In the course of the $[Pt(P\text{-}t\text{-}Bu_3)_2]/Ph_2(S)H$ reaction, the trans → cis rearrangement $[PtH(P\text{-}t\text{-}Bu_3)_2\{P(S)Ph_2\}]$ appears unlikely for steric reasons. **2** should be generated from the trans intermediate or its dissociation product $[PtH(P\text{-}t\text{-}Bu_3)(SPPh_2]$. The stability of **2** against H_2 release may be interconnected with the hindered trans → cis rearrangement or the boat conformation of **2**.

Registry No. **1a**, 96617-58-2; **1b**, 96648-01-0; **2**, 96633-12-4; $Pt(PMePh_2)_4$, 27121-53-5; $Pt(P\text{-}t\text{-}Bu_3)_4$, 96617-59-3.

Supplementary Material Available: A packing diagram and full listings of interatomic distances and angles, anisotropic thermal parameters, hydrogen atom positional parameters, least-squares planes, and observed and calculated structure amplitudes (18 pages). Ordering information is given on any current masthead page.

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Reactions of Coordinated β-Polyketonate Ligands. 2. Ligand Oxidation and Benzilic Acid Type Rearrangement in the Nickel(II) Complex of 2,2-Dimethyl-3,5,7-octanetrione. Molecular Structure of the Binuclear Nickel(II) Complex of the Resultant 2-*tert*-Butyl-2-hydroxy-3,5-dioxohexanoic Acid

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The trinuclear Ni(II) complex of 2,2-dimethyl-3,5,7-octanetrione, H_3PAA, was prepared and characterized as $Ni_3(PAA)_2(OH)_2(CH_3OH)_4$. Crystallization of this product from pyridine in air results in ligand oxidation and migration of the *tert*-butyl group from the 3- to the 4-carbon in a benzilic acid type rearrangement. The binuclear Ni(II) complex recovered contains the new ligand 2-*tert*-butyl-2-hydroxy-3,5-dioxohexanoate (2–), $t\text{-}BHMA^{2-}$, with a molecular formula $Ni_2(t\text{-}BHMA)_2(py)_4$. The blue crystals obtained are suitable for single-crystal X-ray studies. They contain, in addition to two Ni(II) ions, two *t*-BHMA dianions, four coordinated pyridine molecules, one pyridine, and three waters of solvation. The crystal belongs to the triclinic space group $P\bar{1}$ and has 2 asymmetric molecules per unit cell. The lattice constants are $a = 10.324$ (3) Å, $b = 15.646$ (3) Å, $c = 16.018$ (5) Å, $\alpha = 87.00$ (2)°, $\beta = 79.45$ (2)°, $\gamma = 75.86$ (2) Å, and $V = 2466$ (1) $Å^3$. The structure was refined by least-squares analysis to a discrepancy factor of $R = 0.062$ for 2927 independent diffractometer data. The coordination sphere of each Ni(II) consists of two cis pyridine nitrogens, two enolate oxygens from the β-diketonate moiety of one $t\text{-}BHMA^{2-}$, and one carboxylate and a hydroxy oxygen from the second $t\text{-}BHMA^{2-}$, forming a five-membered chelate ring. The two nickel atoms are about 5.5 Å apart. A proposed mechanism for the ligand reaction is presented that depends upon initial oxidation at the 4-carbon to yield an σ-diketone as a precursor to the *tert*-butyl rearrangement. No ligand reaction is observed when the initial trinuclear complex is crystallized from pyridine in an inert atmosphere.

Introduction

The β-polyketones are a versatile class of ligands that constitute an homologous series capable of forming an homologous series of transition-metal complexes. The series members 1,3,5-triketones and above afford the opportunity to systematically assess the consequences of having two or more metal ions in close proximity on the chemical and physical properties of these molecular complexes. One of our fundamental interests in this class of compounds is to investigate the chemical significance of placing two or more metal ions in juxtapositions that allow for reasonably strong electronic/magnetic interactions. In this regard, one of the first general class of reactions to consider is the reaction of the ligand itself. Such reactions are interesting of themselves, but they are also important if the complexes are to be useful as potential reagents and/or catalysts, since the reactivity of the ligands may present competing reactions and destruction of the reagent or catalyst. Understanding ligand reactivity is important in the design of molecules for specific reactive purposes so that synthetic strategies may be planned to either block it or enhance it.

The oxidation of coordinated β-polyketonates has not been discussed in any detail. Complexes of the simplest and most familar homologues, the 1,3-diketones, do not appear to be particularly susceptible to ligand oxidation, since solutions of complexes with metal ions in normal oxidation states are routinely handled in air without difficulty. Since oxidation at the 2-carbon of 1,3-diketonates would result in decomposition of the chelate, such reactions would be obvious if they were important. Oxidation of the 1- or 3-carbons to carboxylates in the 1,3-diketonates does not appear to be of significance either. Incorporation of the 1,3-diketone into a macrocyclic ligand by condensation with a tetraamine and subsequent complexation with Co(II) yield a molecular ion in which the 2-carbon is readily oxidized to a carbonyl.[1-3] The oxidized species are isolated intact. Decomposition that would normally take place once the diketonate is oxidized is prevented by the macrocyclic nature of the complex. We have observed a similar type of oxidation at the 4-carbon of bis(1,7-diphenyl-1,3,5,7-heptanetetraonato)dicobalt(II) upon crystallization from 10% pyridine–90% benzene in air. The Co(II) ions are bound in the 1,3- and 5,7-positions, leaving the central position (3,5) empty. Oxidation of the 4-carbon to a carbonyl does not destroy the dianionic character of the ligand and, therefore, the complex. The structure of the oxidized molecule has been reported.[4] This study and the one reported herein are, to our knowledge, the only reports of oxidations of coordinated ligands involving higher homologues of β-polyketones. In both cases the reactions are sensitive to the number and kind of metal ions present.

Experimental Section

Synthesis of Bis(2,2-dimethyl-3,5,7-octanetrionato)dihydroxotetrakis(methanol)trinickel(II), $Ni_3(PAA)_2(OH)_2(CH_3OH)_4$. A solution containing 1.00 g (5.4 × 10^{-3} *m*) of 2,2-dimethyl-3,5,7-octanetrione, H_2PAA, and 1.07 g (1.46 mL) of $(C_2H_5)_3N$ in 50 mL of MeOH was heated to reflux. A solution of 1.62 g (6.51 × 10^{-3} *m*) of $Ni(H_3C_2O_2)_2(H_2O)_2$ in

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(1) Weiss, M. D.; Goedken, V. L. *J. Am. Chem. Soc.* **1976**, *98*, 1976.

(2) Durham, B.; Anderson, T. J.; Switzer, J. A.; Endicott, J. F.; Glick, M. D. *Inorg. Chem.* **1977**, *16*, 271.

(3) Switzer, J. A.; Endicott, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 80.

(4) Lintvedt, R. L.; Ranger, G.; Ceccarelli, C. *Inorg. Chem.* **1985**, *24*, 456.

(5) The abbreviation is based upon a trivial nomenclature commonly used for β-polyketones in which the compounds are treated as derivatives of simple ketones. In this case, $t\text{-}BHMA^{2-}$ stands for *tert*-butylhydroxymalonylacetonato.

(6) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71–147.

(7) Reference 6, pp 148–51.

(8) Steward, R. F.; Davidson, E. K.; Simpson, E. T. *J. Chem. Phys.* **1965**, *42*, 3175.

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Table I. X-ray Experimental Data for $Ni_2(t\text{-}BHMA)_2(py)_4 \cdot py \cdot 3H_2O$

formula	$Ni_2C_{45}H_{59}N_5O_{13}$
mol wt	994.4
color	blue
size, mm^3	0.35 × 0.30 × 0.25
cryst syst	triclinic
space gp	$P\bar{1}$
a, Å	10.324 (2)
b, Å	15.646 (3)
c, Å	16.018 (5)
α, deg	87.00 (2)
β, deg	79.45 (2)
γ, deg	75.86 (2)
V, Å^3	2466 (1)
ρ, g cm^{-3}	1.340
Z	2
μ, cm^{-1}	8.31
2θ scan range, deg	$K\alpha_1$–1 to $K\alpha_2$–2
max dev of stds, %	~5
$2\theta_{max}$, deg	45
no. of data collcd	7085
no. of data with $F_o^2 \geq 3\sigma(F_o^2)$	2927
no. of variables	505
R_1[a]	0.062
R_2[b]	0.085
S[c]	2.028
resid electron density, e/Å^3	0.6
scattering factors	ref 6–8

[a] $R_1 = \sum[|F_o| - |F_c|]/\sum|F_o|$. [b] $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $S = [\sum w(|F_o| - |F_c|]^2/(NO - NV)]^{1/2}$ where NO is the number of observations and NV is the number of variable parameters.

50 mL of MeOH was added dropwise to the ligand solution. The resulting lime green solution was refluxed overnight, yielding a pale green precipitate. The solid was filtered, washed with MeOH, and dried under vacuum. Anal. Calcd for $Ni_3C_{24}H_{46}O_{12}$: C, 41.02; H, 6.60; Ni, 25.06. Found: C, 40.97; H, 6.11; Ni, 25.34.

Synthesis of Bis(2,2-dimethyl-3,5,7-octanetrionato)dihydroxotetrakis(pyridine)dinickel(II), $Ni_2(PAA)_2(OH)_2(py)_4$. Dissolution and crystallization of $Ni_3(PAA)_2(OH)_2(CH_3OH)_4$ from pyridine under N_2 yielded a green binuclear complex formulated as $Ni_2(PAA)_2(OH)_2(py)_4$. Anal. Calcd for $Ni_2C_{40}H_{50}N_4O_8$: C, 57.73; H, 6.06; N, 6.73; Ni, 14.11. Found: C, 56.85; H, 5.98; N, 6.26; Ni, 14.47.

Synthesis of Bis(2-*tert*-butyl-2-hydroxy-3,5-dioxohexanoato(2−))tetrakis(pyridine)dinickel(II) Pyridine Trihydrate, $Ni_2(t\text{-}BHMA)_2 \cdot py \cdot 3H_2O$. Dissolution and crystallization of $Ni_3(PAA)_2(OH)_2(CH_2OH)_4$ from pyridine in a beaker open to the atmosphere yielded blue crystals of $Ni_2(t\text{-}BHMA)_2 \cdot py \cdot 3H_2O$ suitable for single-crystal structure determination.

Crystallography and Structure Determination. A blue crystal of bis(2-*tert*-butyl-2-hydroxy-3,5-dioxohexanoato(2−))tetrakis(pyridine)dinickel(II) pyridine trihydrate was mounted on a glass fiber with epoxy cement, covered with silicone grease, and placed on a Syntex $P2_1$ four-circle diffractometer. A total of 24 intense reflections were precisely centered and yielded the cell constants. The centric space group $P\bar{1}$ was assumed and gave satisfactory refinement throughout. A summary of the X-ray data collection parameters is given in Table I. The nickel positions were obtained by solution of a Patterson map. A series of Fourier maps based on the nickels yielded all the non-hydrogen atoms. Due to the presence of 2 asymmetric molecules in the unit cell, the variable parameters were partitioned into two large blocks. The effect was such that molecule A was refined on odd-numbered cycles and molecule B on even-numbered cycles. The solvent atoms were initially refined isotropically. They refined poorly and were held fixed in the final stages of the refinement. No effort was made to assign the nitrogen atom of the pyridine of crystallization. The molecule was refined with all carbon atoms. Hydrogen atom positions were calculated and thermal parameters assigned at 11% greater than the atom to which they were bound. The distances were 0.95 Å for C–H bonds and 0.90 Å for O–H bonds.

Intensity data were collected with monochromatic Mo Kα radiation (0.710688 Å). The $\theta/2\theta$ scan technique was used at a scan rate of 2°/min. Backgrounds were measured at each end of the scan for a total time equal to half the scan time. Intensities of three standard reflections were measured every 97 reflections with no indication of crystal decomposition or movement. Lorentz, polarization, and decay corrections were applied. Extinction and absorption corrections were not applied. Data for which $F_o^2 \geq 3\sigma(F_o^2)$ were used in the solution and refinement. Atomic coordinates are in Table II. Bond distances and angles are in Tables III and IV. The labeling scheme for the atoms is shown in Figure 1. Tables of hydrogen parameters, thermal parameters, and observed and calculated structure factors have been deposited as supplementary material. Computer programs used are described in ref 9.

Table II. Atomic Coordinates for $Ni_2(t\text{-}BHMA)_2(py)_4 \cdot py \cdot 3H_2O$[a]

atom	x	y	z
Ni(1)A	0.1596 (2)	0.0741 (1)	−0.1229 (1)
O(1)A	0.2539 (8)	0.1268 (5)	−0.0467 (5)
O(2)A	0.1528 (8)	−0.0283 (5)	−0.0376 (5)
O(3)A	0.0409 (8)	−0.1329 (5)	0.0577 (5)
O(4)A	−0.0428 (10)	−0.0337 (5)	0.1925 (5)
O(5)A	0.1558 (9)	−0.0685 (6)	0.2336 (5)
N(1)A	0.1573 (11)	0.1869 (8)	−0.2010 (7)
N(2)A	0.3354 (12)	0.0040 (7)	−0.1936 (6)
C(1)A	0.3429 (15)	0.1547 (10)	0.0702 (8)
C(2)A	0.2818 (13)	0.0991 (9)	0.0249 (8)
C(3)A	0.2533 (13)	0.0219 (9)	0.0637 (8)
C(4)A	0.1890 (12)	−0.0333 (8)	0.0339 (8)
C(5)A	0.1478 (13)	−0.1090 (8)	0.0920 (8)
C(6)A	0.2648 (14)	−0.1948 (9)	0.0910 (9)
C(7)A	0.3914 (14)	−0.1801 (9)	0.1220 (9)
C(8)A	0.2104 (15)	−0.2653 (10)	0.1481 (10)
C(9)A	0.3098 (15)	−0.2318 (9)	0.0000 (10)
C(10)A	0.0851 (16)	−0.0696 (8)	0.1802 (9)
C(11)A	0.1401 (17)	0.2654 (11)	−0.1704 (10)
C(12)A	0.1272 (28)	0.3391 (15)	−0.2152 (17)
C(13)A	0.1334 (24)	0.3346 (16)	−0.2974 (21)
C(14)A	0.1524 (19)	0.2567 (18)	−0.3376 (11)
C(15)A	0.1629 (15)	0.1825 (11)	−0.2852 (11)
C(16)A	0.4441 (18)	0.0341 (9)	−0.2124 (9)
C(17)A	0.5635 (17)	−0.0093 (13)	−0.2625 (10)
C(18)A	0.5670 (21)	−0.0897 (14)	−0.2940 (11)
C(19)A	0.4544 (25)	−0.1208 (12)	−0.2751 (13)
C(20)A	0.3428 (17)	−0.0730 (11)	−0.2256 (11)
Ni(1)B	−0.0969 (2)	0.3786 (1)	0.4265 (1)
O(1)B	−0.2561 (9)	0.4617 (6)	0.3871 (5)
O(2)B	−0.1228 (9)	0.4590 (5)	0.5296 (5)
O(3)B	−0.0510 (9)	0.5494 (5)	0.6287 (5)
O(4)B	−0.0755 (10)	0.6978 (5)	0.5445 (5)
O(5)B	−0.2979 (11)	0.7377 (6)	0.5812 (6)
N(1)B	−0.0696 (12)	0.3101 (8)	0.3118 (7)
N(2)B	−0.2142 (12)	0.2969 (6)	0.4886 (7)
C(1)B	−0.4384 (14)	0.5809 (9)	0.3744 (9)
C(2)B	−0.3275 (14)	0.5325 (9)	0.4199 (8)
C(3)B	−0.3092 (13)	0.5692 (7)	0.4939 (8)
C(4)B	−0.2071 (14)	0.5326 (9)	0.5413 (8)
C(5)B	−0.1859 (14)	0.5882 (8)	0.6147 (8)
C(6)B	−0.2889 (15)	0.5849 (9)	0.7003 (8)
C(7)B	−0.2634 (15)	0.4884 (10)	0.7332 (9)
C(8)B	−0.4390 (15)	0.6164 (9)	0.6925 (8)
C(9)B	−0.2573 (16)	0.6405 (10)	0.7673 (9)
C(10)B	−0.1893 (18)	0.6834 (9)	0.5793 (8)
C(11)B	−0.1063 (17)	0.3480 (10)	0.2427 (11)
C(12)B	−0.0952 (25)	0.3106 (15)	0.1676 (14)
C(13)B	−0.0413 (23)	0.2261 (21)	0.1626 (13)
C(14)B	−0.0021 (18)	0.1772 (11)	0.2319 (15)
C(15)B	−0.0195 (16)	0.2260 (11)	0.3086 (9)
C(16)B	−0.3138 (16)	0.2786 (9)	0.4565 (9)
C(17)B	−0.3870 (16)	0.2208 (11)	0.4918 (11)
C(18)B	−0.3559 (19)	0.1768 (10)	0.5647 (13)
C(19)B	−0.2584 (19)	0.1968 (12)	0.6014 (10)
C(20)B	−0.1890 (15)	0.2571 (10)	0.5612 (11)

[a] The standard deviations in parentheses refer to the least signifiant digit.

Results and Discussion

The isolation of the trinuclear Ni(II) complex, $Ni_3(PAA)_2(OH)_2(CH_3OH)_4$, under conditions that favor the more usual binuclear complex, $Ni_2(PAA)_2(CH_3OH)_4$, is surprising, but not unprecedented. Recently, we reported the preparation of a similar trinuclear complex with the ligand 1,1,1-trifluoro-2,4,6-heptanetrionate(2−), which was formulated as $Ni_3(TFDAA)_2(OH)_2$-

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(9) Guthrie, J. W.; Lintvedt, R. L.; Glick, M. D. *Inorg. Chem.* **1980**, *19*, 2949.

Table III. Bonds Lengths for the Two Asymmetric Units A and B of the Complex $Ni_2(t\text{-}BHMA)_2(py)_4{\cdot}py{\cdot}3H_2O$

	length, Å	
bond type	molecule A	molecule B
	Nickel–Nickel	
	5.456 (4)	5.509 (3)
	Nickel–Oxygen	
Ni(1)–O(1)	2.012 (8)	2.010 (9)
Ni(1)–O(2)	2.057 (8)	2.067 (8)
Ni(1)–O(3)	2.150 (8)	2.146 (8)
Ni(1)–O(4)	2.004 (9)	2.010 (9)
	Nickel–Nitrogen	
Ni(1)–N(1)	2.107 (11)	2.115 (11)
Ni(1)–N(2)	2.046 (11)	2.068 (11)
	Ligand	
C(2)–O(1)	1.26 (1)	1.25 (1)
C(4)–O(2)	1.26 (1)	1.26 (1)
C(5)–O(3)	1.45 (1)	1.43 (1)
C(10)–O(4)	1.28 (1)	1.27 (2)
C(10)–O(5)	1.23 (1)	1.23 (1)
C(2)–C(1)	1.48 (2)	1.50 (2)
C(2)–C(3)	1.40 (2)	1.41 (2)
C(4)–C(3)	1.36 (2)	1.40 (2)
C(4)–C(5)	1.56 (2)	1.57 (2)
C(5)–C(10)	1.54 (2)	1.56 (2)

Table IV. Bond Angles for the Two Asymmetric Units A and B of the Complex $Ni_2(t\text{-}BHMA)_2(py)_4{\cdot}py{\cdot}3H_2O$

	angles, deg	
	molecule A	molecule B
Coordination Sphere Angles		
O(1)–N2(1)–O(2)	89.1 (3)	89.4 (3)
O(1)–Ni(1)–O(3)	94.7 (3)	96.2 (3)
O(1)–Ni(1)–O(4)	172.2 (4)	173.4 (4)
O(1)–Ni(1)–N(1)	88.0 (4)	86.5 (4)
O(1)–Ni(1)–N(2)	94.6 (4)	93.0 (4)
O(2)–Ni(1)–O(3)	85.6 (3)	83.7 (3)
O(2)–Ni(1)–O(4)	92.5 (3)	92.0 (3)
O(2)–Ni(1)–N(1)	174.8 (5)	173.1 (4)
O(2)–Ni(1)–N(2)	91.7 (4)	95.3 (4)
O(3)–Ni(1)–O(4)	77.9 (3)	77.6 (3)
O(3)–Ni(1)–N(1)	90.3 (4)	91.2 (4)
O(3)–Ni(1)–N(2)	170.3 (4)	170.7 (4)
O(4)–Ni(1)–N(1)	89.9 (4)	91.4 (4)
O(4)–Ni(1)–N(2)	92.9 (4)	93.3 (4)
N(1)–Ni(1)–N(2)	92.9 (4)	90.6 (4)
Ring Angles		
O(4)–C(10)–O(5)	123 (1)	124 (1)
C(10)–C(5)–O(3)	107 (1)	108 (1)
O(1)–C(2)–C(3)	124 (1)	125 (1)
C(2)–C(3)–C(4)	127 (1)	125 (1)
C(3)–C(4)–O(2)	126 (1)	127 (1)
Remaining Bond Angles		
Ni(1)–O(1)–C(2)	128.1 (8)	128.5 (8)
Ni(1)–O(2)–C(4)	125.2 (7)	124.8 (8)
Ni(1)–O(3)–C(5)	113.8 (6)	114.6 (6)
Ni(1)–O(4)–C(10)	118.8 (8)	120.0 (9)
Ni(1)–N(1)–C(11)	122.5 (11)	123.2 (10)
Ni(1)–N(1)–C(15)	121.1 (11)	120.3 (11)
Ni(1)–N(2)–C(16)	122.4 (10)	122.0 (10)
Ni(1)–N(2)–C(20)	121.4 (11)	121.2 (11)
O(1)–C(2)–C(1)	117 (1)	116 (1)
C(1)–C(2)–C(3)	120 (1)	119 (1)
O(2)–C(4)–C(5)	114 (1)	114 (1)
C(3)–C(4)–C(5)	120 (1)	119 (1)
O(3)–C(5)–C(4)	106 (1)	105 (1)
O(3)–C(5)–C(6)	107 (1)	109 (1)
C(4)–C(5)–C(6)	114 (1)	113 (1)
C(4)–C(5)–C(10)	107 (1)	107 (1)
C(6)–C(5)–C(10)	115 (1)	104 (1)
O(4)–C(10)–C(5)	116 (1)	116 (1)
O(5)–C(10)–C(5)	121 (1)	120 (1)

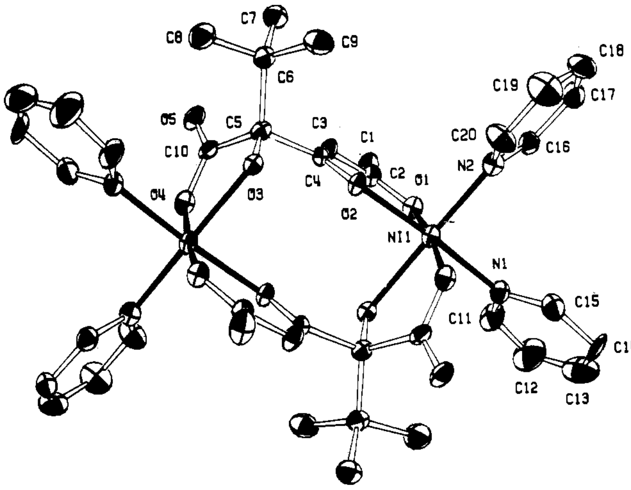

Figure 1. ORTEP drawing and atom-numbering scheme.

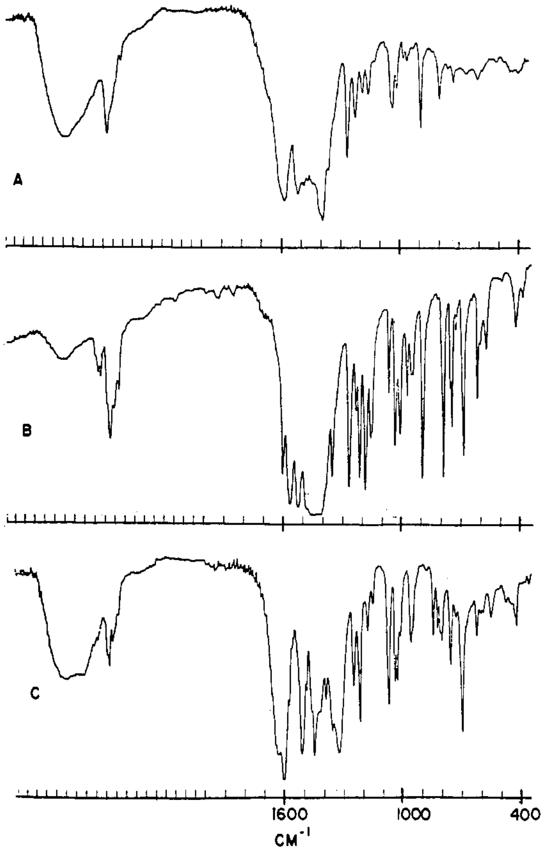

Figure 2. Infrared spectra (KBr pellets): (A) $Ni_3(PAA)_2(OH)_2(CH_3OH)_4$; (B) $Ni_2(PAA)_2(py)_4$; (C) the oxidized product, $Ni_2(t\text{-}BHMA)_2(py)_4{\cdot}py{\cdot}3H_2O$.

$(H_2O)_6$.[9] A complete magnetic susceptiblity study from 4 to 296 K was carried out, and the results were interpreted for a linear array of three Ni(II) ions in which adjacent Ni's are coupled ferromagnetically, J_{12} = 10 cm^{-1}, and terminal Ni's antiferromagnetically, J_{13} = −6 cm^{-1}.[10] These magnetic properties are very similar to those of the trimer $[Ni(acac)_2]_3$ whose structure consists of face-shared octahedra.[11,12] The possibility exists that $Ni_3(PAA)_2(OH)_2(CH_3OH)_4$ has a very similar structure with bridging OH$^-$ ligands as shown below in **1**. This would explain the magnetic similarity to $[Ni(acac)_2]_3$ but may require a sig-

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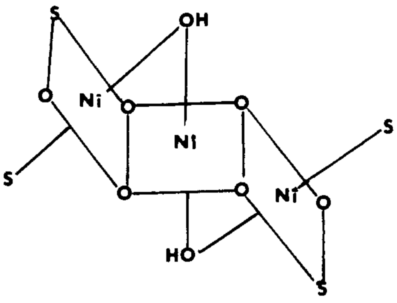
(10) Long, G. L.; Lindner, D.; Lintvedt, R. L.; Guthrie, J. W. *Inorg. Chem.* **1982**, *21*, 1431.

(11) Ginsberg, A. P.; Martin, R. L.; Sherwood, R. C. *Inorg. Chem.* **1968**, *7*, 932.

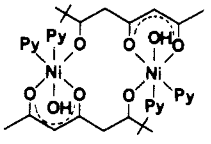
(12) Boyd, P. E. W.; Martin, R. L. *J. Chem. Soc., Dalton Trans.* **1979**, 92.



1

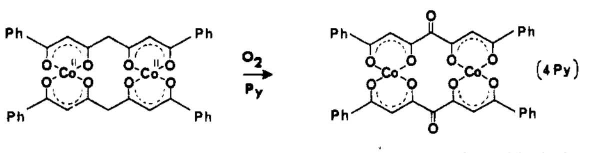
nificant distortion from the usual planarity of the deprotonated 1,3,5-triketonate. Other possibilities are discussed in ref 10. The infrared spectrum of $Ni_3(PAA)_2(OH)_2(CH_3OH)_4$ is shown in Figure 2A.

Recrystallization of the trinuclear Ni(II) complexes from pyridine under a N_2 atmosphere yields a binuclear Ni(II) complex whose molecular formula based upon elemental analysis corresponds to $Ni_2(PAA)_2(OH)_2(py)_4$. While the structure of this compound is not known, the nature of the starting material and the title compound resulting from oxidation of the ligand makes a structure such as **2** a reasonable speculation. Other possibilities exist, of course, but there is no evidence for any ligand reaction having taken place in the absence of O_2. The infrared spectrum is shown in Figure 2B.



2

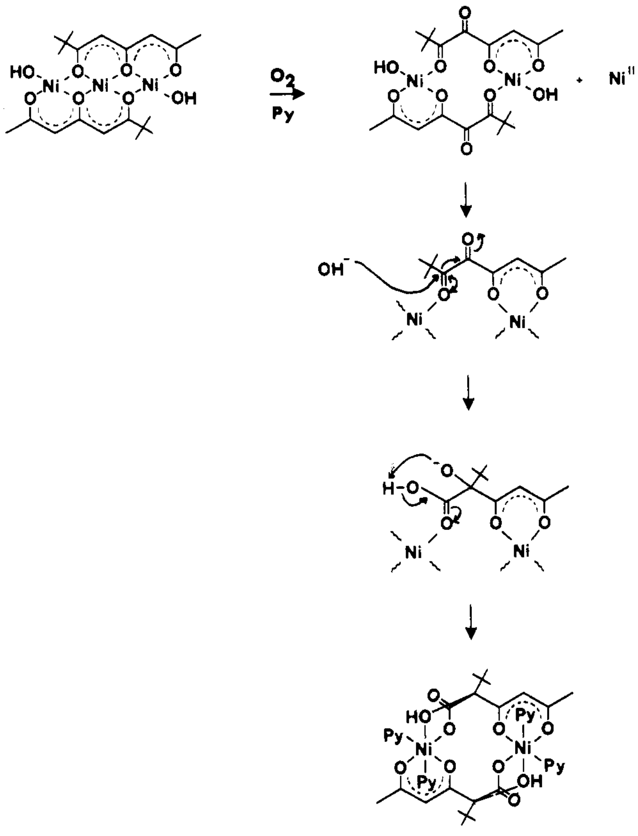
Dissolution of $Ni_3(PAA)_2(OH)_2(CH_3OH)_4$ in pyridine followed by slow evaporation at room temperature in air yields well-formed blue crystals. The infrared spectrum of this product (Figure 2C) indicates that significant changes have taken place in the presence of O_2. The single-crystal X-ray structure determination confirms this. The ligand has undergone both oxidation and a migration of the *tert*-butyl group from the terminal carbonyl 3-carbon to the adjacent 4-carbon. In addition, a hydroxy group resides on the same carbon in the final product. The entire process has converted the original ligand, 2,2-dimethyl-3,5,7-octanetrionate (2−) to 2-*tert*-butyl-2-hydroxy-3,5-dioxohexanoate (2−). The changes that have taken place are explainable by oxidation of the 4-carbon of the original ligand and attack by OH^- on the carbonyl 3-carbon, followed by a benzilic acid type rearrangement. A reasonable mechanism is shown in Scheme I. The benzilic acid type rearrangement requires the formation of an σ-diketone moiety that may be facilitated by the loss of the central Ni(II) to give a compound analogous to $Ni_2(PAA)_2(OH)_2(py)_4$. The fact that the 4-carbon may be more susceptible to oxidation upon loss of the central Ni(II) is supported by the observation that oxidation of the binuclear Co(II) tetraketonate occurs at a similar site under similar conditions[4] (eq 1).



(1)

The final coordination environment of each Ni(II) ion in $Ni_2(t\text{-BHMA})_2(py)_4$ consists of one β-diketonate chelate ring, a carboxylate oxygen, and one OH oxygen that together form a 5-membered σ-hydroxy carboxylate chelate ring and two pyridine nitrogens. An ORTEP drawing of the binuclear molecule is shown in Figure 1. The molecular packing in the cell is composed of 2 asymmetric units A and B. The atomic coordinates and the important bond lengths and angles for both asymmetric molecules are presented in Tables II–IV, respectively. The average bond distances in the coordination spheres are Ni–O(carboxylate) = 2.01 Å, Ni–O(enolate) = 2.06 and 2.01 Å, Ni-O(hydroxy) = 2.15 Å, and Ni–N(pyridine) = 2.08 Å. These distances are quite normal. It is interesting to note that the sum of the trans O_1–Ni–O_4 bond length is significantly less than the sum of the other trans bonds, O_3–NI–N_2 and O_2–Ni–N_1. The difference in these sums is close to 0.2 Å. Thus, the pseudooctahedral coordination sphere is contracted along one axis. This does not appear to be simply due to the fact that the shortened axis is the one with two oxygen donors and the other two have one oxygen and one nitrogen since the Ni–N distances are normal or shorter than expected. That is, axial Ni–N(pyridine) distances in related β-polyketonate complexes are 2.156,[13] 2.112,[14] and 2.175 Å.[15] In the title compound, the Ni–N distances appear to adjust so that trans O–Ni–N sum is about 4.19 Å, i.e. Ni–O_3 + NiN_2 = 2.150 + 2.046 Å and Ni–O_2 + Ni–N_1 = 2.057 + 2.107 Å.

Scheme I



The other distortion from pseudooctahedral geometry is evident in the deviation from 180° for all three pseudoaxes. They all are distorted toward the center of the molecule from about 5–10°. The largest distortion occurs in the O_3–Ni–N_2 angle which is about 170°. This most likely is the result of the constraints placed on the coordination sphere by the five-membered chelate ring and the nature of the bonding at carbon 5.

Not only is the ligand reaction unusual from the standpoint that, to our knowledge, no analogous reactions have been observed for β-diketones or other β-triketones, but it is metal ion specific. Complexes of the same ligand, 2,2-dimethyl-3,5,7-octanetrione, H_2PAA, with Cu(II) and Zn(II) are routinely crystallized in our laboratory from pyridine in air without any observable oxidation of the ligand. Thus, Ni(II) appears to specifically initiate the reaction whereas Cu(II) and Zn(II) do not. There is an imporant difference between the H_2PAA complex of Ni(II) and those of Cu(II) and Zn(II) that may influence the oxidizability of the ligand. This is the fact that Cu(II) and Zn(nII) form "normal"

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(13) Lintvedt, R. L.; Borer, L. L.; Murtha, D. P.; Kuszaj, J. M.; Glick, M. D. *Inorg. Chem.* **1974**, *13*, 18.

(14) Elder, R. C. *Inorg. Chem.* **1968**, *7*, 2316.

(15) Lintvedt, R. L.; Schoenfelner, B. A.; Ceccarelli, C.; Glick, M. D. *Inorg. Chem.* **1984**, *23*, 2867.

binuclear complexes, $M_2(PAA)_2$. Under identical synthetic conditions, only the trinuclear Ni(II) is isolated. Crystallization of the Cu(II) and Zn(II) complexes from pyridine in air yields crystals of the pyridine adduct, $M_2(PAA)_2(py)_2$, in which the metals are bonded to four enolate oxygens, two terminal and two bridging, and one pyridine nitrogen in typical five-coordinate manner. The triketonate moieties in such complexes are very nearly planar as demonstrated in a number of structural studies.[16] Since there is some reason to believe that PAA^{2-} in $Ni_3(PAA)_2(OH)_2(CH_3OH)_4$ might be distorted from planarity, i.e. if the structure is similar to $[Ni(acac)_2]_3$, there is the possibility that such distortions account for the oxidizability of the ligands rather than the metal itself.

Acknowledgment is made to the National Science Foundation, Grant CHE 8300251, for support of this research.

Registry No. H_2PAA, 66734-21-2; $Ni_3(PAA)_2(OH)_2(CH_3OH)_4$, 96504-41-5; $Ni_2(PAA)_2(OH)_2(py)_4$, 96532-46-6; $Ni_2(t\text{-}BHMA)_2(py)_4\cdot py\cdot 3H_2O$, 96504-43-7.

Supplementary Material Available: Complete listing of hydrogen atom parameters, final positional and thermal parameters, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(16) See for example, ref 9 and 13.

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Kinetic Studies on the Rearrangements of *B*-Monochloro Derivatives of *closo*-2,4-$C_2B_5H_7$ and on the Rearrangement of 5,6-Cl_2-*closo*-2,4-$C_2B_5H_5$. Characterization of All *B*,*B'*-Cl_2-*closo*-2,4-$C_2B_5H_5$ Isomers

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The rearrangement patterns for two *B*-monochloro derivatives of *closo*-2,4-$C_2B_5H_7$ suggest that a triangular-face-rotation mechanism for such a reaction in this set of compounds is highly unlikely. The relative stabilities of the *B*,*B'*-dichloro derivatives of this cage carborane system have been determined from a rearrangement rate study on one of the isomers; a correlation of these *B*,*B'*-Cl_2-$C_2B_5H_5$ isomer stabilities with the results from the thermal equilibration of the *B*-monochloro set of isomers leads to the suggestion that, with the exception of the 1,3-Cl_2 isomer, a (substituent) positional additivity effect is operating. An electronic interaction through the cage between a Cl located in an apical position and a Cl located at the unique equatorial 3-position may account for the stability of the 1,3-Cl_2 isomer. All of the *B*,*B'*-Cl_2-*closo*-2,4-$C_2B_5H_5$ isomers are characterized for the first time. A slow side reaction observed during the rearrangement reactions involves intermolecular chlorine exchange; the rate of this halogen exchange is considerably reduced when the rearrangements are carried out at reduced pressures.

Introduction

Preparations of the monochloro-*closo*-dicarbaheptaborane isomer 5-Cl-*closo*-2,4-$C_2B_5H_6$[1] and the dichloro isomer 5,6-Cl_2-*closo*-2,4-$C_2B_5H_5$ are effected by the aluminum chloride catalyzed reactions of the parent *closo*-2,4-$C_2B_5H_7$ with varying quantities of Cl_2.[2,3] Presumed electrophilic halogen attack occurs predominantly at the electron-rich equatorial boron 5- and 6-positions[4] with only trace evidence of attack at the axial 1- (or symmetry-related 7-) position.[5] Both 1- and 3-Cl-$C_2B_5H_6$, as well as the 5-Cl isomer, can be obtained from a light-initiated reaction of $C_2B_5H_7$ with Cl_2,[2] but both the 1- and 3-Cl isomers are more reliably obtained in usable quantities from the thermal rearrangement of 5-Cl-$C_2B_5H_6$.[3] Subjecting the dichloro cage compound, 5,6-Cl_2-$C_2B_5H_5$, to thermal rearrangement conditions leads to a mixture of *B*,*B'*-Cl_2-isomers; however, difficulty in separating the various isomers along with lack of adequate NMR peak resolution made full identification and characterization of the various *B*,*B'*-dichloro isomers uncertain.[3]

In the present study we report a procedure used to characterize all of the *B*,*B'*-Cl_2-$C_2B_5H_5$ isomers; in addition, kinetic studies are carried out on one dichloro and two monochloro isomers.

Experimental Section

Nuclear Magnetic Resonance Spectroscopy. Boron-11 (160.44-MHz) and proton (60-MHz) NMR spectra were obtained on Bruker WM-500 FT and Bruker WP-60 spectrometers, respectively. For the rearrangement studies, proton-decoupled boron spectra were recorded at all time intervals cited in the tables; an occasional proton-coupled boron NMR spectrum was recorded for verifying peak assignments. Triple-resonance studies, observing the proton resonance, while decoupling both ^{11}B and ^{10}B resonances, were conducted with a modified WP-60 probe equipped to accept two decoupling channels; two frequency synthesizers (Fluke 6160B and General Radio 1062), each output modulated by a homemade pseudo-random-noise generator driving an Electronic Navigation Industries Model 320L power amplifier, were used to decouple the two boron isotopes. Delay times between pulses were varied during the course of measuring the spectra of several samples in order to verify the saturation effects were negligible in all *B*-chloro- and *B*,*B'*-dichlorocarborane spectra employed for the determination of the relative carborane concentrations in rearrangement mixtures. All ^{11}B chemical shift data are based on $\delta(BF_3\cdot Et_2O)$ 0.00, with the parent 2,4-$C_2B_5H_7$ used as a secondary standard: $\delta(B(1,7))$ −21.73 (J = 180 Hz), $\delta(B(3))$ 7.02 (J = 184 Hz), $\delta(B(5,6))$ 3.83 (J = 170 Hz). Negative chemical shift values are upfield of the $BF_3\cdot Et_2O$ resonance. Approximate chemical shift and coupling constant errors for all dicarbaheptaboranes (parent and derivatives) are as follows: ±0.02 ppm and ±3 Hz for the cage 1-, 3-, and 7-positions of carborane; ±0.06 ppm and ±10 Hz, for the 5- and 6-positions.

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(1) The compounds reported in the present work have been named, and numbered, by using previously accepted nomenclature rules. It is noted, however, that a new nomenclature scheme has been devised for cage polyboranes; e.g., 5-(chloro)hexahydro-2,4-dicarba[D_{5h}-($1v^5 5v^4 1v^5$)-Δ^{10}-*closo*]heptaborane is recommended for 5-Cl-*closo*-2,4-$C_2B_5H_6$: (a) Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1983**, *22*, 2236–2245. (b) *Ibid.* **1983**, *22*, 2228–2235. (c) *Ibid.* **1981**, *20*, 3556–3561. (d) *Ibid.* **1981**, *20*, 1333–1341.

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(4) Dixon, D. A.; Kleier, D. A.; Halgren, T. A.; Hall, J. H.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1977**, *99*, 6226–6237. A value for the group charge of B(3)H of 2,4-$C_2B_5H_7$ in this reference has been corrected to read +0.06.

(5) Siwapinyoyos, G.; Onak, T. *Inorg. Chem.* **1982**, *21*, 156–163.

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