3444 *Inorg. Chem.* **1984**, *23*, 3444-3449

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Reactions of the Nickel(II) and Copper(II) Complexes of the Dihydrazone Ligand 4,4,9,9-Tetramethyl-5,8-diazadodecane-2,11-dione Dihydrazone with Pentane-2,4-dione. Crystal Structures of Two Resultant Nickel(II) Complexes

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Received October 11, 1983

The nickel(II) and copper(II) complexes of the diamine dihydrazone ligand 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dihydrazone, amhy, react with pentane-2,4-dione to form complexes of the linear, potentially pentadentate, ligand 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione 2-isopropylidenehydrazone 11-acetylhydrazone, tdaa. The structure of [Ni(tdaa)(ClO_4)]ClO_4, determined by X-ray diffractometry [$C_{19}H_{38}Cl_2N_6NiO_9$, orthorhombic, $Pn2_1a$, $a = 26.314$ (3) Å, $b = 9.567$ (1) Å, $c = 11.122$ (1) Å, $Z = 4$, $R = 0.037$, $R_w = 0.049$, for 1851 reflections], shows the tdaa ligand coordinated in a square-pyramidal arrangement, with the isopropylidenehydrazone nitrogen in the axial site, and trans to a weakly coordinated perchlorate oxygen (Ni–O = 2.455 (5) Å). Spectroscopic evidence suggests that other compounds of tdaa such as [Ni(tdaa)(NO_2)]ClO_4 have structures with the amide oxygen not coordinated. [Ni(amhy)]$(ClO_4)_2$ reacts with pentane-2,4-dione in the presence of acetone and base to form the compound [Ni(amba)(acac)]ClO_4, where amba is the bis(isopropylidenehydrazone) derivative of amhy. The structure of [Ni(amba)(acac)]ClO_4 has been determined by X-ray diffractometry [$C_{25}H_{47}ClN_6NiO_6$, orthorhombic, $Pbca$, $a = 25.624$ (4) Å, $b = 13.476$ (3) Å, $c = 18.456$ (2) Å, $Z = 8$, $R = 0.048$, $R_w = 0.060$, for 2412 reflections]. The tetradentate ligand amba is present in a folded conformation similar to that of tdaa in the previous compound, with chelate pentane-2,4-dionato ($acac^-$) completing octahedral coordination, with one donor oxygen trans to a secondary amino nitrogen and the other trans to a diazine nitrogen atom.

Introduction

The preparations of cobalt(II), nickel(II) and copper(II) complexes of the tetradentate bis(secondary amine), dihydrazone ligand 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dihydrazone, amhy, have been reported.[2] The structures of the triplet ground-state nickel(II) compounds *trans*-[Ni(amhy)$(NCS)_2$]H_2O and [Ni(amhy)(NO_2)]ClO_4, with *trans* N-coordinated thiocyanate and symmetrical chelate nitrite, respectively, have been determined.[3] The compounds [Ni(amhy)]$(ClO_4)_2$ and [Cu(amhy)]$(ClO_4)_2$ react with many aliphatic carbonyl compounds to form complexes of 15-membered hexaaza macrocycles, e.g. $[Ni(amac)]^{2+}$, formed with acetone (Scheme I). The structure of a copper(II) analogue of [Ni(amac)]$(ClO_4)_2$, formed from cyclohexanone, has been determined.[4] They also react with 1,2-diketones to form complexes of 16-membered hexaaza macrocycles, e.g. $[Ni(diac)]^{2+}$, formed with butane-2,3-dione (diacetyl) (Scheme I). The structures of singlet ground-state square-planar [Ni(diac)]$(ClO_4)_2$ and of triplet ground-state [$(Ni(diac))_2C_2O_4$]$(ClO_4)_2$·$2H_2O$, with symmetrical bridging bidentate oxalate, have been determined.[5]

This study reports the results of attempts to extend the above series of reactions, hopefully to form complexes of 17-membered hexaaza macrocycles, by reaction of the amhy complexes with the 1,3-diketone pentane-2,4-dione (acetylacetone, acacH). A reaction yielding a macrocycle complex from the condensation of a linear terminal dihydrazine compound and acacH has been reported.[6] Macrocyclic complexes resulting from reactions of complexes of linear tetraamine or diamines with acacH have been described.[7]

For the reaction of the amhy complexes with acacH, the anticipated macrocyclic product was not observed. Nonmacrocyclic products resulting from the reaction of the amhy complexes of Ni(II) and Cu(II) with acacH under various conditions are here described, and the structures of two of these products, determined by X-ray diffractometry, are reported.

Experimental Section

Preparation of amhy Compounds. The compounds [Ni(amhy)]$(ClO_4)_2$ and [Cu(amhy)]$(ClO_4)_2$ (amhy = 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dihydrazone) were prepared as previously reported.[2]

(4,4,9,9-Tetramethyl-5,8-diazadodecane-2,11-dione 2-isopropylidenehydrazone 11-acetylhydrazone)(perchlorato)nickel(II) Perchlorate, [Ni(tdaa)(ClO_4)]ClO_4, Hydrate and Ethanolate. Pentane-2,4-dione (acetylacetone, acacH, 2 g) was added to a warm solution of [Ni(amhy)]$(ClO_4)_2$ (2.7 g) in ca. 50 mL of 1:1 methanol/water. The solution was allowed to evaporate; the blue crystals were filtered off after about 3 days and washed with a little cold water; yield ca. 1.9 g (60%). The anhydrous compound was formed by crystallization from hot methanol/propan-2-ol. Anal. Calcd for $C_{19}H_{37}Cl_2N_6NiO_9$: C, 36.6; H, 6.0; N, 13.5. Found: C, 36.6; H, 6.1; N, 13.0. The hydrate crystallized when a solution in methanol/water or acetone/water was allowed to evaporate. An ethanol solvate crystallized from ethanol.

(Nitrito-*O*,*O*′)(4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione 2-isopropylidenehydrazone 11-acetylhydrazone)nickel(II) Perchlorate, [Ni(tdaa)(NO_2)]ClO_4. Sodium nitrite in excess in water was added to a solution of [Ni(tdaa)]$(ClO_4)_2$ in acetone, and the solution was allowed to evaporate. The mauve crystalline *product* was filtered off, washed with cold water, and recrystallized from hot methanol/propan-2-ol. Anal. Calcd for $C_{19}H_{38}ClN_7NiO_7$: C, 40.0; H, 6.7; Ni, 10.3. Found: C, 40.2; H, 6.8; Ni, 10.2.

(*cis*-Dithiocyanato)(4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione 2-isopropylidenehydrazone 11-acetylhydrazone)nickel(II), Ni(tdaa)$(NCS)_2$, and Aqua(thiocyanato)(4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione 2-isopropylidenehydrazone 11-acetylhydrazone)nickel(II) Thiocyanate, [Ni(tdaa)(NCS)(H_2O)]CNS. Sodium thiocyanate in excess in water was added to an acetone solution of [Ni(tdaa)]$(ClO_4)_2$, and the solution was allowed to evaporate. The blue-violet crystalline *product* was filtered off and recrystallized by evaporation of an acetone/water solution (aqua compound) or from hot acetone/propan-2-ol (anhydrous compound). Anal. Calcd for $C_{21}H_{40}N_8NiO_2S_2$: C, 45.1; H, 7.2; N, 20.0. Found (for hydrate): C, 44.6; H, 7.2; N, 20.0.

(Thiocyanato)(4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione 2-isopropylidenehydrazone 11-acetylhydrazone)nickel(II) Perchlorate, [Ni(tdaa)(NCS)]ClO_4. Equimolar amounts of the diperchlorate and dithiocyanato compounds were dissolved in the minimum volume of

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(2) Curtis, N. F. *Inorg. Chim. Acta* **1982**, *59*, 171.

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Scheme I

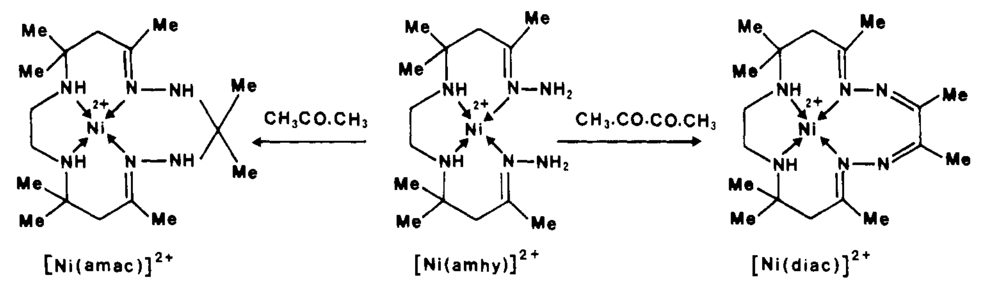


Table I. Crystal Data for $[Ni(tdaa)(ClO_4)]ClO_4$ (1) and $[Ni(amba)(acac)]ClO_4$ (2)

	1	2
formula	$C_{19}H_{38}Cl_2N_6NiO_9$	$C_{25}H_{47}ClN_6NiO_6$
cryst syst	orthorhombic	orthorhombic
space group	$Pn2_1a$[a]	$Pbca$
a, Å	26.314 (3)	25.624 (4)
b, Å	9.567 (1)	13.476 (3)
c, Å	11.122 (1)	18.456 (2)
V, Å^3	2799.9	6373.0
Z	4	8
fw	624.16	621.85
μ, cm^{-1}	6.36	7.39
ρ_{obsd}, g cm^{-3}	1.47[b]	1.31[c]
ρ_{calcd}, g cm^{-3}	1.480	1.296

[a] Nonstandard setting of $Pna2_1$. Equivalent positions: (x, y, z); $(\bar{x}, {}^1/_2 + y, \bar{z})$; $({}^1/_2 - x, {}^1/_2 + y, {}^1/_2 + z)$; $(x + {}^1/_2, y, {}^1/_2 - z)$. [b] Flotation in $CHBr_3/CH_2Cl_2$. [c] Flotation in $CCl_4/C_6H_5CH_3$.

hot water. The blue-violet crystalline *product* was filtered off from the cold solution. Anal. Calcd for $C_{20}H_{38}ClN_7NiO_5S$: C, 41.2; H, 6.6; N, 16.8. Found: C, 41.1; H, 6.8; N, 16.8.

(4,4,9,9-Tetramethyl-5,8-diazadodecane-2,11-dione 2-isopropylidenehydrazone 11-acetylhydrazone)(perchlorato)copper(II) Perchlorate, $[Cu(tdaa)(ClO_4)]ClO_4$. The compound was prepared in low yield as for the nickel(II) analogue. It was more conveniently prepared by boiling $[Ni(tdaa)](ClO_4)_2$ with 1.2 mol of $[Cu(H_2O)_4](ClO_4)_2$ in 1:1 methanol/water for 5 min and then allowing the solution to evaporate. The bright blue *product* was filtered off, washed with ethanol, and recrystallized from hot methanol/propan-2-ol. Anal. Calcd for $C_{19}H_{37}Cl_2CuN_6O_9$: C, 36.3; H, 5.9; N, 13.4. Found: C, 36.5; H, 6.3; N, 13.4.

(Pentane-2,4-dionato)(4,4,7,7-tetramethyl-5,8-diazadodecane-2,11-dione dihydrazone)nickel(II) Perchlorate, $[Ni(amhy)(acac)]ClO_4$. $[Ni(amhy)](ClO_4)_2$ (2.7 g) was dissolved in a hot mixture of water (20 mL), methanol (40 mL), and ammonia (5 mL of 2 mol L^{-1}) and acacH (0.5 g, 1 mol) added. The pale blue *product* was filtered from the cold solution, and recrystallized from hot methanol/propan-2-ol, or by evaporation of a methanol/water solution; yield nearly quantitative. Anal. Calcd for $C_{19}H_{39}ClN_6NiO_6$: C, 42.1; H, 7.3; N, 15.5; Ni, 10.8. Found: C, 42.7; H, 7.7; N, 15.6; Ni, 10.8.

(Pentane-2,4-dionato)(4,4,7,7-tetramethyl-5,8-diazadodecane-2,11-dione 2,11-bis(isopropylidenehydrazone))nickel(II) Perchlorate, $[Ni(amba)(acac)]ClO_4$. This *compound* was prepared and recrystallized as for the previous preparation, substituting acetone for the methanol; yield nearly quantitative. Anal. Calcd for $C_{25}H_{45}ClN_6NiO_6$: C, 48.4; H, 7.3; Ni, 9.5. Found: C, 47.9; H, 7.9; Ni, 9.6.

Analogous compounds with other aliphatic ketones and aldehydes were prepared similarly in water/methanol containing an excess of the appropriate carbonyl compound.

Magnetic Susceptibilities. Magnetic susceptibilities were measured at 25 °C by the Faraday method, using $HgCo(CNS)_4$ as calibrant. Effective magnetic moments, calculated with diamagnetic corrections using Pascal's constants and on the assumption of the Curie relationship, confirm the presence of triplet ground-state nickel(II) and the absence of appreciable spin coupling for $[Cu(tdaa)](ClO_4)_2$. Results are as follows, where χ_m is the corrected molar susceptibility: $[Ni(tdaa)(H_2O)](ClO_4)_2$, χ_m 5.03×10^{-8} mol^{-1} m^3, μ_{eff} 3.09 μ_B; $[Ni(tdaa)(NO_2)]ClO_4$, χ_m 4.95×10^{-8} mol^{-1} m^3, μ_{eff} 3.09 μ_B; $[Ni(tdaa)(NCS)]ClO_4$, χ_m 4.86×10^{-8} mol^{-1} m^3, μ_{eff} 3.04 μ_B; $[Cu(tdaa)](ClO_4)_2$, χ_m 1.73×10^{-8} mol^{-1} m^3, μ_{eff} 1.81 μ_B; $[Ni(amba)(acac)]ClO_4$, χ_m 5.08×10^{-8} mol^{-1} m^3, μ_{eff} 3.11 μ_B.

Table II. Data Collection and Refinement for $[Ni(tdaa)(ClO_4)]ClO_4$ (1) and $[Ni(amba)(acac)]ClO_4$ (2)

	1	2
cryst size, mm	0.40 × 0.36 × 0.36	0.06 × 0.55 × 0.44
scan width, deg ($2\theta < 25°$)[a] ($2\theta > 25°$)	1.4	1.2
bkgd counts,[b] s	20	0.1 (× scan time)
line profile anal.[c]	no	yes
total no. of unique reflcns	1961	4189
no. of obsd reflcns[d]	1851	2412
final R[e]	0.037	0.048
final R_w[f]	0.049	0.060
no. of variables	234	352

[a] Also corrected for $K\alpha_1$-$K\alpha_2$ dispersion. [b] At each side of scan. Stationary counter–stationary crystal. [c] Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* 1978, *11*, 114. [d] $I > 2.3\sigma(I)$. [e] $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ (observed reflctions only). [f] $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma |F_o|^2)^{1/2}$ (observed reflections only).

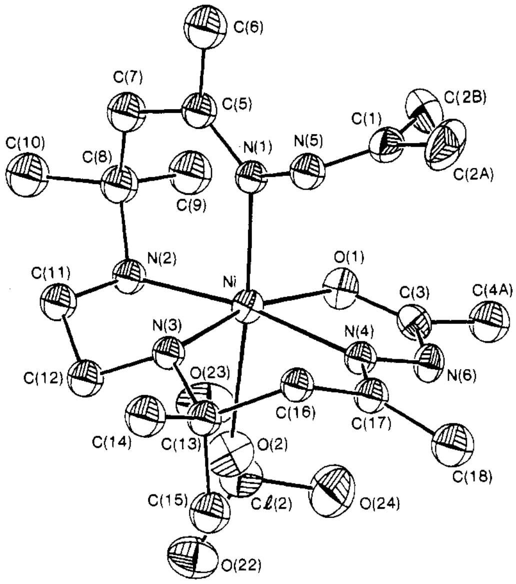


Figure 1. ORTEP projection of the cation $[Ni(tdaa)(ClO_4)]^+$, showing atomic labeling. Thermal ellipsoids show 35% probability levels.

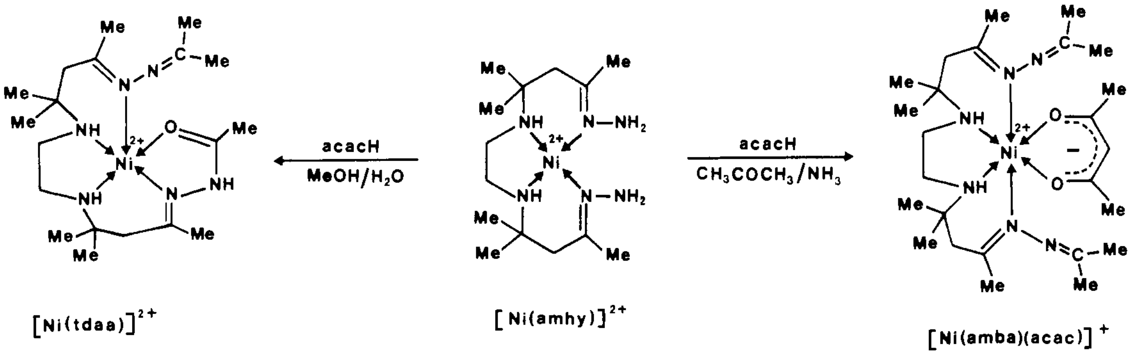
Structure Determinations. The structures of $[Ni(tdaa)(ClO_4)]ClO_4$ (**1**) and $[Ni(amba)(acac)]ClO_4$ (**2**) were determined by X-ray diffractometry. Data were collected in the range 3° < 2θ < 45° on a Picker FACS-I four-circle diffractometer with graphite crystal monochromatized Mo Kα radiation (λ(Mo Kα_1) = 0.7093 Å). Crystal data are shown in Table I and details of diffraction data collection in Table II. The structures were solved by heavy-atom methods and refined by least-squares analysis (full matrix for **1**, block diagonal for **2**).

Hydrogen atoms were located and incorporated in the structure factor calculations, but their parameters were not refined. For **2** all non-hydrogen atoms were refined with anisotropic temperature factors while for **1** only the nickel, perchlorates, and some ligand atoms (all of which had shown evidence of anisotropic thermal motion in difference maps) were refined anisotropically. Final agreement factors are given in Table II.

Table III. Fractional Atomic Coordinates of Non-Hydrogen Atoms

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
[Ni(tdaa)(ClO_4)] ClO_4 (1)							
Ni	0.86194 (3)	0.75000	0.77356 (6)	C(11)	0.9438 (3)	0.8242 (8)	0.9305 (6)
O(1)	0.7864 (2)	0.7050 (5)	0.8057 (4)	C(12)	0.9494 (3)	0.9129 (8)	0.8187 (6)
N(1)	0.8871 (2)	0.5464 (6)	0.7667 (4)	C(13)	0.9364 (2)	0.8986 (7)	0.5923 (6)
N(2)	0.8920 (2)	0.7685 (6)	0.9443 (4)	C(14)	0.9924 (3)	0.9031 (8)	0.5576 (7)
N(3)	0.9308 (2)	0.8310 (6)	0.7149 (4)	C(15)	0.9142 (3)	1.0433 (8)	0.5910 (6)
N(4)	0.8303 (2)	0.7670 (6)	0.6056 (4)	C(16)	0.9082 (2)	0.8049 (7)	0.5016 (5)
N(5)	0.8906 (2)	0.4995 (6)	0.6469 (5)	C(17)	0.8520 (2)	0.8028 (7)	0.5047 (6)
N(6)	0.7783 (2)	0.7590 (7)	0.6100 (4)	C(18)	0.8222 (3)	0.8362 (9)	0.3936 (7)
C(1)	0.8539 (3)	0.4285 (8)	0.6049 (6)	Cl(1)	0.56241 (6)	0.62891 (23)	0.70115 (15)
C(2A)	0.8577 (4)	0.3886 (11)	0.4770 (8)	O(11)	0.5744 (3)	0.7705 (9)	0.7227 (6)
C(2B)	0.8092 (3)	0.3811 (10)	0.6711 (8)	O(12)	0.5132 (2)	0.5979 (9)	0.7485 (7)
C(3)	0.7583 (2)	0.7217 (7)	0.7177 (6)	O(13)	0.5597 (4)	0.6200 (12)	0.5771 (6)
C(4A)	0.7026 (3)	0.7029 (8)	0.7212 (6)	O(14)	0.5970 (3)	0.5402 (10)	0.7503 (9)
C(5)	0.9092 (2)	0.4719 (7)	0.8475 (6)	Cl(2)	0.79278 (6)	1.04019 (22)	0.88469 (16)
C(6)	0.9322 (3)	0.3348 (9)	0.8168 (7)	O(2)	0.8331 (2)	0.9909 (6)	0.8073 (4)
C(7)	0.9163 (3)	0.5185 (8)	0.9743 (6)	O(22)	0.8008 (2)	1.1845 (6)	0.9145 (5)
C(8)	0.8883 (2)	0.6446 (8)	1.0265 (6)	O(23)	0.7938 (2)	0.9596 (7)	0.9921 (5)
C(9)	0.8320 (3)	0.6106 (10)	1.0446 (7)	O(24)	0.7458 (2)	1.0274 (8)	0.8250 (6)
C(10)	0.9130 (3)	0.6775 (9)	1.1486 (7)				
[Ni(amba)(acac)] ClO_4 (2)							
Ni	0.13638 (3)	0.06953 (5)	0.18379 (3)	C(12)	0.2329 (2)	0.1745 (4)	0.1823 (3)
N(1)	0.1469 (2)	−0.0579 (3)	0.1166 (2)	C(13)	0.2362 (2)	0.0476 (5)	0.2822 (3)
N(2)	0.1621 (2)	0.1555 (3)	0.0922 (2)	C(14)	0.2951 (3)	0.0349 (6)	0.2820 (3)
N(3)	0.2163 (2)	0.0760 (3)	0.2088 (2)	C(15)	0.2206 (2)	0.1269 (5)	0.3371 (3)
N(4)	0.1216 (2)	−0.0107 (3)	0.2831 (2)	C(16)	0.2126 (2)	−0.0530 (5)	0.3004 (3)
N(5)	0.1428 (2)	−0.1464 (3)	0.1578 (2)	C(17)	0.1555 (3)	−0.0625 (4)	0.3170 (3)
N(6)	0.0692 (2)	−0.0330 (3)	0.3009 (2)	C(18)	0.1420 (3)	−0.1373 (5)	0.3746 (4)
C(1)	0.0994 (3)	−0.1929 (4)	0.1558 (3)	O(1)	0.0599 (1)	0.0640 (3)	0.1594 (2)
C(2A)	0.0957 (3)	−0.2831 (5)	0.2021 (4)	O(2)	0.1232 (1)	0.1998 (3)	0.2353 (2)
C(2B)	0.0541 (3)	−0.1667 (5)	0.1120 (4)	C(101)	−0.0263 (3)	0.1114 (6)	0.1336 (4)
C(3)	0.0488 (3)	0.0204 (5)	0.3497 (3)	C(102)	0.0271 (2)	0.1328 (4)	0.1658 (3)
C(4A)	−0.0064 (3)	−0.0031 (6)	0.3697 (4)	C(103)	0.0355 (2)	0.2231 (4)	0.1989 (3)
C(4B)	0.0740 (3)	0.1020 (5)	0.3909 (3)	C(104)	0.0817 (2)	0.2511 (4)	0.2326 (3)
C(5)	0.1633 (2)	−0.0676 (4)	0.0510 (3)	C(105)	0.0845 (3)	0.3504 (5)	0.2687 (3)
C(6)	0.1741 (3)	−0.1664 (5)	0.0176 (3)	Cl(1)	0.17042 (7)	0.46457 (13)	0.07195 (8)
C(7)	0.1751 (2)	0.0201 (4)	0.0045 (3)	O(11)	0.1311 (2)	0.3924 (4)	0.0801 (3)
C(8)	0.1517 (2)	0.1222 (4)	0.0166 (3)	O(12)	0.2160 (2)	0.4349 (4)	0.1119 (3)
C(9)	0.0924 (2)	0.1169 (5)	0.0053 (3)	O(13)	0.1551 (3)	0.5561 (4)	0.0961 (4)
C(10)	0.1759 (3)	0.1920 (5)	−0.0397 (3)	O(14)	0.1863 (2)	0.4670 (5)	0.0004 (3)
C(11)	0.2175 (2)	0.1816 (4)	0.1040 (3)				

Scheme II[a]



[a] For clarity, the ion [Ni(tdaa)]$^{2+}$ is represented with no ligand in the sixth coordination site. Also for clarity, the ion [Ni(amba)(acac)]$^+$ is represented in a symmetrical configuration. The structural study of [Ni(amba)(acac)] ClO_4 shows a less symmetrical arrangement (Figure 2).

The atomic coordinates of the non-hydrogen atoms are given in Table III and selected bond lengths and angles in Table IV. The atomic labeling scheme is similar to that used in ref 3 and 5 and is shown on the ORTEP diagrams[8] displayed in Figures 1 and 2. Thermal parameters, hydrogen atom coordinates, additional bond lengths and angles, selected torsion angles, least-squares planes, structure factor listings, and details of the data collection and structure refinement have been deposited as supplementary material.

Results and Discussion

Reaction of [Ni(amhy)](ClO_4)$_2$ and [Cu(amhy)](ClO_4)$_2$ with acacH under Neutral Conditions. In methanol/water (3:1) [Ni(amhy)](ClO_4)$_2$ reacts with 1 mol of acacH over a period of hours–days to yield a blue-violet, triplet ground-state product, isolated by slow evaporation. This is of composition $Ni(C_{19}H_{38}N_6O)(H_2O)(ClO_4)_2$, i.e. incorporating one amhy and one acacH residue, condensed with elimination of one mol of H_2O. An X-ray diffractometric study of the anhydrous form of this compound, below, revealed the presence of the pentadentate ligand 4,4,9,9-tetramethyl-5,8-diazadodecane-

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Table IV. Selected Bond Lengths (Å) and Angles (deg) in [Ni(tdaa)(ClO$_4$)]ClO$_4$ (1) and [Ni(amba)(acac)]ClO$_4$ (2)

	1	2		1	2
Ni-N(1)	2.058 (5)	2.135 (4)	Ni-N(4)	2.052 (4)	2.161 (4)
Ni-N(2)	2.064 (5)	2.153 (4)	Ni-N(3)	2.075 (5)	2.100 (4)
Ni-O(1)	2.065 (4)	2.013 (4)	Ni-O(2)	2.455 (5)	2.025 (3)
C(1)-N(5)	1.270 (8)	1.275 (8)	C(3)-N(6)	1.356 (7)	1.265 (7)
N(5)-N(1)	1.409 (7)	1.418 (6)	N(6)-N(4)	1.370 (6)	1.415 (6)
N(1)-C(5)	1.288 (8)	1.288 (6)	N(4)-C(17)	1.305 (8)	1.279 (7)
C(8)-N(2)	1.501 (9)	1.491 (7)	C(13)-N(3)	1.517 (8)	1.497 (7)
N(2)-C(11)	1.473 (8)	1.477 (7)	N(3)-C(12)	1.479 (8)	1.477 (7)
			C(3)-O(1)	1.237 (7)	
O(1)-C(102)		1.256 (7)	O(2)-C(104)		1.268 (6)
C(102)-C(103)		1.380 (8)	C(104)-C(103)		1.389 (8)

	1	2		1	2
N(1)-Ni-N(2)	89.6 (2)	86.5 (2)	N(2)-Ni-O(2)	84.1 (2)	87.3 (2)
N(1)-Ni-N(3)	93.5 (2)	92.2 (2)	N(3)-Ni-N(4)	92.2 (2)	90.3 (2)
N(1)-Ni-N(4)	99.9 (2)	96.4 (2)	N(3)-Ni-O(1)	166.5 (2)	179.6 (2)
N(1)-Ni-O(1)	96.8 (2)	87.9 (2)	N(3)-Ni-O(2)	88.1 (2)	91.4 (2)
N(1)-Ni-O(2)	173.3 (2)	172.3 (2)	N(4)-Ni-O(1)	77.5 (2)	90.0 (2)
N(2)-Ni-N(3)	85.6 (2)	81.5 (2)	N(4)-Ni-O(2)	86.5 (2)	90.4 (2)
N(2)-Ni-N(4)	170.4 (2)	171.4 (2)	O(1)-Ni-O(2)	82.7 (2)	88.5 (1)
N(2)-Ni-O(1)	103.1 (2)	98.2 (2)			
C(1)-N(5)-N(1)	117.9 (5)	117.6 (5)	C(3)-N(6)-N(4)	115.7 (5)	115.9 (5)
N(5)-N(1)-Ni	111.0 (4)	110.9 (3)	N(6)-N(4)-Ni	111.6 (3)	118.1 (3)
N(5)-N(1)-C(5)	117.0 (5)	116.3 (4)	N(6)-N(4)-C(17)	118.8 (5)	114.5 (5)
Ni-N(1)-C(5)	130.1 (4)	131.9 (4)	Ni-N(4)-C(17)	128.8 (4)	124.7 (4)
C(8)-N(2)-Ni	117.9 (4)	121.2 (3)	C(13)-N(3)-Ni	121.8 (4)	121.4 (3)
C(8)-N(2)-C(11)	114.1 (5)	112.4 (4)	C(13)-N(3)-C(12)	116.3 (5)	115.5 (4)
Ni-N(2)-C(11)	106.9 (4)	107.9 (3)	Ni-N(3)-C(12)	104.0 (4)	104.2 (3)
Ni-O(1)-C(3)	114.3 (4)		Ni-O(2)-Cl(2)	128.6 (3)	
O(1)-C(3)-C(4A)	123.9 (6)		O(1)-C(3)-N(6)	120.0 (5)	
Ni-O(1)-C(102)		127.1 (4)	Ni-O(2)-C(104)		126.5 (3)
O(1)-C(102)-C(101)		115.2 (5)	O(2)-C(104)-C(105)		115.5 (5)
O(1)-C(102)-C(103)		126.0 (5)	O(2)-C(104)-C(103)		125.7 (5)
C(102)-C(103)-C(104)		124.8 (5)			

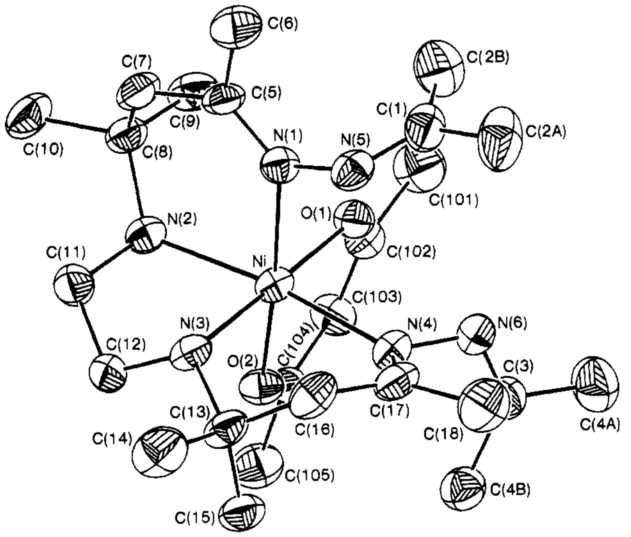

Figure 2. ORTEP projection of the cation [Ni(amba)(acac)]$^+$, showing atomic labeling. Thermal ellipsoids show 50% probability levels.

2,11-dione 2-isopropylidenehydrazone 11-acetylhydrazone, tdaa, i.e. amhy with an isopropylidenehydrazone function at one carbonyl group and an acetylhydrazone function at the other (Scheme II). This ligand *could* be considered to arise from the hydrolysis of the pentane-2,4-dione moiety of the putative 17-membered macrocycle resulting from the condensation of [Ni(amhy)]$^{2+}$ and acacH, but it is not known if this is the mechanism by which it *is* formed. [Ni(tdaa)(H$_2$O)](ClO$_4$)$_2$ was isolated in ca. 60% yield, the other major product being (ethanediimine)bis(pentane-2,4-dionato)nickel(II).

When [Ni(amhy)](ClO$_4$)$_2$ was reacted with acacH in the absence of water (e.g. in methanol/acetonitrile (3:1), the acetonitrile being added to increase the solubility), a rapid reaction yielded [Ni(amhac)](ClO$_4$)$_2$ (the macrocyclic product formed by reaction of [Ni(amhy)]$^{2+}$ with acetone—see Scheme I), which was isolated by evaporation or by addition of propan-2-ol. The mechanism of the formation of this compound is unknown. The acetone required for its formation could arise from hydrolysis of some acacH but is considered more likely to have come from hydrolysis of some of the [Ni(amhy)]$^{2+}$. [Ni(amhac)]$^{2+}$ is also formed when [Ni(amhy)]$^{2+}$ reacts with a variety of other carbonyl compounds, e.g. benzaldehyde. The suggested mechanism involves abstraction of hydrazine from some of the [Ni(amhy)]$^{2+}$ by the carbonyl compound, followed by hydrolysis of the residue of the [Ni(amhy)]$^{2+}$ to release acetone by retro Michael reaction; this acetone then reacts with further [Ni(amhy)]$^{2+}$ to form [Ni(amhac)]$^{2+}$.

The compound [Ni(tdaa)(ClO$_4$)]ClO$_4$ crystallizes from methanol, propan-2-ol, acetone, etc., as the nonsolvated form described above. It crystallizes from water, or solvents containing appreciable amounts of water, as a blue monohydrate, which is relatively resistant to dehydration. An ethanol solvate, apparently structurally similar to the hydrate, crystallizes from ethanol.

Structure of [Ni(tdaa)(ClO$_4$)]ClO$_4$. The structure of [Ni(tdaa)(ClO$_4$)]ClO$_4$ has been determined by X-ray diffractometry, and the complex cation is represented in Figure 1. The compound has the ligand tdaa coordinated by the two secondary amine (N(2), N(3)), two hydrazone nitrogen atoms (N(4), N(5)) of the amhy residue, and also the acetyl amide oxygen atom (O(1)). These are arranged in a square pyramid about the nickel(II) with the isopropylidenehydrazone nitrogen atom N(5) in the axial position. A perchlorate oxygen atom O(2) is weakly coordinated in the sixth coordination site, trans to N(5), to produce a very distorted-octahedral coordination environment about the nickel(II) ion.

The four Ni–N bonds are of approximately equal length, ranging from 2.052 (4) to 2.075 (5) Å, and lie on the short side of the ranges previously observed for high-spin nickel(II) in similar systems.[9–11] The distances to the imine nitrogen atoms are only marginally shorter than those to the amine nitrogen atoms.

The bond lengths and angles within the acetyl amide group and the location of the hydrogen atom on N(6) indicate that it is present in the keto, rather than the possible enol, form. The amide oxygen and adjacent hydrazone nitrogen are both bonded to the nickel atom and subtend an angle of 77.5 (2)°, which is a major cause of distortion of the Ni(II) coordination environment from regular octahedral. The Ni–O(1) distance of 2.065 (4) Å is comparable with the nickel(II)–oxalate oxygen bond lengths in $[(Ni(diac))_2C_2O_4](ClO_4)_2$.[5]

Dimensions within the six-membered amine–imine chelate rings and ethanediamine residue portions of the tdaa ligand are similar to the equivalent parts of the amhy and diac systems previously reported, particularly those with a folded conformation. The ethanediamine residue chelate ring is in a gauche conformation, with NH groups on opposite sides of the equatorial plane.

Torsion angles around the ligand are given in supplementary table III. Most lie reasonably close to the strain-free values, but C(8)–N(2)–C(11)–C(12) (160.4 (5)° cf. 180° for strain free), C(13)–C(16)–C(17)–N(4) (−57.6 (9)° cf. −30°), and C(17)–N(4)–N(6)–C(3) (−179.8 (6)° cf. 90°) are exceptions. The first is imposed by the folding of the ligand and is similar for the other structure reported below. The last two arise from the bidentate nature and small bite of the acetylhydrazone portion of the ligand.

The nickel(II)–perchlorate oxygen distance is long (2.455 (5) Å), and atoms N(2), N(3), N(4), and O(1) are close to coplanar, with the nickel(II) ion displaced 0.17 Å from this plane toward N(1), the atom *trans* to the perchlorate, a value typical of the five-coordinate metalloporphyrins.[12] However, a dimethyl[13] and two dimethyl diisopropyl[14] substituted (1,4,8,11-tetraazacyclotetradecane)nickel(II) (cyclam) complexes have revealed nickel(II)–perchlorate oxygen distances of ca. 2.23, 2.202 (2), and 2.42 (1) Å, respectively. In these compounds, nickel(II)–nitrogen distances are typical of high-spin nickel(II), confirming that they are six-coordinate. Therefore the nickel(II)–perchlorate oxygen contact in $[Ni(tdaa)(ClO_4)]ClO_4$, being of comparable length, should also be regarded as a real, though weak, bond. Metal–perchlorate bonds have also been observed for (*trans*-diperchlorato)(1,4,8,11-tetraazacyclotetradecane)cobalt(II) (2.409 (3) Å)[15] and for a pentaaza macrocyclic complex of Mn(II) (2.30 (4) Å).[16]

Other Compounds of tdaa. Sparingly soluble blue-violet $[Ni(tdaa)(NO_2)]ClO_4$ crystallizes from solutions of $[Ni(tdaa)](ClO_4)_2$ containing nitrite. A blue-violet dithiocyanate was similarly prepared from solutions containing excess thiocyanate. This compound crystallizes as a hydrate from water, or solvents containing appreciable water, and as an anhydrous form from nonaqueous solvents. The thiocyanate perchlorate compound $[Ni(tdaa)(NCS)]ClO_4$ crystallizes from solutions containing 1 mol of thiocyanate.

The Cu(II) compound $[Cu(amhy)](ClO_4)_2$ reacts with acacH in aqueous methanol in a manner similar to that of the Ni(II) compound to form deep blue $[Cu(tdaa)](ClO_4)_2$, in low yield. The compound is more conveniently prepared by substitution of Cu(II) for Ni(II) in $[Ni(tdaa)]^{2+}$. This metal ion substitution reaction is also observed with the amhy complexes and with the complexes of the 15-membered hexaaza macrocycles derived from amhy such as amhac (Scheme I).

The cations $[Ni(tdaa)]^{2+}$ and $[Cu(tdaa)]^{2+}$ are stable in water but are rapidly hydrolyzed by dilute acid.

Spectroscopic Properties. The $\nu_3(ClO_4^-)$ band in the IR spectrum of $[Ni(tdaa)(ClO_4)]ClO_4$ occurs as a well-resolved triplet (1100, 1050 cm^{-1} coordinated; 1083 cm^{-1} ionic). The spectrum of the Cu(II) analogue is similar (1112, 1087 sh, 1072 cm^{-1}), indicating one coordinated perchlorate ion. The Ni(II) perchlorate hydrate has a single broad $\nu_3(ClO_4^-)$ band (1083 cm^{-1}), suggesting that the water has displaced the perchlorate from the coordination sphere.

The IR bands of $[Ni(tdaa)(NO_2)]ClO_4$ assignable to nitrite (ν_{as} 1372, ν_s 1200, δ 845 cm^{-1}) are at similar frequencies to those of $[Ni(amhy)(NO_2)]ClO_4$[2] and other compounds with symmetrical chelate nitrite.[3,17]

$Ni(tdaa)(NCS)_2$ shows sharp doublet $\nu(C\equiv N)$ absorption (2048, 2074 cm^{-1}; Δ 26 cm^{-1}) typical of cis N-coordinated dithiocyanato compounds of octahedral triplet ground-state Ni(II).[18] For the hydrate the bands are at 2024 and 2088 cm^{-1} (Δ 64 cm^{-1}), indicating the presence of one N-coordinated and one ionic thiocyanate. $[Ni(tdaa)(NCS)]ClO_4$ shows a single sharp $\nu(C\equiv N)$ band at 2093 cm^{-1}, indicative of N-coordinated thiocyanate. The $\nu_3(ClO_4^-)$ band of this compound is sharp, with components at 1115 sh (?), 1095, and 1075 cm^{-1}, which could arise from a hydrogen-bonding interaction rather than coordination. The compound crystallizes from methanol and ethanol as solvates that effloresce on exposure to the atmosphere. The IR spectrum of the resultant material is different from that of the compound crystallized from water, but the $\nu(C\equiv N)$ and amide bands occur at about the same frequencies, indicating that the forms have similar coordination environments.

All the compounds show two bands in the 1650–1500-cm^{-1} region assignable to the amide group.[19] For $[Ni(tdaa)(ClO_4)]ClO_4$, with the amide group coordinated, the bands are at 1640 and 1530 cm^{-1} (Δ 110 cm^{-1}). For $[Ni(tdaa)(NO_2)]ClO_4$ and $Ni(tdaa)(NCS)_2$, which have the anions occupying two coordination sites and hence must have tdaa as a tetradentate ligand, presumably with the amide oxygen not coordinated, the bands are at 1630 and 1548 cm^{-1} (Δ 82 cm^{-1}) and 1628 and 1550 br cm^{-1} (Δ 78 cm^{-1}), respectively. Coordination of the amide oxygen thus increases the separation between the bands from ca. 80 to ca. 110 cm^{-1}. $[Ni(tdaa)(NCS)]ClO_4$ has amide bands at 1638 and 1528 cm^{-1} (Δ 110 cm^{-1}), confirming that the amide oxygen is coordinated, while the dithiocyanate hydrate has bands at 1632 and 1545 br cm^{-1} (Δ 87 cm^{-1}), which indicates that the amide group is not coordinated and therefore presumably the water is. The Ni(II) perchlorate hydrate and Cu(II) perchlorate have amide bands at 1630 and 1535 cm^{-1} (Δ 95 cm^{-1}) and 1637 and 1538 cm^{-1} (Δ 89 cm^{-1}), which suggest only very weak amide oxygen coordination is present.

All the Ni(II) compounds, except $[Ni(tdaa)(ClO_4)]ClO_4$, have reflectance spectra with the ν_1 band ($^3T_{2g} \leftarrow {}^3A_{2g}$ of O_h)

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present as a singlet, as is usual for *cis*-NiN_4X_2 chromophores. However, $[Ni(tdaa)(ClO_4)]ClO_4$ of known cis structure has this band as a doublet (8700, 11 600 cm^{-1}), which may be a consequence of the distorted-octahedral geometry about the ion. $[Cu(tdaa)(ClO_4)]ClO_4$ is bright blue, the reflectance spectrum showing a strong band at 15 000 cm^{-1} with a shoulder at ca. 12 000 cm^{-1}, and the spectrum in acetone is similar (15 300 cm^{-1}, ϵ 13.6 m^3 mol^{-1}; ca. 1200 sh cm^{-1}, ϵ 9.6 m^3 mol^{-1}). These values can be compared with those of the compound of the similar but tetradentate ligand amhy, $[Cu(amhy)](ClO_4)_2$, where the solution in acetone has a band at 17 100 cm^{-1}. The shift to lower energy and appearance of a shoulder on the low-energy side of the band for the tdaa compound is indicative of tetragonal interactions.

Reactions of $[Ni(amhy)](ClO_4)_2$ with acacH under Basic Conditions. A rapid reaction occurs between $[Ni(amhy)](ClO_4)_2$ and acacH in the presence of base (e.g., stoichiometric triethylamine in methanol or on addition of a little aqueous ammonia to a methanol solution), to yield a blue product, $[Ni(amhy)(acac)]ClO_4$, which contains discrete tetradentate amhy and bidentate $acac^-$ ligands and is analogous to previously reported[2] compounds $[Ni(amhy)A]ClO_4$, where A represents chelates such as NO_2^-,[2] NO_3^-, $CH_3CO_2^-$, or $^1/_2C_2O_4^{2-}$. The infrared spectrum of this product shows bands at 1583 and 1510 cm^{-1}, lower frequencies than usually observed for compounds of nickel(II) with chelate $acac^-$ (cf. 1590 and 1523 cm^{-1} for [Ni(*rac*-5,5,7,11,11,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)(acac)]ClO_4[20] or 1598 and 1514 cm^{-1} for $Ni(acac)_2(H_2O)$).[21] The compound is stable and shows no tendency to convert to the tdaa species in the solid state or in solution.

Reaction of $[Ni(amhy)](ClO_4)_2$ with acacH in the presence of a higher concentration of ammonia resulted in the formation of the very sparingly soluble blue polymeric μ-hydrazine compound $[Ni(acac)(N_2H_4)]$.

Reactions of $[Ni(amhy)](ClO_4)_2$ with acacH in Acetone. $[Ni(amhy)](ClO_4)_2$ reacts slowly (days) with acetone at room temperature to form the 15-membered macrocyclic compound $[Ni(amac)](ClO_4)_2$ (Scheme I). This reaction is base catalyzed. Reaction of $[Ni(amhy)](ClO_4)_2$, acacH, and acetone in the presence of base (e.g., stoichiometric triethylamine or a little aqueous ammonia) rapidly yields a blue product of composition $[Ni(C_{25}H_{47}N_6O_2)]ClO_4$, i.e. incorporating one amhy, two acetone, and one acacH residues, condensed with the loss of 2 mol of water and 1 mol of H^+. The infrared spectrum of this product shows bands at 1602 and 1517 cm^{-1}, indicative of discrete chelating $acac^-$.

Structure of $[Ni(amba)(acac)]ClO_4$. An X-ray diffractometric study of the compound shows it to be $[Ni(amba)(acac)]ClO_4$, where amba is the tetradentate ligand 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione the bis(isopropylidenehydrazone derivative of amhy. The nickel atom is in an irregular octahedral coordination environment. Two secondary amine nitrogen atoms and one hydrazone nitrogen occupy adjacent meridional sites, with the remaining hydrazone nitrogen axial. The oxygen atoms of the chelating $acac^-$ ligands occupy the two remaining (cis) sites. The complex cation is represented in Figure 2. The Ni–N distances range from 2.100 (4) to 2.161 (4) Å, which are considerably longer than in the tdaa complex and are comparable with the six-coordinate amhy and diac complexes. Those opposite the $acac^-$ oxygen atoms are the shortest, in contrast to $[(Ni(diac))_2C_2O_4](ClO_4)_2$ where those trans to the oxalate oxygen atoms are slightly longer than the others.[5]

Bond lengths and angles within the ligand are comparable with the equivalent dimensions of the tdaa complex, which has the same folding conformation. Although the amba ligand is formally symmetric, the folding of the ligand causes many of the "equivalent" angles to be significantly different.

The only torsion angle markedly divergent from its strain-free value is C(8)–N(2)–C(11)–C(12) (156.6 (4)° cf. strain free 180°), which is imposed by the folding of the ligand, as in the tdaa complex. The torsion angles C(14)–C(16)–C(17)–N(4) and C(17)–N(4)–N(6)–C(3) now have values near to strain free, as restrictions arising from the bonding of the keto oxygen to tdaa to the metal do not apply for amba.

The $acac^-$ chelate is planar and symmetrical, with the nickel atom 0.226 (1) Å out of the ligand plane.[22-24]

$[Ni(amac)]^{2+}$–$[Ni(amba)]^{2+}$ Interconversion. The formation of the bis(isopropylidenehydrazone) ligand, amba, by reaction of $[Ni(amhy)]^{2+}$ with acetone in the presence of $acac^-$ is unusual, since in the absence of the $acac^-$ the macrocylic compound $[Ni(amac)]^{2+}$ (Scheme I) is formed.

The nickel(II) macrocyclic ligand cation $[Ni(amac)]^{2+}$ occurs as the singlet ground-state square-planar perchlorate salt and as triplet ground-state, octahedral compounds with coordinated anions such as *trans*-$[Ni(amac)(NCS)_2]$ and as the cis, folded amac, compounds $[Ni(amac)A]ClO_4$, where A = NO_2^-, NO_3^-, $CH_3CO_2^-$, $^1/_2C_2O_4^{2-}$, etc., similar to $[Ni(amhy)]^{2+}$.[2] Attempts to prepare $[Ni(amac)(acac)]ClO_4$, analogous to $[Ni(amhy)(acac)]ClO_4$, described above, were unsuccessful, $[Ni(amba)(acac)]ClO_4$ being obtained in low yield instead. This yield is improved if the reaction is carried out in acetone. It is concluded that the macrocyclic cation $[Ni(amac)]^{2+}$ and the bisisopropylidenehydrazone) cation $[Ni(amba)]^{2+}$ are interconvertible, the reaction being base catalyzed. The macrocycle amac is the stable form for poorly coordinating anions such as perchlorate and for sterically nondemanding coordinating anions such as thiocyanate and chelate oxyanions, but the bis(isopropylidenehydrazone) amba is the stable form with chelating $acac^-$. The effect is presumably steric in origin, the cation $[Ni(amac)]^{2+}$ with eight methyl substituents is already crowded, and the added bulk of the $acac^-$ chelate, compared with chelating NO_2^-, is sufficient to tip the balance in favor of the more flexible noncyclic amba ligand.

Acknowledgment. We are grateful for the financial support of the Natural Sciences and Engineering Council of Canada through an operating grant (F.W.B.E.) and to the New Zealand Universities Research Grants Committee for support (N.F.C.).

Registry No. 1, 91549-88-1; **2**, 91549-90-5; $[Ni(tdaa)(NO_2)]ClO_4$, 91549-92-7; $[Ni(tdaa)(NCS)(H_2O)]CNS$, 91549-94-9; $[Ni(tdaa)(NCS)]ClO_4$, 91549-96-1; $[Cu(tdaa)(ClO_4)]ClO_4$, 91549-98-3; $[Cu(amhy)](ClO_4)_2$, 82429-34-3; $[Ni(amhy)(acac)]ClO_4$, 91550-00-4; $[Ni(tdaa)(H_2O)](ClO_4)_2$, 91550-02-6; $[Ni(amhy)](ClO_4)_2$, 82429-26-3; amhy, 82424-16-6; acacH, 123-54-6; acetone, 67-64-1.

Supplementary Material Available: Details of X-ray data collection and structure refinement and tables of thermal parameters, hydrogen atom coordinates, selected torsion angles, structure factor listings, and selected bond lengths and angles (47 pages). Ordering information is given on any current masthead page.

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