

identical, with $g \approx 2.09$. The solution spectrum (CHCl₃) showed $g^* = 2.122$ and $A^* = 64$ G, while the spectrum in frozen chloroform solution had $g_{\parallel} = 2.214$ and $A_{\parallel} = 184$ G, with $g_{\perp} \approx 2.030$. No hyperfine A_{\perp} was observed, and a calculation shows that it would be only 4 G. The spectra of [Cu(2,3-cbpN)] are again similar.

Registry No. Cu(2,3-mmbpN)·2H₂O, 68876-55-1; Ni(2,3-mmbpN)·H₂O, 68876-56-2; Cu(2,3-cbpN), 68876-57-3; Ni(2,3-cbpN), 68876-58-4; Cu(2,3-mbpN), 68876-59-5; Ni(2,3-mbpN), 68876-60-8; Cu(3,4-cbpN), 68876-61-9; Ni(3,4-cbpN), 68876-62-0; Cu(3,3-cbpN), 56861-98-4; Ni(3,3-cbpN), 56861-99-5; Cu(3,3-mbpN), 56811-15-5; Ni(3,3-mbpN), 56811-16-6; Hmnbp, 26880-95-5.

Supplementary Material Available: Listings of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

References and Notes

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Synthesis and Structure of the Acetone Adduct of the Macrocyclic Complex (Tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine)nickel(II)

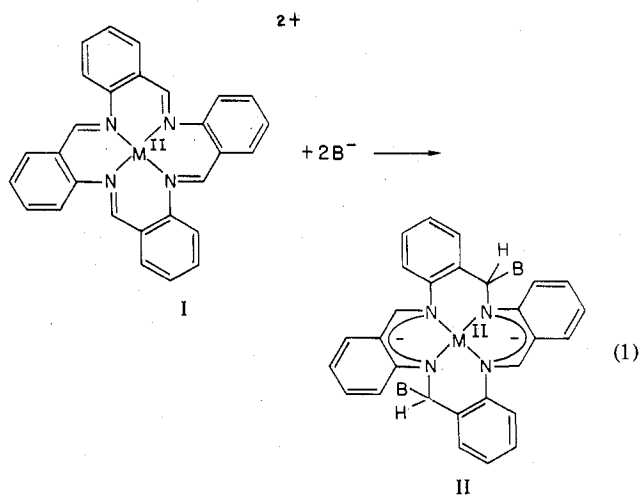
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New derivatives of the macrocyclic ligand TAAB, tetrabenzo[*b,f,j,n*][1,3,5,9]tetraazacyclohexadecine, have been prepared in which the substituents are bound by C-C linkages. They are produced by the displacement of diethylamide groups from the azomethine carbon atoms of TAAB with the enolate of acetone. The new compounds have the composition M^{II}-(TAAB)(CH₂COCH₃)₂. An X-ray structure determination (Ni²⁺ complex) shows the crystals to be triclinic, $\rho_0 = 1.37$ g cm⁻³ (floatation), $\rho_c = 1.363$ g cm⁻³, space group *P* $\bar{1}$, Mo K α , λ 0.7107 Å. The structure refined to $R = 0.061$ and $R_w = 0.081$. The two enolate groups have added to trans imine-carbon atoms but the substituents are on the same side of the approximate NiN₄ plane. The overall conformation of the macrocycle is saddle shaped and bond distances confirm the general electronic structures assigned to this class of nucleophilic ligand adducts of TAAB.

Introduction

The incorporation of substituent groups on macrocyclic ligands is of considerable interest because of the possibility of using such materials either as models for biological systems or as precursors for the development of such models.³ Examples are especially abundant in the area of porphyrin chemistry, e.g., the picket fence porphyrins,⁴ capped porphyrin,⁵ and strapped porphyrins.^{6,7} Earlier studies have shown that the nickel(II) and copper(II) complexes of the anhydrotetramer of *o*-aminobenzaldehyde⁸ will add nucleophiles to two of the azomethine groups, thereby forming neutral complexes,⁹⁻¹¹ structures I and II, eq 1. Alkoxides and amides have been found to react in this manner and the first examples of "strapped" macrocyclic complexes were the adducts of Cu(TAAB)²⁺ and Ni(TAAB)²⁺ with RN(CH₂CH₂O)₂, R = H, CH₃, and S(CH₂CH₂O)₂.^{10,11} The results presented here are significant in two general ways. First, examples of adducts are reported in which the substituent is attached to the ring through carbon-carbon bonds. This opens the possibility of producing acid-stable derivatives and should greatly extend the applicability of TAAB complexes to model systems. Secondly, an X-ray crystal structure determination on the bis(acetone) adduct of Ni(TAAB)²⁺ establishes the detailed structures of this class of compounds.



Experimental Section

Preparation of Ni(TAAB)(CH₂COCH₃)₂. This compound was prepared by the reaction of the diethylamine adduct Ni(TAAB)-(NEt₂)₂ with acetone. The latter was prepared by the method previously reported.¹¹ One gram of Ni(TAAB)(NEt₂)₂ was dissolved in 200 mL of acetone. A few milliliters of water was added and the

Table 1. Fractional Coordinates and Thermal Parameters ($\times 10^4$) for Ni(TAAB)(CH₂COCH₃)₂^a

atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ni	4492.7 (0.9)	2309.9 (0.6)	2960.3 (0.7)	445 (5)	351 (4)	297 (4)	24 (3)	202 (3)	87 (3)
N(1)	3600 (5)	2308 (4)	1163 (4)	550 (33)	402 (28)	336 (25)	3 (23)	243 (25)	120 (22)
N(2)	2812 (5)	1661 (4)	2794 (4)	475 (31)	353 (26)	354 (26)	53 (22)	237 (25)	122 (21)
N(3)	5218 (5)	2848 (3)	4800 (4)	453 (28)	384 (26)	302 (23)	77 (22)	186 (22)	83 (20)
N(4)	6340 (5)	2442 (4)	3093 (4)	518 (31)	399 (27)	417 (27)	32 (23)	308 (25)	107 (23)
C(1)	2218 (7)	2406 (4)	496 (5)	567 (42)	341 (32)	322 (30)	8 (28)	171 (31)	86 (26)
C(2)	1669 (8)	2795 (5)	-659 (6)	786 (53)	473 (40)	363 (34)	22 (35)	174 (36)	144 (31)
C(3)	254 (9)	2900 (6)	-1297 (7)	836 (59)	578 (45)	447 (39)	103 (40)	161 (41)	158 (35)
C(4)	-773 (9)	2607 (6)	-918 (7)	770 (55)	688 (50)	450 (41)	57 (41)	173 (40)	150 (38)
C(5)	-292 (7)	2216 (6)	140 (6)	554 (45)	608 (44)	440 (38)	74 (34)	92 (35)	122 (34)
C(6)	1178 (7)	2114 (5)	858 (6)	528 (39)	438 (34)	366 (31)	18 (28)	199 (30)	114 (27)
C(7)	1532 (7)	1645 (5)	1906 (6)	544 (41)	426 (34)	390 (34)	79 (29)	238 (32)	119 (28)
C(8)	2988 (6)	1029 (5)	3668 (6)	471 (36)	468 (35)	478 (35)	142 (28)	313 (31)	240 (30)
C(9)	2391 (7)	-33 (5)	3200 (7)	652 (45)	399 (35)	725 (47)	107 (31)	439 (40)	225 (34)
C(10)	2618 (9)	-610 (6)	4098 (8)	835 (58)	564 (45)	877 (61)	133 (40)	540 (52)	371 (44)
C(11)	3448 (9)	-164 (7)	5405 (9)	836 (57)	739 (54)	923 (62)	276 (44)	598 (52)	535 (50)
C(12)	4033 (7)	914 (6)	5865 (7)	662 (46)	766 (50)	594 (43)	228 (38)	411 (39)	408 (40)
C(13)	3795 (6)	1510 (5)	4984 (6)	474 (37)	500 (37)	431 (34)	145 (29)	281 (30)	214 (29)
C(14)	4330 (7)	2653 (5)	5433 (6)	562 (40)	524 (37)	380 (32)	160 (30)	308 (31)	155 (29)
C(15)	3133 (7)	3419 (5)	5158 (7)	520 (42)	564 (41)	633 (43)	164 (32)	358 (37)	133 (35)
C(16)	1932 (16)	3117 (12)	5351 (17)	1706 (153)	1896 (159)	2521 (213)	1366 (144)	1839 (172)	1660 (173)
C(17)	639 (8)	2845 (8)	4209 (8)	420 (47)	1250 (77)	744 (52)	112 (48)	240 (42)	241 (52)
C(18)	6363 (6)	3578 (4)	5550 (5)	477 (36)	384 (31)	331 (29)	130 (27)	160 (28)	123 (25)
C(19)	6582 (7)	4263 (5)	6799 (6)	640 (45)	519 (39)	391 (34)	114 (33)	137 (33)	72 (31)
C(20)	7759 (8)	5007 (5)	7546 (7)	611 (46)	550 (41)	493 (39)	88 (35)	96 (37)	102 (34)
C(21)	8806 (8)	5113 (5)	7143 (7)	591 (46)	498 (40)	569 (44)	65 (33)	56 (38)	76 (35)
C(22)	8659 (7)	4471 (5)	5984 (6)	522 (40)	438 (36)	522 (39)	78 (30)	98 (33)	134 (32)
C(23)	7438 (6)	3704 (4)	5175 (6)	449 (35)	372 (31)	403 (31)	85 (26)	150 (28)	104 (26)
C(24)	7435 (6)	3040 (4)	4027 (6)	430 (35)	364 (30)	456 (33)	18 (26)	199 (30)	134 (27)
C(25)	6574 (7)	1733 (5)	2090 (6)	756 (40)	409 (33)	522 (37)	-37 (29)	369 (33)	85 (29)
C(26)	7672 (7)	1076 (5)	2396 (7)	683 (45)	427 (36)	921 (54)	59 (32)	602 (43)	138 (36)
C(27)	7856 (8)	384 (6)	1391 (9)	797 (54)	503 (41)	1027 (66)	-63 (37)	663 (53)	30 (43)
C(28)	6942 (9)	370 (5)	88 (9)	953 (60)	435 (40)	1045 (65)	-113 (40)	803 (56)	-6 (41)
C(29)	5829 (8)	1009 (5)	-217 (7)	937 (56)	492 (39)	667 (45)	-181 (38)	610 (44)	-14 (34)
C(30)	5639 (7)	1700 (5)	796 (6)	763 (46)	390 (33)	501 (36)	-136 (31)	461 (36)	26 (28)
C(31)	4473 (7)	2418 (5)	489 (6)	684 (43)	427 (33)	422 (33)	-18 (30)	344 (32)	129 (27)
C(32)	5077 (8)	3615 (5)	897 (7)	804 (50)	551 (40)	569 (41)	-140 (35)	364 (38)	204 (34)
C(33)	5831 (9)	3751 (6)	73 (8)	967 (63)	617 (47)	676 (51)	-144 (42)	388 (48)	232 (41)
C(34)	7281 (9)	4212 (8)	712 (11)	573 (53)	1116 (74)	1599 (102)	0 (49)	578 (62)	308 (72)
O(1)	1833 (10)	2798 (9)	6322 (9)	1963 (89)	3042 (115)	2107 (85)	865 (80)	1442 (75)	1323 (82)
O(2)	5161 (9)	3539 (8)	-1095 (7)	1812 (78)	2222 (93)	801 (50)	-799 (68)	641 (52)	410 (55)

^a The complete temperature factor expression is $\exp[-2\pi^2(a^*U_{11}h^2 + b^*U_{22}k^2 + c^*U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

acetone was slowly evaporated by bubbling air through the solution for several hours. The product separated as dark red crystals which were isolated by filtration and dried in vacuo. Anal. Calcd for Ni(TAAB)(CH₂COCH₃)₂: C, 69.76; H, 5.18; N, 9.57; Ni, 10.03. Found: C, 69.30, 69.81; H, 5.02, 5.32; N, 9.93, 9.46; Ni, 9.96, 10.80.

Preparation of Cu(TAAB)(CH₂COCH₃)₂. The starting material, Cu(TAAB)(NEt₂)₂, was prepared by dissolving 0.3 g of Cu(TAAB)(BF₄)₂ in 300 mL of water and then adding 100 mL of diethylamine diluted with 100 mL of water. The brown NEt₂⁻ adduct separated after being stirred for 10 min. It was isolated by filtering, washing with water, and drying at room temperature. The preparation of Cu(TAAB)(CH₂COCH₃)₂ is similar to that described for Ni(TAAB)(CH₂COCH₃)₂. Anal. Calcd for Cu(TAAB)(CH₂COCH₃)₂: C, 69.18; H, 5.13; N, 9.49; Cu, 10.76. Found: C, 68.65; H, 5.21; N, 9.29; Cu, 10.41.

Structure Analysis. Crystal data for Ni(TAAB)(CH₂COCH₃)₂ are as follows: triclinic, $a = 10.538$ (3) Å, $b = 13.093$ (5) Å, $c = 11.859$ (3) Å, $\alpha = 104.19$ (2)°, $\beta = 115.63$ (2)°, $\gamma = 89.41$ (2)°, $V = 1421.7$ Å³, $\rho_c = 1.37$ g cm⁻³ (by flotation), $Z = 2$, $\rho_c = 1.363$ g cm⁻³, space group $P\bar{1}$, Mo K α radiation, $\lambda 0.7107$ Å, $\mu(\text{Mo K}\alpha) = 12.51$ cm⁻¹.

A cleaved fragment of a dark red crystal was ground to approximately spherical shape with $r = 0.115$ mm and used for data collection. Preliminary oscillation and Weissenberg photographs showed the permissible space groups to be $P1$ and $P\bar{1}$. The space group $P\bar{1}$ was confirmed by the structure solution. The lattice constants were determined from least-squares refinement of the setting angles of 23 reflections on a Philips PW 1100 automated diffractometer.

Diffraction data were collected using graphite-monochromated molybdenum radiation. The intensity data were collected by ω - 2θ scan technique (scan width, 1.20°; scan speed, 0.03° s⁻¹) in the range of $4^\circ \leq 2\theta \leq 60^\circ$. Three standard reflections were monitored after

every 2 h and they were fairly stable during the data collection period. The PW 1100's software provides an automatic reorientation of the crystal if the azimuths of the standard reflections reveal a little misalignment. The intensities were corrected for Lorentz and polarization effects but no absorption correction was applied. A total of 4039 independent reflections were measured of which 3876 with $I \geq 3\sigma(I)$ were considered observed.

Structure Determination and Refinement. A three-dimensional Patterson synthesis gave the position of the nickel atom. The parameters of the Ni atom were refined together with the scale factor; the value of R was 0.35, where $R = \sum(|F_o| - |F_c|)/|F_o|$. A Fourier map phased on the nickel atom afforded the coordinates of all nonhydrogen atoms. Refinement of the scale and the appropriate atomic coordinates gave $R = 0.13$. Refinement of positional and isotropic thermal parameters for all atoms except hydrogens converged with $R = 0.105$, while the refinement with anisotropic temperature factors reduced R to 0.066. Hydrogen atom positions were then included in the calculation with their geometrically determined positions at 1.0 Å from carbon atoms and with the isotropic thermal factors equal to the isotropic thermal factors of the carrier atoms. It was verified that these calculated hydrogen atom positions coincide with regions of significant positive electron density in a difference-Fourier synthesis. Hydrogen atom positions were not refined. The R index dropped to the final value of 0.061 (the corresponding weighted R_w was 0.081). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights, w , taken as $1/\sigma^2(F_o)$. The atomic scattering factors were taken from Cromer and Mann.¹² The effects of anomalous dispersion were included in F_c ; the values of $\Delta f'$ and $\Delta f''$ for Ni were taken from Cromer and Liberman.¹³

Calculations were carried out on the UNIVAC 1100 of the University Computing Centre, Zagreb, and were performed in part with the system of programs developed by Domenicano, Spagna, and

Table II. Fractional Coordinates ($\times 10^3$) for Hydrogen Atoms of Ni(TAAB)(CH₂COCH₃)₂^a

atom	x	y	z
H(1)	233	299	-99
H(2)	-7	320	-207
H(3)	-180	269	-141
H(4)	-99	199	43
H(5)	74	128	196
H(6)	182	-36	225
H(7)	218	-136	379
H(8)	364	-60	603
H(9)	461	124	682
H(10)	336	255	469
H(11)	357	414	575
H(12)	277	345	424
H(13)	43	347	384
H(14)	76	224	358
H(15)	-19	264	434
H(16)	587	420	713
H(17)	786	548	839
H(18)	965	565	770
H(19)	941	454	570
H(20)	834	304	394
H(21)	831	111	332
H(22)	862	-10	159
H(23)	710	-11	-63
H(24)	518	97	-114
H(25)	535	284	123
H(26)	428	407	75
H(27)	577	383	184
H(28)	732	493	127
H(29)	784	376	128
H(30)	777	430	18

^a Hydrogen atoms were not refined. All hydrogen atoms were assigned a constant isotropic temperature factor of the carrier atom.

Vaciago¹⁴ and in part with Stewart's X-ray 72 system.¹⁵ The observed and calculated structure factors ($\times 10$) are available.¹⁶ The final positional and thermal parameters are given in Tables I and II.

Discussion

The acetone adducts of Ni(TAAB)²⁺ and Cu(TAAB)²⁺ were prepared by a reaction in which the enolate anion of acetone replaces the diethylamide group (eq 2). Only the two M^{II}(TAAB)(NET₂)₂ + 2CH₃C(=O)CH₃ → M^{II}(TAAB)(CH₂C(=O)CH₃)₂ + 2NH₂Et (2)

metal ions have been investigated. Preliminary results¹⁷ indicate that enamines and, in some cases, the enolates of ketones will add directly to the azomethine carbon atoms of M^{II}(TAAB)²⁺. Once formed, the acetone adducts appear to be relatively stable; however, their solubilities are very low in the solvents that have been tested. Consequently, straightforward judgments concerning their reactivities are difficult to make. It is clear that the acetone groups can be removed by the action of strong acids, regenerating M^{II}(TAAB)²⁺.

The nickel(II) complex formed by the reaction of eq 2 contains low-spin nickel(II), exhibiting a small residual paramagnetism. The copper(II) complex has a value of μ_{eff} equal to 1.82 μ_B at 293 K. The peak of highest mass number in the mass spectrum of the copper complex appears at 533 amu, corresponding to Cu(TAAB)(CH₂COCH₃)⁺. The prominence of this fragment in the mass spectra of base adducts of M^{II}(TAAB)²⁺ has been pointed out earlier.¹¹ The infrared spectra of M(TAAB)(CH₂COCH₃)₂, M = Ni or Cu, are also very similar to those reported earlier for alkoxide⁹ and amide¹¹ adducts. The only distinctive absorption in their infrared spectra is due to the C=O stretching mode of the ketone groups at 1720 cm⁻¹.

The crystal structure consists of the packing of individual Ni(TAAB)(CH₂COCH₃)₂ molecules. All intermolecular contacts are quite normal with the closest carbon-carbon

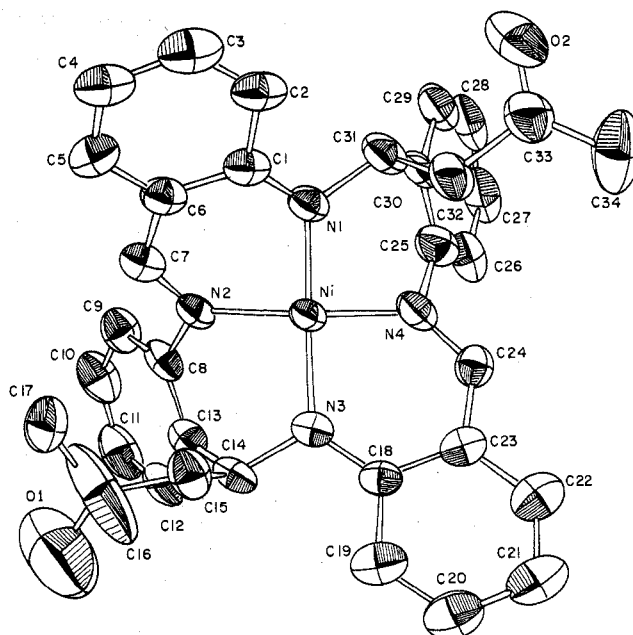


Figure 1. Structure of Ni(TAAB)(CH₂COCH₃)₂ viewed from above the coordination plane.

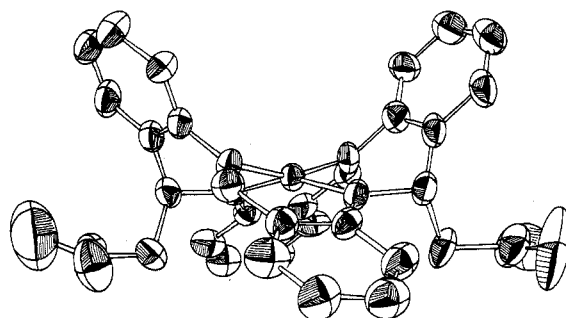


Figure 2. Structure of Ni(TAAB)(CH₂COCH₃)₂ looking toward the edge of the coordination plane.

Table III. Bond Distances and Standard Deviations (Å) for Nonhydrogen Atoms in Ni(TAAB)(CH₂COCH₃)₂^a

Ni-N(1)	1.921 (5)	C(12)-C(13)	1.391 (11)
Ni-N(2)	1.883 (6)	C(13)-C(14)	1.486 (9)
Ni-N(3)	1.912 (4)	C(14)-C(15)	1.576 (10)
Ni-N(4)	1.890 (6)	C(15)-C(16)	1.454 (23)
N(1)-C(1)	1.346 (8)	C(16)-C(17)	1.413 (15)
N(1)-C(31)	1.486 (7)	C(16)-O(1)	1.361 (26)
N(2)-C(7)	1.300 (7)	C(18)-C(19)	1.452 (9)
N(2)-C(8)	1.431 (9)	C(18)-C(23)	1.408 (11)
N(3)-C(14)	1.487 (6)	C(19)-C(20)	1.388 (9)
N(3)-C(18)	1.356 (7)	C(20)-C(21)	1.398 (14)
N(4)-C(24)	1.288 (6)	C(21)-C(22)	1.369 (10)
N(4)-C(25)	1.430 (9)	C(22)-C(23)	1.440 (8)
C(1)-C(2)	1.455 (10)	C(23)-C(24)	1.423 (9)
C(1)-C(6)	1.424 (12)	C(25)-C(26)	1.407 (10)
C(2)-C(3)	1.374 (11)	C(25)-C(30)	1.410 (8)
C(3)-C(4)	1.426 (15)	C(26)-C(27)	1.395 (13)
C(4)-C(5)	1.360 (12)	C(27)-C(28)	1.418 (12)
C(5)-C(6)	1.433 (9)	C(28)-C(29)	1.403 (11)
C(6)-C(7)	1.425 (10)	C(29)-C(30)	1.404 (11)
C(8)-C(9)	1.404 (9)	C(30)-C(31)	1.512 (9)
C(8)-C(13)	1.391 (8)	C(31)-C(32)	1.573 (9)
C(9)-C(10)	1.391 (13)	C(32)-C(33)	1.543 (15)
C(10)-C(11)	1.379 (11)	C(33)-C(34)	1.437 (12)
C(11)-C(12)	1.422 (11)	C(33)-O(2)	1.209 (11)

^a The C-H bond distance is 1.0 Å.

distance of 3.30 Å. The molecular structure is shown in projection in Figure 1 and the interatomic distances and angles are shown in Tables III and IV. The conformation of the ring is clear from Figure 2. The molecule is saddle shaped with

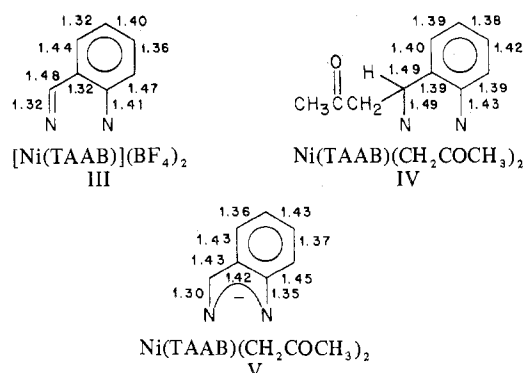
Table IV. Bond Angles and Standard Deviations (deg) for Nonhydrogen Atoms in Ni(TAAB)(CH₂COCH₃)₂

N(1)-Ni-N(2)	90.9 (2)	N(3)-C(18)-C(19)	122.6 (7)
N(2)-Ni-N(3)	92.9 (2)	N(3)-C(18)-C(23)	121.8 (5)
N(3)-Ni-N(4)	90.6 (2)	N(4)-C(24)-C(23)	124.0 (7)
N(1)-Ni-N(4)	93.5 (2)	N(4)-C(25)-C(26)	120.7 (6)
N(1)-Ni-N(3)	158.4 (1)	N(4)-C(25)-C(30)	117.4 (6)
N(2)-Ni-N(4)	158.8 (2)	C(1)-C(6)-C(7)	121.7 (6)
Ni-N(1)-C(1)	124.3 (5)	C(15)-C(6)-C(7)	116.4 (7)
Ni-N(1)-C(31)	120.2 (3)	C(8)-C(13)-C(14)	120.2 (6)
Ni-N(2)-C(7)	127.3 (5)	C(12)-C(13)-C(14)	121.0 (5)
Ni-N(2)-C(8)	115.7 (4)	C(13)-C(14)-C(15)	114.2 (5)
Ni-N(3)-C(14)	118.9 (2)	C(14)-C(15)-C(16)	115.2 (9)
Ni-N(3)-C(18)	124.2 (5)	C(15)-C(16)-C(17)	114.3 (1.6)
Ni-N(4)-C(24)	127.6 (5)	C(15)-C(16)-O(1)	132.7 (1.2)
Ni-N(4)-C(25)	116.0 (3)	C(17)-C(16)-O(1)	110.8 (1.4)
C(1)-N(1)-C(31)	114.4 (5)	C(18)-C(23)-C(24)	122.4 (5)
C(7)-N(2)-C(8)	116.6 (6)	C(22)-C(23)-C(24)	115.9 (7)
C(14)-N(3)-C(18)	115.5 (4)	C(25)-C(30)-C(31)	121.0 (6)
C(24)-N(4)-C(25)	116.2 (6)	C(29)-C(30)-C(31)	119.8 (5)
N(1)-C(1)-C(2)	122.9 (7)	C(30)-C(31)-C(32)	111.9 (5)
N(1)-C(1)-C(6)	122.1 (6)	C(31)-C(32)-C(33)	108.8 (6)
N(1)-C(31)-C(30)	110.3 (5)	C(32)-C(33)-C(34)	119.3 (8)
N(1)-C(31)-C(32)	108.9 (5)	C(32)-C(33)-O(2)	119.2 (8)
N(2)-C(7)-C(6)	124.5 (7)	C(34)-C(33)-O(2)	121.3 (1.2)
N(2)-C(8)-C(9)	120.7 (5)	C(6)-C(1)-C(2)	115.0 (6)
N(2)-C(8)-C(13)	116.8 (5)	C(1)-C(2)-C(3)	121.0 (9)
N(3)-C(14)-C(13)	109.5 (5)	C(2)-C(3)-C(4)	123.2 (8)
N(3)-C(14)-C(15)	108.5 (6)	C(3)-C(4)-C(5)	116.9 (7)
C(4)-C(5)-C(6)	122.0 (8)	C(19)-C(20)-C(21)	121.4 (7)
C(5)-C(6)-C(1)	121.8 (6)	C(20)-C(21)-C(22)	119.2 (6)
C(13)-C(8)-C(9)	122.4 (7)	C(21)-C(22)-C(23)	120.8 (8)
C(8)-C(9)-C(10)	118.0 (6)	C(22)-C(23)-C(18)	121.5 (6)
C(9)-C(10)-C(11)	120.9 (7)	C(30)-C(25)-C(26)	121.9 (7)
C(10)-C(11)-C(12)	120.4 (9)	C(25)-C(26)-C(27)	119.1 (7)
C(11)-C(12)-C(13)	119.5 (6)	C(26)-C(27)-C(28)	119.2 (7)
C(12)-C(13)-C(8)	118.7 (6)	C(27)-C(28)-C(29)	121.7 (8)
C(23)-C(18)-C(19)	115.6 (5)	C(28)-C(29)-C(30)	119.0 (7)
C(18)-C(19)-C(20)	121.5 (8)	C(29)-C(30)-C(25)	119.1 (6)

an approximate twofold symmetry axis. Further, both -CH₂COCH₃ groups are cis to each other with respect to the plane of the macrocyclic ligand. This confirms the predictions made earlier for structures of this kind.

The nickel atom exhibits a distorted planar coordination sphere. The least-squares best plane of the nickel atom and four coordinating nitrogen atoms is defined by the equation $-2.723X + 12.574Y - 0.644Z = 1.495$, referred to the crystal axes, with the N(1) and N(3) +0.35 Å out of the plane. The mean value of the Ni-N bond lengths is 1.902 Å, although it might be considered that two nickel-to-nitrogen bond lengths are slightly shorter (mean value 1.887 Å) than the other two (mean value 1.917 Å). The value of 1.902 Å is in very good agreement with Ni-N bond length of 1.90 Å observed for Ni(TAAB)(BF₄)₂¹⁸ and other nickel(II) complexes with square-planar coordination of the Ni atom to four coordinating N atoms.¹⁹ Two of the N-Ni-N bond angles are approximately 91° while the other two are about 93°.

In contrast to TAAB, the new ligand (TAAB)-(CH₂COCH₃)₂²⁻ contains two pairs of dissimilar chelate rings, the like rings appearing trans to each other (structure II). As partial structures III, IV, and V show, the chelate ring to which the -CH₂C(=O)CH₃ group is appended contains only saturated C-N linkages (structure IV), while the π-electron system is more delocalized in the other (TAAB)-(CH₂COCH₃)₂²⁻ chelate ring (compare structures IV and V).



Structure III is included in order to show the chelate rings of TAAB. It is interesting that the slightly shorter Ni-N distances (N₂ and N₄) occur for the nitrogens remote from positions of the added enolate groups. This is consistent with the conclusion that the ligand charge is largely delocalized over the chelate rings having structure V. The relative lengths of the bonds between nitrogen atoms and aromatic carbons emphasize these relationships. The long aromatic C-N bond in structure IV and the relatively short C-N bonds in structure V indicate that the π-delocalization is mostly confined to chelate ring V.

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Registry No. Ni(TAAB)(CH₂COCH₃)₂, 68907-95-9; Cu-(TAAB)(CH₂COCH₃)₂, 68890-51-7; Ni(TAAB)(NEt₂)₂, 31564-07-5; Cu(TAAB)(NEt₂)₂, 68890-50-6; Cu(TAAB)(BF₄)₂, 68890-49-3.

Supplementary Material Available: A listing of structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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