	1099	1269
-1	11	1091	1101
1	12	1132	1133
-1	12	1142	1120
-3	0	2496	2594
3	1	1608	1854
-3	1	2093	2177
3	2	1445	1697
-3	2	1765	2039
3	3	1404	1434
-3	3	1374	1412
3	4	2036	2134
-3	4	1741	1713
3	5	1614	1612
-3	5	1241	1596
3	6	1766	1715
-3	6	2654	2647
3	7	1281	1214
-3	7	1383	1433
3	8	1948	1476
-3	8	1533	1555
3	9	1393	1230
-3	9	1333	1410
3	10	1249	1106
-3	10	1050	1244
3	12	1016	1236
-3	12	1277	1197
-5	0	2028	[illegible]
5	1	1351	[illegible]
-5	1	1630	1778
5	2	2326	2433
-5	2	1931	[illegible]
5	3	1399	[illegible]
-5	3	1647	1630
5	4	1415	[illegible]
-5	4	1400	[illegible]
5	5	1764	[illegible]
-5	5	1692	1775
5	6	1418	1416
-5	6	1770	1651
5	7	1474	1396
-5	7	1427	1359
5	8	1257	1316
-5	8	1254	1334
5	9	807	1174
-5	9	812	[illegible]
5	10	1148	1234
-5	10	1346	1231
5	11	1158	927
5	12	1149	[illegible]
-7	0	1693	[illegible]
7	1	1299	[illegible]
-7	1	1671	[illegible]
7	2	1290	1305
-7	2	1298	1326
7	3	1374	[illegible]
-7	3	1250	1199
7	4	1072	1241
-7	4	1485	[illegible]
-7	5	1188	[illegible]
7	6	2009	[illegible]
-7	6	2598	[illegible]
7	7	1055	910
-7	7	985	1274
7	8	1419	1047
-7	8	1297	1193
-7	9	1330	1267
7	10	1059	[illegible]
-7	10	995	[illegible]
7	11	1280	[illegible]
-7	11	998	926
-9	0	1767	1676
9	1	1169	954
-9	1	1285	854
9	2	1529	[illegible]
9	3	1095	[illegible]
-9	3	783	1204
-9	4	1237	1311
-9	5	1105	954
9	6	1008	1244
-9	6	1130	1087
9	7	836	925
-9	8	1200	1090
11	1	361	756
11	2	1327	1002
-11	2	1100	[illegible]
11	4	866	924
-11	4	1326	[illegible]
-11	5	1012	[illegible]
****K = 12****			
0	3	605	720
0	5	1002	[illegible]
2	1	743	[illegible]
-2	1	823	814
2	2	493	330
2	3	916	909
-2	3	1195	1157
2	4	713	314
2	5	847	780
2	7	952	709
-2	7	1245	1074
-2	8	801	412
2	9	1057	707
4	1	1070	1032
4	3	574	842
-4	5	1093	1150
6	1	710	879
6	3	749	117
-6	4	752	296
6	5	818	687
-6	5	315	643
-6	7	833	60
6	8	862	411
-6	11	893	350
-9	1	774	437
-9	5	713	457
-8	8	952	247
-10	5	938	117
12	4	847	276

the basis of maintaining equal temperature factors of these atoms for both orientations of the molecule. During the refinement of Ni(TAAB)$I_2 \cdot H_2O$ it was found that both DC(8) and DC(16) tended to move toward C(8) and C(16) and could not be resolved as distinct positions (they had originally been placed less than 0.5 Å apart). In the case of Ni(TAAB)$(BF_4)_2$ the bridging carbon atoms remained fairly well resolved (being 0.8–1.2 Å apart, except for DC(26) and C(18) which are 0.5 Å apart). This refinement procedure yielded occupancies of 0.3 for the atoms prefixed by "D" and 0.7 for the corresponding unprefixed atoms in the Ni(TAAB)$(BF_4)_2$ structure. The corresponding values in the Ni(TAAB)$I_2 \cdot H_2O$ structure are 0.33 and 0.6, where the estimated accuracy of the procedure is about 10%.

The final refinement of both structures included anisotropic temperature parameters for the heavy atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where for Ni(TAAB)$I_2 \cdot H_2O$ the weights were defined as $1/\sqrt{w} = 3$ for $|F_o| \leq 13$, $1/\sqrt{w} = |F_o|/40$ for $|F_o| > 40$, and $1/\sqrt{w} = 1$ otherwise. The scale factor applied to the F_o values in this procedure was 4.33, while for Ni(TAAB)$(BF_4)_2$ the weights were defined as $1/\sqrt{w} = 2$ for $|F_o| \leq 16$, $1/\sqrt{w} = |F_o|/60$ for $|F_o| > 60$, and $1/\sqrt{w} = 1$ otherwise. The corresponding scale was 1.03. The weighting schemes were shown to be satisfactory by the relative independence of $w\{|F_o| - |F_c|\}$ on F_o as demonstrated by appropriate plots of the quantities. In the case of Ni(TAAB)$I_2 \cdot H_2O$, full-matrix least-squares refinement yielded R factors of $R = 0.109$ and $wR = 0.115$ where $R = \Sigma||F_o| - |F_c||/$

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES FOR Ni(TAAB)$(BF_4)_2$



$\Sigma|F_o|$ and $wR = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$. The refinement of the Ni(TAAB)$(BF_4)_2$ was carried out by block-diagonal least-squares methods (using half the calculated shifts) and yielded R factors of $R = 0.141$ and $wR = 0.163$. Throughout the refinement scattering factors used were those of the neutral atoms[15] and no corrections were applied for anomalous dispersion effects. A final difference Fourier map calculated for Ni(TAAB)$I_2 \cdot H_2O$ showed residual density about the iodine atoms of ~ 2 $e^-/Å^3$ and none greater than 1 $e^-/Å^3$ elsewhere. No hydrogen atoms could be located reliably. The corresponding difference Fourier map for Ni(TAAB)$(BF_4)_2$ was substantially clearer but again hydrogen atoms could not be consistently located.

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(15) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1965, Table 3.3.1.A.

TABLE V

BOND DISTANCES (Å) FOR $Ni(TAAB)I_2 \cdot H_2O$[a]

Ni–N(1)	2.09 (3)	Ni–DN(1)	2.00 (5)
Ni–N(9)	2.09 (3)	Ni–DN(9)	2.10 (6)
N(1)–C(2)	1.41 (4)	DN(1)–C(7)	1.55 (6)
N(9)–C(10)	1.42 (4)	DN(9)–C(15)	1.47 (7)
N(1)–C(16)′	1.18 (4)[b]	DN(1)–C(8)	1.06 (5)[b]
N(9)–C(8)	1.14 (4)[b]	DN(9)–C(16)	1.01 (6)[b]
C(15)–C(16)	1.64 (4)[b]	C(2)–C(16)′	2.07 (4)[b]
C(7)–C(8)	1.67 (4)[b]	C(8)–C(10)	2.09 (4)[b]
Ni–O	2.20 (3)	Ni–I(1)	2.903 (7)
C(2)–C(3)	1.32 (4)	C(10)–C(11)	1.32 (4)
C(2)–C(7)	1.41 (3)	C(10)–C(15)	1.45 (3)
C(3)–C(4)	1.43 (4)	C(11)–C(12)	1.47 (4)
C(4)–C(5)	1.40 (4)	C(12)–C(13)	1.35 (4)
C(5)–C(6)	1.38 (4)	C(13)–C(14)	1.33 (4)
C(6)–C(7)	1.39 (4)	C(14)–C(15)	1.50 (4)

[a] Primed atoms are related by twofold rotation. [b] Values are unreliable owing to unresolved atoms (C(8), DC(16) and C(16), DC(8)). Those distances associated with atoms prefixed by "D" are also less reliable.

TABLE VI

BOND DISTANCES (Å) FOR $Ni(TAAB)(BF_4)_2$[a]

Ni–N(1)	1.87	Ni–DN(1)	1.90
Ni–N(9)	1.89	Ni–DN(9)	1.95
Ni–N(17)	1.92	Ni–DN(17)	1.91
Ni–N(25)	1.91	Ni–DN(25)	1.77
N(1)–C(2)	1.41	DN(1)–C(23)	1.55
N(9)–C(10)	1.42	DN(9)–C(15)	1.38
N(17)–C(18)	1.37	DN(17)–C(7)	1.57
N(25)–C(26)	1.42	DN(25)–C(31)	1.64
N(1)–C(32)	1.32	DN(1)–DC(32)	1.32
N(9)–C(8)	1.37	DN(9)–DC(8)	1.25
N(17)–C(16)	1.28	DN(17)–DC(16)	1.21
N(25)–C(24)	1.29	DN(25)–DC(24)	1.26
C(7)–C(8)	1.46	C(18)–DC(8)	1.99
C(15)–C(16)	1.47	C(10)–DC(16)	1.62
C(23)–C(24)	1.51	C(2)–DC(24)	1.57
C(31)–C(32)	1.49	C(26)–DC(32)	1.59
C(2)–C(3)	1.47	C(18)–C(19)	1.42
C(3)–C(4)	1.36	C(19)–C(20)	1.40
C(4)–C(5)	1.40	C(20)–C(21)	1.36
C(5)–C(6)	1.32	C(21)–C(22)	1.40
C(6)–C(7)	1.44	C(22)–C(23)	1.34
C(7)–C(2)	1.32	C(23)–C(18)	1.37
C(10)–C(11)	1.32	C(26)–C(27)	1.40
C(11)–C(12)	1.39	C(27)–C(28)	1.39
C(12)–C(13)	1.42	C(28)–C(29)	1.34
C(13)–C(14)	1.41	C(29)–C(30)	1.39
C(14)–C(15)	1.38	C(30)–C(31)	1.38
C(15)–C(10)	1.41	C(31)–C(26)	1.36
B(1)–F(1)	1.36	B(2)–F(5)	1.33
B(2)–F(2)	1.40	B(2)–F(6)	1.28
B(1)–F(3)	1.34	B(2)–F(7)	1.31
B(1)–F(4)	1.32	B(2)–F(8)	1.29
B(1)–F(4)	1.32	B(2)–F(8)	1.29
Ni–F(1)[b]	2.70		

[a] Distances associated with atoms prefixed by "D" are less reliable. Estimated deviations are given in Table IX. They were not calculated from the least-squares procedure because of the lack of covariance terms in the block-diagonal method. [b] Atom at position $1 - x, -{}^1/_2 + y, {}^1/_2 - z$.

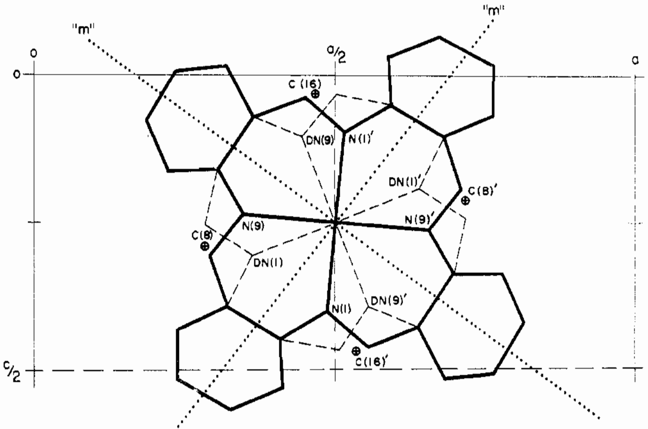

Figure 2.—Projection of the TAAB ligand down the [010] axis in $Ni(TAAB)I_2 \cdot H_2O$. The dotted lines show the pseudomirror planes by which one molecule goes into the other packing alternative. The crosses mark the actual refined positions of C(8) and C(16).

TABLE VII

BOND ANGLES (DEG) FOR $Ni(TAAB)I_2 \cdot H_2O$[a]

N(1)′–Ni–N(1)	171 (1)	DN(1)′–Ni–DN(1)	175 (3)
N(9)′–Ni–N(9)	166 (1)	DN(9)′–Ni–DN(9)	169 (3)
N(1)–Ni–N(9)	90 (1)	DN(1)–Ni–DN(9)	92 (2)
N(9)–Ni–N(1)′	90 (1)	DN(9)–Ni–DN(1)′	88 (2)
N(1)–Ni–O	94 (1)	DN(1)–Ni–O	92 (1)
N(9)–Ni–O	83 (1)	DN(9)–Ni–O	84 (1)
N(1)–Ni–I(1)	85 (1)	DN(1)–Ni–I(1)	87 (1)
N(9)–Ni–I(1)	96 (1)	DN(9)–Ni–I(1)	87 (1)
Ni–N(1)–C(16)′	131 (2)[b]	C(8)–DN(1)–Ni	148 (4)[b]
C(16)′–Ni(1)′–C(2)	106 (2)[b]	C(7)–DN(1)–C(8)	77 (3)[b]
C(2)–N(1)–Ni	122 (2)	Ni–DN(1)–C(7)	130 (3)
Ni–N(9)–C(8)	129 (2)[b]	C(16)–DN(9)–Ni	149 (5)[b]
C(8)–N(9)–C(10)	108 (2)[b]	C(15)–DN(9)–C(16)	80 (4)[b]
C(10)–N(9)–Ni	121 (1)	Ni–DN(9)–C(15)	126 (3)
C(7)–C(8)–N(9)	117 (2)[b]	C(10)–C(8)–DN(1)	91 (3)[b]
C(15)–C(16)–N(1)′	112 (2)[b]	C(2)′–C(16)–DN(9)	91 (4)[b]
C(7)–C(2)–N(1)	114 (2)	C(2)–C(7)–DN(1)	95 (2)
C(15)–N(10)–N(9)	111 (2)	C(10)–C(15)–DN(9)	101 (3)
C(2)–C(7)–C(8)	132 (2)	C(7)–C(2)–C(16)′	142 (2)[b]
C(10)–C(15)–C(16)	137 (2)[b]	C(15)–C(10)–C(8)	138 (2)[b]
C(3)–C(2)–N(1)	127 (2)	C(6)–C(7)–DN(1)	144 (2)
C(11)–C(10)–N(9)	127 (2)	C(14)–C(15)–DN(9)	143 (3)
C(6)–C(7)–C(8)	106 (2)[b]	C(3)–C(2)–C(16)′	98 (2)[b]
C(14)–C(15)–C(16)	106 (2)[b]	C(11)–C(10)–C(8)	98 (2)[b]
C(7)–C(2)–C(3)	117 (2)	C(15)–C(10)–C(11)	120 (2)
C(2)–C(3)–C(4)	122 (2)	C(10)–C(11)–C(12)	122 (2)
C(3)–C(4)–C(5)	120 (2)	C(11)–C(12)–C(13)	118 (3)
C(4)–C(5)–C(6)	116 (3)	C(12)–C(13)–C(14)	122 (3)
C(5)–C(6)–C(7)	122 (3)	C(13)–C(14)–C(15)	120 (2)
C(6)–C(7)–C(2)	120 (2)	C(14)–C(15)–C(10)	115 (7)

[a] Primed atoms are related by a twofold rotation. [b] Values are unreliable owing to unresolved atoms (C(8), DC(16) and C(16), DC(8)). Those angles associated with atoms prefixed by "D" are also less reliable.

The final positional and thermal parameters are given in Table I for $Ni(TAAB)I_2 \cdot H_2O$ and in Table II for $Ni(TAAB)(BF_4)_2$. The observed and calculated structure factor amplitudes for $Ni(TAAB)I_2 \cdot H_2O$ are given in Table III and are to be multiplied by 0.0623 to be placed on an absolute scale, while for $Ni(TAAB)(BF_4)_2$ they are given in Table IV with a corresponding scale of 0.0400.

Results and Discussion

In both structures the tetradentate TAAB ligand has approximately S_4 symmetry and presents a decidedly

Table VIII

Bond Angles (deg) for $Ni(TAAB)(BF_4)_2$[a]

N(1)–Ni–N(17)	162	DN(1)–Ni–DN(17)	167
N(9)–Ni–N(25)	168	DN(9)–Ni–DN(25)	169
N(1)–Ni–N(9)	92	DN(1)–Ni–DN(9)	92
N(9)–Ni–N(17)	90	DN(9)–Ni–DN(17)	83
N(17)–Ni–N(25)	89	DN(17)–Ni–DN(25)	92
N(25)–Ni–N(1)	90	DN(25)–Ni–DN(1)	92
Ni–N(1)–(C(32)	123	Ni–DN(1)–DC(32)	124
C(32)–N(1)–C(2)	114	C(23)–DN(1)–DC(32)	103
C(2)–N(1)–Ni	121	C(23)–DN(1)–Ni	129
Ni–N(9)–C(8)	122	Ni–DN(9)–DC(8)	132
C(8)–N(9)–C(10)	114	C(15)–DN(9)–DC(8)	88
C(10)–N(9)–Ni	123	C(15)–DN(9)–Ni	136
Ni–N(17)–C(16)	121	Ni–DN(17)–DC(16)	130
C(16)–N(17)–C(18)	118	C(7)–DN(17)–DC(16)	106
C(18)–N(17)–Ni	120	C(7)–DN(17)–Ni	122
Ni–N(25)–C(24)	124	Ni–DN(25)–DC(24)	131
C(24)–N(25)–C(26)	114	C(31)–DN(25)–DC(24)	100
C(26)–N(25)–Ni	120	C(31)–DN(25)–Ni	128
C(7)–C(8)–N(9)	117	C(18)–DC(8)–DN(9)	96
C(15)–C(16)–N(17)	122	C(10)–DC(16)–DN(17)	105
C(23)–C(24)–N(25)	119	C(2)–DC(24)–DN(25)	105
C(31)–C(32)–N(1)	118	C(26)–DC(32)–DN(1)	108
C(7)–C(2)–N(1)	114	C(18)–C(23)–DN(1)	86
C(15)–C(10)–N(9)	109	C(10)–C(15)–DN(9)	88
C(23)–C(18)–N(17)	116	C(2)–C(7)–DN(17)	95
C(31)–C(26)–N(25)	112	C(26)–C(31)–DN(25)	90
C(2)–C(7)–C(8)	132	C(23)–C(18)–DC(8)	150
C(10)–C(15)–C(16)	130	C(15)–C(10)–DC(16)	149
C(18)–C(23)–C(24)	127	C(7)–C(2)–DC(24)	151
C(26)–C(31)–C(32)	131	C(31)–C(26)–DC(32)	148
C(3)–C(2)–N(1)	125	C(22)–C(23)–DN(1)	149
C(11)–C(10)–N(9)	127	C(14)–C(15)–DN(9)	154
C(19)–C(18)–N(17)	125	C(6)–C(7)–DN(17)	145
C(27)–C(26)–N(25)	127	C(30)–C(31)–DN(25)	146
C(6)–C(7)–C(8)	108	C(19)–C(18)–DC(8)	89
C(14)–C(15)–C(16)	112	C(11)–C(10)–DC(16)	87
C(22)–C(23)–C(24)	109	C(3)–C(2)–DC(24)	88
C(30)–C(31)–C(32)	106	C(27)–C(26)–DC(32)	89
C(7)–C(2)–C(3)	120	C(23)–C(18)–C(19)	117
C(2)–C(3)–C(4)	118	C(18)–C(19)–C(20)	118
C(3)–C(4)–C(5)	121	C(19)–C(20)–C(21)	120
C(4)–C(5)–C(6)	118	C(20)–C(21)–C(22)	120
C(5)–C(6)–C(7)	122	C(21)–C(22)–C(23)	118
C(6)–C(7)–C(2)	118	C(22)–C(23)–C(18)	123
C(15)–C(10)–C(11)	122	C(31)–C(26)–C(27)	120
C(10)–C(11)–C(12)	122	C(26)–C(27)–C(28)	116
C(11)–C(12)–C(13)	116	C(27)–C(28)–C(29)	122
C(12)–C(13)–C(14)	119	C(28)–C(29)–C(30)	121
C(13)–C(14)–C(15)	121	C(29)–C(30)–C(31)	116
C(14)–C(15)–C(10)	116	C(30)–C(31)–C(26)	122
F(1)–B(1)–F(2)	105	F(5)–B(2)–F(6)	113
F(2)–B(1)–F(3)	109	F(6)–B(2)–F(7)	114
F(3)–B(1)–F(1)	108	F(7)–B(2)–F(5)	104
F(4)–B(1)–F(1)	112	F(8)–B(2)–F(5)	114
F(4)–B(1)–F(2)	107	F(8)–B(2)–F(6)	109
F(4)–B(1)–F(3)	113	F(8)–B(2)–F(7)	99
N(1)–Ni–F(1)[b]	96	N(9)–Ni–F(1)[b]	82
N(17)–Ni–F(1)[b]	101	N(25)–Ni–F(1)[b]	86

Ni–F(1)[b]–B(1)[b] 143.7

[a] Angles associated with atoms prefixed by "D" are less reliable. Estimated deviations are given in Table IX. [b] Atoms at position $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

Table IX

Average Bond Parameters for TAAB and TRI Ligands

Atoms	$Ni(TRI)(H_2O)_2(NO_3)_2$[a]	$Ni(TAAB)I_2 \cdot H_2O$[b]	$Ni(TAAB)(BF_4)_2$[b]
	Distances, Å		
Ni—N	2.03 (1)	2.09 (3)	1.90 (2)
N—$C_{benzene}$	1.44 (2)	1.42 (4)	1.41 (2)
C—$C_{benzene}$	1.48 (2)	1.65[c]	1.48 (2)
C=N	1.27 (2)	1.16[c]	1.32 (4)
$C_{benzene}$—$C_{benzene}$	1.40 (2)	1.40 (4)	1.38 (4)
	Angles, deg		
Ni—N=C	. . .	130[c]	123 (2)
N=C—$C_{benzene}$	123 (2)	115[c]	119 (2)
C—$C_{benzene}$—$C_{benzene}$	124 (2)	135[c]	130 (3)
$C_{benzene}$—$C_{benzene}$—N	118 (2)	113 (3)	113 (3)
$C_{benzene}$—N—Ni	. . .	122 (3)	121 (2)
C=N—$C_{benzene}$	119 (2)	107[c]	116 (2)
$C_{benzene}$—$C_{benzene}$—$C_{benzene}$	120 (2)	120 (4)	120 (2)

[a] Reference 5. [b] Present study; errors are given as rms deviations of the mean for chemically equivalent bonds in $Ni(TAAB)(BF_4)_2$. [c] These values are unreliable owing to unresolved atoms (see text).

saddle-shaped appearance (Figure 3). The nickel(II) ion has planar coordination in the structure of $Ni(TAAB)(BF_4)_2$ and tetragonal coordination in the structure of $Ni(TAAB)I_2 \cdot H_2O$ with an iodide ion and a water molecule occupying the axial positions. The numbering system used for the TAAB ligand is shown in Figure 4, and it should be noted that the second 16 atoms are related to the first 16 atoms in $Ni(TAAB)I_2 \cdot H_2O$ as required by the crystallographic point group symmetry C_2. Bond distances with estimated standard deviations for $Ni(TAAB)I_2 \cdot H_2O$ are given in Table V. Bond distances for $Ni(TAAB)(BF_4)_2$ are given in Table VI. Correspondingly the bond angles for the two compounds are presented in Tables VII and VIII. The estimated deviations of the values in Table VI may be found in Table IX where they have been derived as rms deviations of the mean for chemically equivalent bonds.

The averages of chemically equivalent bond distances and angles which are given in Table IX are compared with those found in $Ni(TRI)(H_2O)_2(NO_3)_2$.[5] In general, the distances are quite similar except for the angles involving the bridging carbon atom and benzene ring and the nitrogen atom and benzene ring. In TRI, the C–$C_{benzene}$–$C_{benzene}$ angle is 124° and the $C_{benzene}$–$C_{benzene}$–N angle is 118°, not greatly different from the expected angle of 120°. However, in the TAAB ligand the corresponding angles are 130 and 113° which may reflect the additional strain introduced into the tetradentate ligand over that in the tridentate ligand. It should be noted that the angles and distances in the $Ni(TAAB)I_2 \cdot H_2O$ molecule which involve the bridge carbon atom seem to be unreasonable (*cf.* C–$C_{benzene}$ = 1.65 Å). This is due to the fact that these atoms were not resolved from the atoms produced by the packing disorder (the two positions being less than 0.5 Å apart). However, those distances and angles not involving these atoms compare quite favorably with those found in $Ni(TAAB)(BF_4)_2$. Apparently atoms C(8) and C(16) have refined to positions which are the weighted averages of the positions in the two alternative molecules in the disordered structure. This is illustrated in

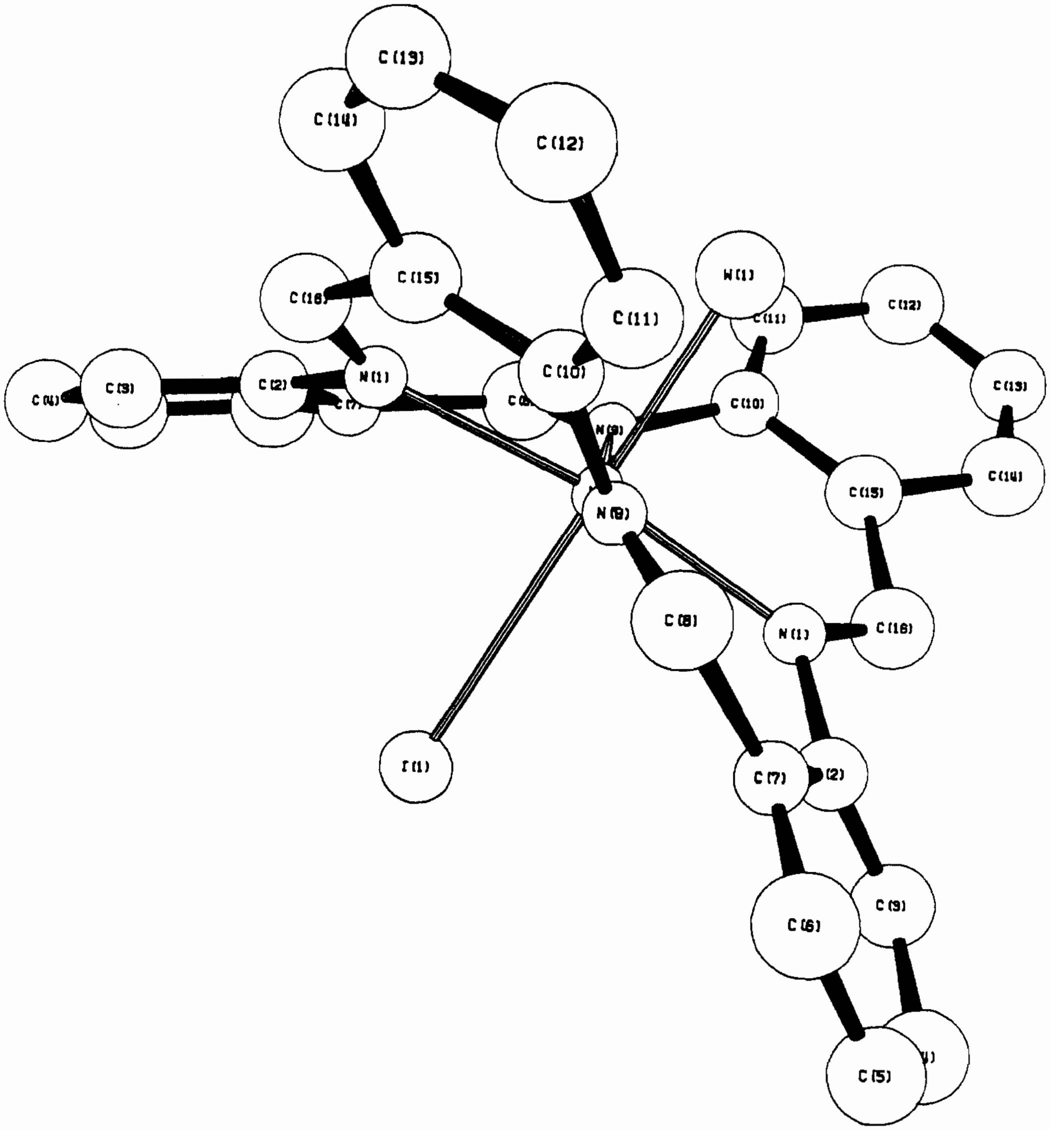

Figure 3.—A persepective view of the TAAB ligand in $Ni(TAAB)I_2 \cdot H_2O$.

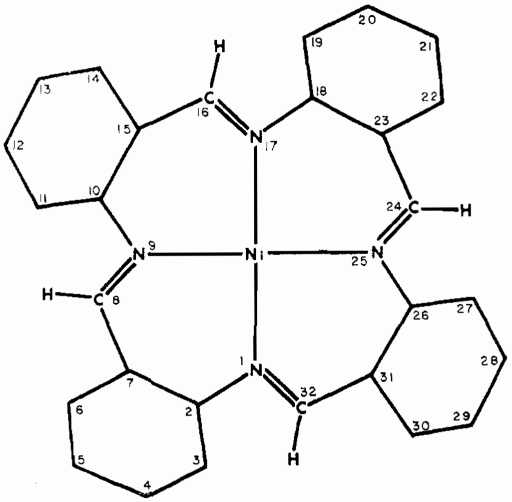

Figure 4.—The numbering system used for the TAAB ligand. The second 16 atoms are related to the first 16 atoms by a twofold rotation in $Ni(TAAB)I_2 \cdot H_2O$.

Figure 2 where the refined positions of C(8) and C(16) are indicated by crosses.

The nitrogen atoms in both molecules lie on a saddle-shaped surface with the nickel ion in the mean plane of the four nitrogen atoms to within the estimated error of the mean plane (~0.05 Å). In the case of $Ni(TAAB)I_2 \cdot H_2O$ the mean plane of the nitrogen atoms is perpendicular to the b axis with N(1) −0.20 Å and N(9) +0.20 Å out of the plane. For $Ni(TAAB)(BF_4)_2$ the mean plane of the nitrogen atoms is given by the equation $2.03x + 13.53y - 2.65z = 2.63$, referred to the crystal axes, with N(1) and N(17) +0.24 Å and N(9) and N(25) −0.24 Å out of the plane.

A point of particular interest is the correspondence of Ni–N bond lengths with the spin state of the nickel(II) ion. In the paramagnetic complex $Ni(TAAB)I_2 \cdot H_2O$ the Ni–N bond length is 2.09 ± 0.03 Å while in the diamagnetic complex $Ni(TAAB)(BF_4)_2$ the Ni–N bond length is 1.90 ± 0.02 Å. These distances are typical of those found in high- and low-spin nickel(II) complexes with four planar nitrogen donors.[16] This effect may be explained by the absence of electrons in the d orbitals which are antibonding with respect to the Ni–N interaction in the case of the diamagnetic nickel(II) complex as compared to their presence in the antibonding orbitals in the paramagnetic complexes. These antibonding electrons produce the lengthening of the Ni–N bond in the tetragonal (and octahedral) complexes which are paramagnetic as proposed by Cotton and Wise.[17]

All intermolecular contacts in the structure of Ni(TAAB)$I_2 \cdot H_2O$ appear to be quite normal with the closest carbon–carbon approaches of 3.4 Å. However, in the Ni(TAAB)$(BF_4)_2$ structure there is one contact which deserves special mention. This is the Ni–F(1) distance of 2.70 Å which seems to be rather short, although not so short as to be bonding. The next shortest nickel–fluorine distance is Ni–F(7) at 4.0 Å on the other side of the ligand plane. The fluorine ligand contacts are greater than 3.1 Å and seem to be normal, with the exception of DC(26)–F(5) at 2.9 Å which is probably due to the badly positioned atom DC(26).[18] The carbon–carbon contacts in Ni(TAAB)$(BF_4)_2$ are all greater than 3.4 Å. The BF_4^- anions are normal within the errors of the determination of Ni(TAAB)$(BF_4)_2$. The average B–F distance is 1.33 ± 0.04 Å and the average F–B–F angle is 109 ± 4°, where the errors are the rms deviations from the mean. The B–F distance seems short as compared to reported values of 1.40 and 1.43 Å,[19] but some of this discrepancy may be due to the large thermal motion of the BF_4^- anions; the data do not permit the analysis required for this correction.

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[16] F. Madaule-Aubry and G. M. Brown, *Acta Cryst.*, **B24**, 745, 754 (1968), and references contained therein.

[17] F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **5**, 1200 (1966).

[18] See the section on structure determination.

[19] "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958.

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The Crystal and Molecular Structures of Zinc and Cadmium O,O-Diisopropylphosphorodithioates

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The crystal and molecular structures of zinc O,O-diisopropylphosphorodithioate and isomorphous cadmium O,O-diisopropylphosphorodithioate have been solved by single-crystal X-ray diffraction techniques. Three-dimensional scintillation counter data were used to refine the structures by full-matrix least-squares procedures to final conventional R factors of 0.088 and 0.083, respectively (based on F). The crystals are monoclinic, space group C2/c (no. 15), with $a = 10.934 \pm 0.008$ Å, $b = 17.098 \pm 0.006$ Å, $c = 25.587 \pm 0.012$ Å, $\beta = 99.23 \pm 0.04°$, $d_{\text{obsd}} = 1.37 \pm 0.02$ g/cm^3, and $d_{\text{calcd}} = 1.384 \pm 0.002$ g/cm^3 for the zinc complex and $a = 10.964 \pm 0.006$ Å, $b = 16.906 \pm 0.008$ Å, $c = 26.490 \pm 0.008$ Å, $\beta = 99.91 \pm 0.02°$, $d_{\text{obsd}} = 1.46 \pm 0.02$ g/cm^3, and $d_{\text{calcd}} = 1.480 \pm 0.002$ g/cm^3 for the cadmium complex. Both complexes are binuclear. These dimers, four per unit cell of formula $M_2[(i\text{-}C_3H_7O)_2PS_2]_4$, where M = Zn or Cd, lie on the twofold axes of the unit cell. Each metal atom is coordinated with four sulfur atoms in a distorted tetrahedral environment. The metal–sulfur bonds range in length from 2.302 (6) to 2.409 (5) Å in the zinc complex and from 2.486 (7) to 2.590 (8) Å in the cadmium complex. The metal···metal approach within each dimer is 4.108 (5) and 4.059 (4) Å, respectively. Associated with each metal atom are two $(i\text{-}C_3H_7O)_2PS_2$ groups, one which functions as an *intrachelating* group bound wholly to one metal atom and the other which functions as a bridging, or *interchelating*, group linking two monomeric molecules together to form the dimer; the result is a molecule consisting of two four-membered rings joined to a central eight-membered ring through the metal atoms. The inter- and intrachelating groups deviate only slightly from planarity with the metal atoms and the central eight-membered ring possesses the "cradle" configuration. The phosphorus–sulfur bonds average 1.970 (11) and 1.965 (8) Å in length in the zinc and cadmium structures, respectively; the phosphorus–oxygen bonds average 1.58 (2) Å in length. The molecules pack in the crystals to form layers or sheets and, like the molecules within these sheets, are held together by van der Waals forces.

Introduction

Metal derivatives of O,O-dialkylphosphorodithioic acid[1] are important lubricating oil additives and, depending upon the metal atom and alkyl group, have good antioxidant and antiwear properties. One of these, the zinc derivative, is widely used as a lubricant additive to reduce wear under boundary or thin-film lubrication conditions; it is also known to be an oxidation and corrosion inhibitor.

Our present understanding of the metal O,O-dialkylphosphorodithioates has been advanced through a number of investigations, such as association studies, thermal decomposition studies, and infrared analyses.

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[1] The following names have been used interchangeably in the literature for the $-(RO)_2PS_2$ group: O,O-dialkylphosphorodithioate, O,O-dialkyldithiophosphato, and dialkyldithiophosphate.