interactions along the chains. The number of bromide complexes that have been studied is significantly smaller than the number of chlorides. From magnetic interests, this is unfortunate, since exchange couplings are typically larger for copper(II) bromide complexes.

Acknowledgment. The support of NSF Grant DMR 8803382 is acknowledged. The WSU X-ray diffraction laboratory was established through funds from NSF Grant CHE-8408407 and The Boeing Corp.

Supplementary Material Available: Listings of hydrogen positional coordinates, anisotropic thermal parameters, and bond distances and angles for $(HAmpym)CuCl_3(H_2O)$ (Table 1s) and $(H_2Me_2pipz)[CuCl_3(H_2O)]_2$ (Tables 3s-5s), hydrogen positional coordinates and anisotropic thermal parameters for $(HAmpym)_2Cu_2Cl_6$ (Tables 7s and 8s), and data collection and refinement parameters (Table 10s), a packing diagram for $(HAmpym)_2Cu_2Cl_6$, and Appendix A, containing text discussing stacked copper complexes and a listing of structural parameters for stacked copper species (Table 11s) (22 pages); listings of observed and calculated structure factors (Tables 2s, 6s, and 9s) (38 pages). Ordering information is given on any current masthead page.

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Trialkoxysiloxy Complexes of Nickel. Molecular Structures of $Na_3(\mu_3\text{-}I)\{Ni[\mu_3\text{-}OSi(O^tBu)_3]_3I\}\cdot 0.5THF\cdot 0.5C_5H_{12}$ and $\{(\eta^3\text{-}C_3H_5)Ni[\mu_2\text{-}OSi(O^tBu)_3]\}_2$

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Received September 25, 1989

The nickel siloxide complex $Na_3(\mu_3\text{-}I)\{Ni[\mu_3\text{-}OSi(O^tBu)_3]_3I\}\cdot 0.5THF\cdot 0.5C_5H_{12}$ (**1**) is prepared by reaction of $NiI_2(THF)_2$ with $NaOSi(O^tBu)_3$ in refluxing tetrahydrofuran. The dimeric allyl derivative $\{(\eta^3\text{-}C_3H_5)Ni[\mu_2\text{-}OSi(O^tBu)_3]\}_2$ (**2**) is obtained from $Ni(\eta^3\text{-}C_3H_5)_2$ and $HOSi(O^tBu)_3$. Complex **1** crystallizes in space group $P\bar{1}$ with $a = 13.953$ (2) Å, $b = 14.042$ (2) Å, $c = 18.934$ (3) Å, $\alpha = 80.61$ (1)°, $\beta = 87.27$ (1)°, $\gamma = 60.02$ (1)°, $V = 3168$ (1) Å^3, $Z = 2$, and $R_F = 4.65\%$. Complex **2** crystallizes in space group $P2_1$ with $a = 14.474$ (4) Å, $b = 10.336$ (2) Å, $c = 15.651$ (3) Å, $\beta = 117.42$ (2)°, $V = 2078.2$ (8) Å^3, $Z = 4$, and $R_F = 6.20\%$.

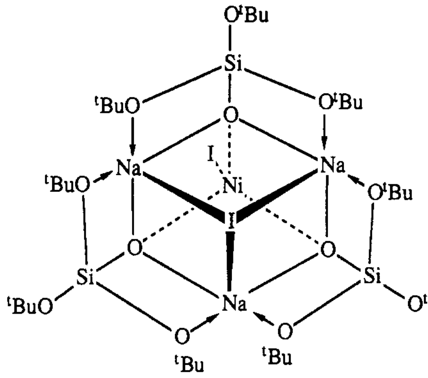
There is renewed interest in alkoxy and siloxy complexes of the transition metals, partly because such species are being shown to display unusual and interesting reactivity patterns.[1] Also, these compounds are becoming popular as precursors to oxide ceramic materials.[2] Trialkoxysiloxy ligands, $-OSi(OR)_3$,[3-6] can potentially provide unique electronic and structural properties for transition-metal derivatives. For example, the presence of four donor atoms creates the possibility for these ligands to behave in a multidentate fashion. We are therefore interested in exploring the coordination chemistry of such ligands and in delineating structural and chemical properties that result from their coordination to transition metals. One goal of this work is to develop complexes that may function as convenient molecular precursors to transition-metal oxide and silicate materials via hydrolysis or thermolysis.

The chemistry of nickel alkoxides has not been extensively developed,[1f,g] and to our knowledge the only previous reports of siloxide derivatives describe $[(PMe_3)(Me)Ni(\mu_2\text{-}OSiMe_3)]_2$[7] and $PhSi(OH)_2ONiOSi(OH)PhOSi(OH)_2Ph$,[8] although polymeric species with Ni–O–Si linkages have been prepared.[9] In this paper, we describe the synthesis and characterization of two tri-*tert*-butoxysiloxy derivatives of nickel, $Na_3(\mu_3\text{-}I)\{Ni[\mu_3\text{-}OSi(O^tBu)_3]_3I\}\cdot 0.5THF\cdot 0.5C_5H_{12}$ (**1**) and $\{(\eta^3\text{-}C_3H_5)Ni[\mu_2\text{-}OSi(O^tBu)_3]\}_2$ (**2**).

Results and Discussion

Anhydrous nickel halides $NiCl_2$ and $NiBr_2$ are unreactive toward either $NaOSi(O^tBu)_3$ or $LiOSi(O^tBu)_3$ in diethyl ether or dichloromethane, presumably because of the insolubility of the metal dihalide. However, $NiI_2(THF)_2$ reacts slowly with $NaOSi(O^tBu)_3$ in refluxing tetrahydrofuran to form a nickel siloxide complex that crystallizes from pentane as the blue solvate $Na_3(\mu_3\text{-}I)\{Ni[\mu_3\text{-}OSi(O^tBu)_3]_3I\}\cdot 0.5THF\cdot 0.5C_5H_{12}$ (**1**, eq 1).

$$NiI_2(THF)_2 + 2\,NaOSi(O^tBu)_3 \xrightarrow[\text{reflux}]{\text{THF}} \qquad (1)$$



1

Crystals of this compound decompose slowly over a few months when stored under nitrogen at room temperature. Once isolated, compound **1** decomposes when redissolved in pentane, diethyl ether, benzene, or dichloromethane, as evidenced by rapid discoloration of the solution and precipitation of NaI. The compound is more stable in tetrahydrofuran, and recrystallization from pentane is possible in the presence of a small amount of tetrahydrofuran. The room-temperature EPR spectrum of a powdered

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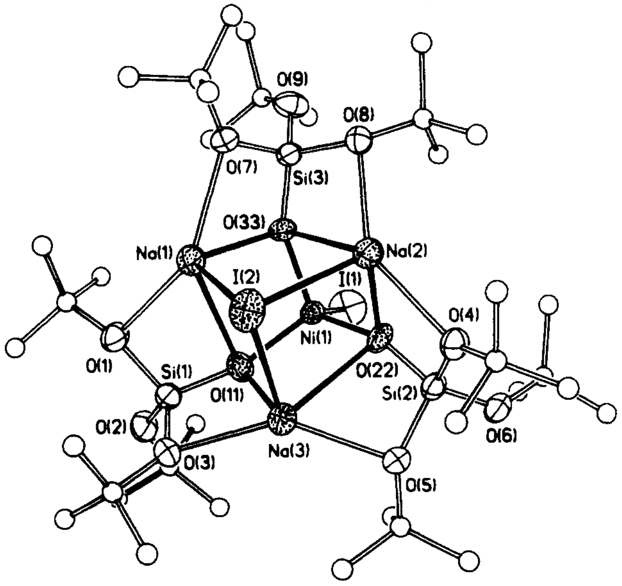

Figure 1. ORTEP view of the nickel complex in $Na_3(\mu_3\text{-}I)\{NiI[\mu_3\text{-}OSi(O^tBu)_3]_3\}\cdot 0.5THF\cdot 0.5C_5H_{12}$ (**1**), with the atom-labeling scheme.

Table I. Crystallographic Data for Compounds **1** and **2**

formula	$C_{40.5}H_{91}I_2Na_3NiO_{12.5}Si_3$	$C_{15}H_{32}NiO_4Si$
fw	1243.8	726.36
space group	$P\bar{1}$	$P2_1$
a, Å	13.953 (2)	14.474 (4)
b, Å	14.042 (2)	10.336 (2)
c, Å	18.934 (3)	15.651 (3)
α, deg	80.61 (1)	90
β, deg	87.27 (1)	117.42 (2)
γ, deg	60.02 (1)	90
V, Å^3	3168 (1)	2078.2 (8)
Z	2	2
D(calcd), g cm^{-3}	1.304	1.161
μ, cm^{-1} (Mo Kα)	13.92	10.03
temp, °C	23	23
T(max)/T(min)	1.052	1.042
R_F	4.65	6.20
R_{wF}	4.87	6.13

sample contains a broad resonance at $g = 1.750$.

Figure 1 provides a view of $Na_3(\mu_3\text{-}I)\{Ni[\mu_3\text{-}OSi(O^tBu)_3]_3I\}$, and relevant bonding parameters are listed in Tables II and III. The molecule forms a cubelike structure, with vertices defined by a nickel(II) center, three sodium ions, three silanolate oxygens, and an iodide. Angles between least-squares planes of the cube range from 73.9 to 104.9°. Distortions in the cube are such that the angles at Ni(1) are greater than 90° (average 98.6°), and the Na-I-Na (average 71.2°) and O-Na-O (average 71.3°) angles are significantly less than 90°. There is an approximate (noncrystallographic) 3-fold axis of rotation that is coincident with the Ni(1)-I(1) bond and passes through I(2). The molecule contains the $Ni[OSi(O^tBu)_3]_3(I)^{2-}$ anion, which binds three sodium ions. The sodium ions are held together by a triply bridging iodide and by bridging interactions with the three siloxy groups of $Ni[OSi(O^tBu)_3]_3(I)^{2-}$. Each tri-*tert*-butoxysiloxy ligand is triply bridging to the nickel and two sodium ions through the silanolate oxygen and bridges a pair of sodium ions via two butoxy groups. The $OSi(O^tBu)_3$ ligands therefore contribute five bonding interactions apiece to the cluster. This bridging mode results in three "wings" that extend from adjacent edges of the cube, pointing away from I(1) and toward I(2).

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for **1**

	x	y	z	U^a
I(1)	3395.4 (6)	8352.9 (6)	4623.2 (3)	84.2 (4)*
I(2)	2884.9 (5)	9082.2 (5)	670.5 (3)	69.3 (3)*
Ni(1)	3306.0 (7)	8513.6 (7)	3260.1 (4)	36.3 (4)*
Na(1)	4535 (2)	8879 (2)	1788 (2)	57 (1)*
Na(2)	1603 (2)	10286 (2)	1930 (2)	54 (1)*
Na(3)	3115 (2)	7312 (2)	1946 (2)	57 (2)*
Si(1)	5460 (2)	6420 (2)	2485 (1)	47 (1)*
Si(2)	925 (2)	8654 (2)	2681 (1)	43 (1)*
Si(3)	3210 (2)	10947 (2)	2486 (1)	43 (1)*
O(11)	4310 (4)	7340 (4)	2721 (3)	52 (2)*
O(22)	1900 (4)	8853 (4)	2840 (2)	48 (3)*
O(33)	3492 (4)	9701 (4)	2708 (3)	48 (2)*
O(1)	6113 (4)	7034 (4)	2051 (3)	58 (3)*
O(2)	6339 (4)	5449 (4)	3079 (3)	61 (3)*
O(3)	5078 (4)	5934 (4)	1892 (3)	54 (3)*
O(4)	256 (4)	9657 (4)	2005 (2)	51 (2)*
O(5)	1439 (4)	7454 (4)	2390 (3)	54 (3)*
O(6)	107 (4)	8619 (4)	3300 (3)	57 (3)*
O(7)	3879 (4)	10881 (4)	1745 (3)	57 (3)*
O(8)	1876 (4)	11740 (4)	2262 (2)	48 (2)*
O(9)	3475 (4)	11557 (4)	3027 (3)	62 (3)*
C(1)	7108 (7)	7069 (7)	2199 (6)	86 (5)*
C(11)	7102 (9)	7943 (9)	1638 (7)	138 (8)*
C(12)	7020 (10)	7399 (11)	2921 (7)	148 (10)*
C(13)	8096 (7)	5935 (8)	2201 (7)	138 (8)*
C(2)	6307 (7)	4726 (7)	3702 (5)	76 (5)*
C(21)	7384 (8)	3691 (8)	3779 (6)	148 (7)*
C(22)	5354 (10)	4572 (12)	3693 (7)	164 (11)*
C(23)	6208 (11)	5291 (11)	4336 (6)	153 (10)*
C(3)	5668 (7)	5233 (7)	1351 (5)	71 (5)*
C(31)	5836 (9)	5923 (9)	717 (5)	109 (7)*
C(32)	4909 (10)	4838 (11)	1127 (7)	151 (11)*
C(33)	6744 (9)	4265 (9)	1650 (6)	138 (8)*
C(4)	−609 (7)	9918 (7)	1484 (4)	64 (5)*
C(41)	−837 (9)	10980 (8)	1022 (5)	122 (7)*
C(42)	−1587 (8)	9958 (12)	1856 (6)	150 (10)*
C(43)	−170 (9)	9023 (9)	1014 (5)	116 (8)*
C(5)	1569 (7)	6390 (7)	2738 (6)	73 (5)*
C(51)	440 (7)	6465 (7)	2758 (6)	97 (6)*
C(52)	2343 (9)	5558 (8)	2283 (7)	122 (7)*
C(53)	2069 (8)	6086 (9)	3481 (6)	117 (7)*
C(6)	−475 (7)	9233 (8)	3871 (4)	68 (5)*
C(61)	−1532 (8)	9193 (10)	3928 (6)	121 (8)*
C(62)	−655 (11)	10384 (8)	3739 (6)	132 (9)*
C(63)	237 (10)	8561 (11)	4560 (5)	130 (10)*
C(7)	3931 (8)	11696 (8)	1190 (5)	83 (6)*
C(71)	3400 (23)	11742 (16)	577 (7)	401 (30)*
C(72)	5043 (13)	11258 (16)	1014 (13)	477 (21)*
C(73)	3506 (13)	12760 (10)	1387 (7)	184 (12)*
C(8)	969 (6)	12430 (6)	2680 (4)	57 (4)*
C(81)	1065 (8)	11855 (8)	3429 (4)	88 (6)*
C(82)	963 (7)	13521 (6)	2672 (5)	77 (5)*
C(83)	−84 (6)	12666 (7)	2300 (5)	87 (5)*
C(9)	4320 (8)	11307 (7)	3541 (5)	89 (6)*
C(91)	5288 (10)	10244 (11)	3513 (9)	217 (12)*
C(92)	4550 (12)	12222 (10)	3453 (7)	176 (12)*
C(93)	3873 (12)	11205 (13)	4285 (6)	182 (13)*
Cp(1)	0	5000	0	294 (16)
Cp(2)	277 (31)	5647 (30)	94 (21)	381 (20)
Cp(3)	693 (26)	6198 (28)	142 (18)	338 (16)
Ot(1)	1610 (27)	3842 (32)	5033 (22)	535 (22)
Ct(1)	623 (27)	4171 (27)	4829 (20)	432 (20)
Ct(2)	−557 (62)	5044 (60)	4611 (23)	416 (23)

[a] An asterisk denotes the equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The nickel center in **1** has a distorted tetrahedral coordination geometry, with I-Ni-O angles (average 118.9°) that are ca. 10° greater than the O-Ni-O angles (average 98.6°). The Ni-O distances (average 1.95 Å) are slightly shorter than comparable distances found in the related cluster $[Ni_4(OMe)_4(OAc)_2$(2,5-dimethyl-2,5-diisocyanohexane)$_4](BPh_4)_2$, which also has a

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Table III. Selected Distances and Angles for **1**

(a) Distances (Å)

Ni(1)–I(1)	2.557 (1)	Na(3)–O(22)	2.770 (5)
Ni(1)–O(11)	1.955 (5)	Na(3)–O(3)	2.449 (5)
Ni(1)–O(22)	1.949 (5)	Na(3)–O(5)	2.369 (6)
Ni(1)–O(33)	1.944 (5)	Si(1)–O(11)	1.579 (4)
Na(1)–I(2)	3.077 (3)	Si(2)–O(22)	1.571 (7)
Na(2)–I(2)	3.104 (3)	Si(3)–O(33)	1.574 (5)
Na(3)–I(2)	3.072 (3)	Si(1)–O(1)	1.652 (7)
Na(1)–O(11)	2.695 (6)	Si(1)–O(2)	1.609 (5)
Na(1)–O(33)	2.285 (5)	Si(1)–O(3)	1.636 (7)
Na(1)–O(1)	2.406 (4)	Si(2)–O(4)	1.644 (4)
Na(1)–O(7)	2.472 (6)	Si(2)–O(5)	1.648 (6)
Na(2)–O(22)	2.300 (5)	Si(2)–O(6)	1.608 (6)
Na(2)–O(33)	2.756 (6)	Si(3)–O(7)	1.639 (5)
Na(2)–O(4)	2.435 (7)	Si(3)–O(8)	1.653 (4)
Na(2)–O(8)	2.434 (7)	Si(3)–O(9)	1.599 (7)
Na(3)–O(11)	2.293 (7)		

(b) Angles (deg)

Na(1)–I(2)–Na(2)	70.4 (1)	Na(1)–I(2)–Na(3)	71.6 (1)
Na(2)–I(2)–Na(3)	71.6 (1)	O(11)–Ni(1)–O(33)	96.7 (2)
O(11)–Ni(1)–O(22)	99.0 (2)	O(22)–Ni(1)–O(33)	100.1 (2)
I(2)–Na(1)–O(33)	105.7 (2)	I(2)–Na(1)–O(11)	93.7 (2)
O(11)–Na(1)–O(33)	71.1 (2)	I(2)–Na(2)–O(22)	103.8 (1)
I(2)–Na(2)–O(33)	94.2 (1)	O(22)–Na(2)–O(33)	71.7 (2)
I(2)–Na(3)–O(11)	102.7 (2)	I(2)–Na(3)–O(22)	94.1 (1)
O(11)–Na(3)–O(22)	71.1 (2)	Na(1)–O(11)–Na(3)	91.9 (2)
Na(1)–O(11)–Ni(1)	89.1 (2)	Ni(1)–O(11)–Na(3)	102.3 (2)
Ni(1)–O(22)–Na(2)	101.0 (3)	Ni(1)–O(22)–Na(3)	87.4 (2)
Na(2)–O(22)–Na(3)	90.4 (2)	Ni(1)–O(33)–Na(1)	89.1 (2)
Ni(1)–O(33)–Na(2)	86.9 (2)	Na(1)–O(33)–Na(2)	89.5 (2)
I(1)–Ni(1)–O(11)	124.6 (1)	I(1)–Ni(1)–O(22)	115.8 (1)
I(1)–Ni(1)–O(33)	116.3 (2)	O(11)–Si(1)–O(1)	108.9 (3)
O(11)–Si(1)–O(2)	119.8 (3)	O(11)–Si(1)–O(3)	102.0 (3)
O(1)–Si(1)–O(2)	106.0 (3)	O(1)–Si(1)–O(3)	106.9 (3)
O(2)–Si(1)–O(3)	112.5 (3)	O(22)–Si(2)–O(4)	101.6 (3)
O(22)–Si(2)–O(5)	108.9 (3)	O(22)–Si(2)–O(6)	120.9 (3)
O(4)–Si(2)–O(5)	108.1 (3)	O(5)–Si(2)–O(6)	105.0 (3)
O(4)–Si(2)–O(6)	111.9 (2)	O(33)–Si(3)–O(7)	101.4 (3)
O(33)–Si(3)–O(8)	109.3 (3)	O(33)–Si(3)–O(9)	120.7 (3)
O(7)–Si(3)–O(8)	106.8 (2)	O(7)–Si(3)–O(9)	111.9 (3)
O(8)–Si(3)–O(9)	106.0 (3)	Na(1)–O(1)–C(1)	111.3 (5)
Na(1)–O(1)–Si(1)	97.4 (2)	Si(1)–O(1)–C(1)	134.6 (5)
Si(1)–O(2)–C(2)	136.6 (4)	Na(3)–O(3)–C(3)	130.5 (5)
Na(3)–O(3)–Si(1)	93.2 (2)	Si(1)–O(3)–C(3)	133.3 (5)
Na(2)–O(4)–C(4)	128.9 (5)	Na(2)–O(4)–Si(2)	93.7 (3)
Si(2)–O(4)–C(4)	135.3 (6)	Si(2)–O(6)–C(6)	138.1 (7)
Na(3)–O(5)–C(5)	113.0 (4)	Na(3)–O(5)–Si(2)	98.7 (3)
Si(2)–O(5)–C(5)	130.7 (5)	Na(1)–O(7)–C(7)	131.3 (5)
Na(1)–O(7)–Si(3)	93.2 (3)	Si(3)–O(7)–C(7)	134.7 (5)
Si(3)–O(9)–C(9)	138.9 (5)	Si(3)–O(8)–C(8)	129.5 (5)
Na(2)–O(8)–Si(3)	96.8 (2)	Na(2)–O(8)–C(8)	110.4 (5)

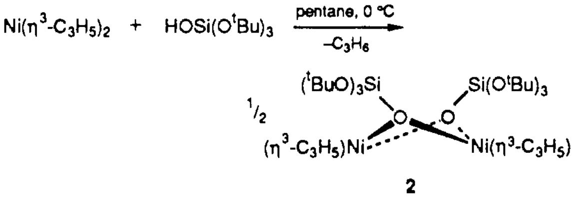
cubelike structure (average 2.07 Å).[10] The Ni(1)–I(1) distance of 2.557 (1) Å is comparable to the Ni–I distances found in $[AsPh_4][NiI_3PPh_3]$ (average 2.54 Å).[11] The Na–I distances, which average 3.08 Å, are somewhat less than that found in crystalline NaI, 3.231 Å, but greater than that measured for gaseous NaI, 2.7115 Å.[12] The Na(1)–O(33), Na(2)–O(22), and Na(3)–O(11) bond lengths (2.285 (5), 2.300 (5), and 2.293 (7) Å, respectively) are much shorter than the other three Na–O distances in the cube (2.695 (6), 2.756 (6), and 2.770 (5) Å). The remaining Na–O bonds, which result from interactions with the ${}^tBuO$– groups, are intermediate in length (range: 2.37–2.47 Å). The silicon atoms of **1** have distorted tetrahedral coordination environments, with bond angles at silicon ranging from 101 to 121°. Many of the bonding parameters observed for **1** are consistent with those recently reported for a related cobalt cluster, $Na_6[(PhSiO_{1.5})_{22}Co_3O_6]\cdot 7H_2O$.[13]

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **2**

	x	*y*	*z*	U^a
Ni(1)	4875 (1)	4652	3775 (1)	60.9 (7)*
Ni(2)	4521 (1)	2639 (2)	2600 (1)	65.7 (8)*
Si(1)	2536 (2)	4391 (3)	1882 (2)	55 (2)*
Si(2)	6611 (3)	4372 (4)	3067 (3)	67 (2)*
O(1)	3682 (5)	4045 (7)	2653 (5)	69 (4)*
O(2)	2246 (7)	5892 (9)	1893 (8)	102 (6)*
O(3)	1671 (7)	3563 (10)	1954 (7)	105 (6)*
O(4)	2436 (8)	4011 (12)	876 (7)	129 (6)*
O(5)	5605 (5)	3907 (8)	3135 (5)	66 (4)*
O(6)	6488 (7)	5916 (9)	2896 (7)	97 (6)*
O(7)	7636 (7)	4207 (14)	4026 (8)	139 (7)*
O(8)	6739 (8)	3653 (11)	2233 (7)	112 (7)*
C(1)	2609 (12)	7156 (13)	1843 (11)	86 (8)*
C(2)	1878 (14)	7786 (18)	882 (13)	140 (11)*
C(3)	2468 (28)	7880 (23)	2630 (17)	252 (24)*
C(4)	3661 (14)	7134 (22)	1973 (26)	249 (21)*
C(5)	1098 (10)	3505 (16)	2491 (10)	93 (8)*
C(6)	727 (26)	2223 (27)	2391 (25)	281 (27)*
C(7)	207 (17)	4246 (34)	1992 (23)	274 (23)*
C(8)	1787 (22)	3764 (43)	3503 (16)	293 (25)*
C(9)	1670 (13)	3769 (17)	−95 (10)	109 (9)*
C(10)	715 (12)	4613 (24)	−372 (12)	141 (10)*
C(11)	2231 (19)	4144 (35)	−698 (15)	232 (20)*
C(12)	1545 (18)	2263 (21)	−192 (13)	174 (14)*
C(13)	7066 (13)	7027 (16)	3053 (11)	115 (10)*
C(14)	6411 (15)	7949 (18)	2211 (13)	148 (14)*
C(15)	7172 (23)	7578 (27)	4004 (15)	214 (20)*
C(16)	8140 (12)	6739 (22)	3076 (14)	154 (12)*
C(17)	8334 (11)	3098 (25)	4492 (13)	157 (12)*
C(18)	9067 (20)	2997 (43)	4128 (21)	307 (25)*
C(19)	9027 (19)	3750 (44)	5649 (19)	294 (24)*
C(20)	7828 (19)	2000 (27)	4577 (23)	274 (22)*
C(21)	6294 (17)	3626 (19)	1205 (12)	128 (13)*
C(22)	6964 (20)	4376 (27)	919 (5)	199 (17)*
C(23)	5197 (17)	4201 (30)	801 (14)	214 (17)*
C(24)	6335 (31)	2219 (27)	1008 (18)	265 (25)*
C(25)	4235 (12)	5188 (17)	4610 (10)	100 (9)*
C(26)	5208 (16)	5766 (19)	4911 (1)	116 (10)*
C(27)	6070 (10)	4981 (21)	5096 (9)	116 (9)*
C(28)	3442 (12)	1200 (14)	2304 (13)	104 (10)*
C(29)	4185 (14)	974 (13)	1994 (13)	118 (10)*
C(30)	5294 (15)	1000 (13)	2706 (14)	119 (12)*

[a] An asterisk denotes the equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Attempts to obtain a neutral nickel complex from $HOSi(O^tBu)_3$ and $NiCp_2$ (pentane, 1 day), $Ni(NH_3)_2(NH_2)_2$ (diethyl ether, 2 days), or $NiCO_3$ (THF, 1 day) did not succeed due to incomplete reaction. Bis(allyl)nickel does react slowly at 0 °C with the silanol to form the siloxide dimer **2** (eq 2). The best yields for this



(2)

2

reaction (ca. 25%) are obtained at 0 °C, where formation of **2** competes most favorably with decomposition of the $Ni(\eta^3\text{-}C_3H_5)_2$ starting material. This diamagnetic compound is thermally stable (mp 141–146 °C) and crystallizes from pentane as orange-red prisms.

The molecular structure of **2** is shown in Figure 2, and geometrical parameters are provided in Tables IV and V. Compound **2** is dimeric, as expected for a $[(\eta^3\text{-allyl})NiX]_2$ complex.[14] The

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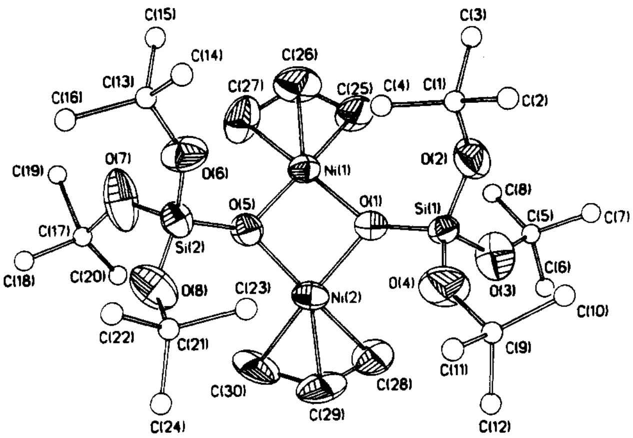

Figure 2. ORTEP view of $\{(\eta^3\text{-}C_3H_5)Ni[\mu_2\text{-}OSi(O^tBu)_3]\}_2$ (**2**), with the atom-labeling scheme.

Table V. Selected Distances and Angles for **2**

(a) Distances (Å)

Ni(1)–Ni(2)	2.665 (2)	Si(1)–O(4)	1.56 (1)
Ni(1)–O(1)	1.914 (6)	Si(2)–O(6)	1.61 (1)
Ni(1)–O(5)	1.92 (1)	Si(2)–O(7)	1.560 (9)
Ni(2)–O(1)	1.919 (8)	Si(2)–O(8)	1.58 (1)
Ni(2)–O(5)	1.915 (8)	C(1)–O(2)	1.42 (2)
Ni(1)–C(25)	2.00 (2)	C(5)–O(3)	1.42 (2)
Ni(1)–C(26)	1.98 (2)	C(9)–O(4)	1.43 (2)
Ni(1)–C(27)	2.02 (1)	C(13)–O(6)	1.38 (2)
Ni(2)–C(28)	2.05 (2)	C(17)–O(7)	1.48 (2)
Ni(2)–C(29)	1.92 (2)	C(21)–O(8)	1.43 (2)
Ni(2)–C(30)	2.00 (2)	C(25)–C(26)	1.40 (3)
O(1)–Si(1)	1.579 (7)	C(26)–C(27)	1.40 (3)
O(5)–Si(2)	1.58 (1)	C(28)–C(29)	1.39 (3)
Si(1)–O(2)	1.61 (1)	C(29)–C(30)	1.47 (2)
Si(1)–O(3)	1.56 (1)		

(b) Angles (deg)

Ni(1)–O(1)–Ni(2)	88.1 (3)	Ni(1)–O(5)–Ni(2)	88.1 (4)
C(25)–C(26)–C(27)	119 (2)	C(28)–C(29)–C(30)	119 (2)
Ni(1)–O(1)–Si(1)	144.4 (5)	Ni(2)–O(1)–Si(1)	127.0 (5)
Ni(1)–O(5)–Si(2)	131.1 (5)	Ni(2)–O(5)–Si(2)	140.5 (6)
O(1)–Ni(1)–O(5)	82.6 (3)	O(1)–Ni(2)–O(5)	82.5 (3)
O(1)–Si(1)–O(2)	113.4 (4)	O(1)–Si(1)–O(3)	114.6 (5)
O(1)–Si(1)–O(4)	106.9 (6)	O(2)–Si(1)–O(3)	107.8 (6)
O(2)–Si(1)–O(4)	110.4 (6)	O(3)–Si(1)–O(4)	103.3 (6)
O(5)–Si(2)–O(6)	106.1 (6)	O(5)–Si(2)–O(7)	113.6 (6)
O(5)–Si(2)–O(8)	111.9 (6)	O(6)–Si(2)–O(7)	104.6 (6)
O(6)–Si(2)–O(8)	111.9 (7)	O(7)–Si(2)–O(8)	108.7 (7)

Ni_2O_2 core of the dimer is bent in a butterfly fashion along the O(1)–O(5) vector, resulting in a fold angle of 135.3° (angle between the two NiO_2 planes). This feature of the structure is similar to that observed for the methoxy-bridged dimer $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}OMe)]_2$, which has a fold angle of 124.3°.[15] Note that both planar and folded Ni_2X_2 cores have been observed for $[(\eta^3\text{-allyl})NiX]_2$ complexes.[14] The Ni–O bond lengths are nearly equivalent (1.92 Å), as are the two Ni–O–Ni angles (88.1°). The Ni(1)–Ni(2) distance, 2.665 (2) Å, is somewhat longer than a typical Ni–Ni single bond, which falls in the range 2.32–2.60 Å.[14,16] The Ni–O–Si angles (127.0 (5)–144.4 (5)°), the O–Si–O angles (103.3–114.6 (5)°), and the Si–O distances (1.560 (9)–1.614 (10) Å) cover relatively wide ranges, but are consistent with comparable distances and angles observed in $Cu[OSi(O^tBu)_3]_2(pyr)_2$.[6] Overall structural parameters for **2** resemble those reported for the related compound $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu_2\text{-}OH)]_2\cdot HNC_4H_2Me_2$, which has a fold angle of 133.6°.[17]

The two allyl groups in **2** have different geometries. In one, C(25)–C(27), the two C–C bonds are identical (1.396 (27) and 1.402 (28) Å) and all Ni–C bond lengths are the same (1.997 (19), 1.983 (18), and 2.023 (11) Å). The other allyl group, C(28)–C(30), possesses two different C–C distances (1.388 (32) and 1.473 (23) Å) and is bound such that the middle carbon is closer to Ni(2) (1.917 (15) Å vs 2.049 (16) and 1.995 (17) Å). Both types of nickel–allyl interactions have been observed previously.[14]

Experimental Section

All manipulations were performed under an atmosphere of nitrogen by using Schlenk techniques and/or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Mikroanalytisches Labor Pascher. Infrared spectra were recorded on a Perkin-Elmer 1330 instrument. ^1H NMR spectra were recorded at 300 MHz with a GE QE-300 instrument or at 90 MHz with a Varian EM-390 instrument. ^{13}C NMR spectra were recorded at 75.5 MHz on the GE QE-300 instrument. EPR spectra were recorded on a Varian E-3 EPR spectrometer. The silanol $(^tBuO)_3SiOH$ was prepared from $(^tBuO)_3SiCl$[18] and converted to $NaOSi(O^tBu)_3$[6] by literature procedures. $NiI_2(THF)_2$ was obtained by Soxhlet extraction of NiI_2, which was prepared from $NiCO_3$ and HI by a published method.[19] $Ni(\eta^3\text{-}C_3H_5)_2$ was prepared according to the literature.[20]

$Na_3(\mu_3\text{-}I)\{Ni[\mu_3\text{-}OSi(O^tBu)_3]_3I\}\cdot 0.5THF\cdot 0.5C_5H_{12}$ (1). A mixture of tetrahydrofuran (50 mL), $NiI_2(THF)_2$ (0.50 g, 1.09 mmol), and $NaOSi(O^tBu)_3$ (1.03 g, 3.60 mmol) was refluxed for 18 h. Nearly all the tetrahydrofuran was removed under reduced pressure, and the resulting residue was extracted with pentane (20 mL). Concentration and extended cooling of this solution (−40 °C, 11 days) afforded the product as blue crystals in 54% yield (0.72 g). Crystallization of this product requires the presence of some residual tetrahydrofuran. Compound **1** has a decomposition temperature of ca. 85 °C. Anal. Calcd for $C_{40.5}H_{91}I_2Na_3NiO_{12.5}Si_3$: C, 39.1; H, 7.37; I, 20.4. Found: C, 39.2; H, 7.35; I, 19.9. IR (Nujol, CsI, cm^{-1}): 1375 m, 1360 s, 1254 m sh, 1238 s br, 1210 m sh, 1190 vs br, 1062 vs br, 1038 vs br, 1020 vs br, 990 vs br, 908 w, 818 s, 695 s, br, 525 w sh, 510 m, 488 m, 472 m sh, 425 w, 380 w br, 365 w br, 350 w sh, 300 m br. EPR (powdered sample, room temperature): $g = 1.750$.

$\{(\eta^3\text{-}C_3H_5)Ni[\mu_2\text{-}OSi(O^tBu)_3]\}_2$ (2). At 0 °C, $HOSi(O^tBu)_3$ (10.25 g, 0.0387 mol) in pentane (100 mL) was added dropwise to $Ni(\eta^3\text{-}C_3H_5)_2$ (5.01 g, 0.0356 mol) in pentane (150 mL). The resulting solution was stirred for 24 h at 0 °C, and stirring was continued for another 24 h at room temperature. Volatiles were removed in vacuo, and the orange-brown residue was washed with acetonitrile (3 × 15 mL) to remove unreacted silanol. The remaining crude product was crystallized from pentane (ca. 5 mL, −40 °C) as orange-red prisms (mp 141–146 °C dec) in 23% yield (2.97 g). Anal. Calcd for $C_{15}H_{32}NiO_4Si$: C, 49.6; H, 8.88. Found: C, 49.6; H, 8.84. IR (Nujol, CsI, cm^{-1}): 1389 m, 1364 s, 1260 w, 1240 m br, 1218 w sh, 1192 s, 1060 vs br, 1022 s br, 1000 m sh, 960 m br, 910 w br, 825 m, 699 m br, 555 w br, 514 w br, 420 w br. ^1H NMR (300 MHz, benzene-d_6): δ 1.48 (s, 54 H, $OSi(O^tBu)_3$), 2.06 (d, $J = 13$ Hz, 4 H, $HC(CH_2)_2$), 5.27, 5.56 (m, 2 H, $HC(CH_2)_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6): δ 32.20 ($OSi(OCMe_3)_3$), 48.50 ($OSi(OCMe_3)_3$), 71.84 ($HC(CH_2)_2$), 105.16 ($HC(CH_2)_2$).

X-ray Structure Determinations for 1 and 2. General Data. A summary of the crystallographic data is provided in Table I. Crystals were mounted in glass capillary tubes in an inert-atmosphere glovebox and then flame-sealed. Unit-cell dimensions were obtained from the angular settings of 25 reflections (21° ≤ 2θ ≤ 26°). Empirical corrections for absorption were applied to both data sets. All calculations and sources of scattering factors used the SHELXTL (5.1) software library (G. Sheldrick, Nicolet XRD, Madison, WI).

1. Photographic evidence and cell reduction routines revealed triclinic symmetry, and the centrosymmetric alternative was initially assumed and subsequently confirmed by the chemically reasonable results of refinement. The structure was solved by an autointerpreted Patterson map routine that located the I and Ni atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were incorporated as idealized contributions.

2. Photographic evidence and systematic absences in the diffraction data indicated either of the monoclinic space groups, $P2_1$ or $P2_1/m$. The former, acentric alternative was initially suggested by the statistical

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distribution of E values, and subsequently confirmed by the absence of crystallographic mirror-plane symmetry perpendicular to the b axis (although the molecule itself possesses two obvious, potential mirror planes). All non-hydrogen atoms were refined as in **1**. Hydrogen atoms were ignored.

Acknowledgment for financial support is made to the Air Force Office of Scientific Research, Air Force Systems Command, USAF (Grant No. AFOSR-88-0273), and to Chevron Research Co. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes. T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–90).

Supplementary Material Available: Tables of crystallographic data, bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates (13 pages); listings of calculated and observed structure factors (43 pages). Ordering information is given on any current masthead page.

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Synthesis and Magnetic Properties of Binuclear Iron(III) Complexes with Oxalate, 2,5-Dihydroxy-1,4-benzoquinone Dianion, and Squarate as Bridging Ligands. Crystal Structure of (μ-1,3-Squarato)bis[(N,N'-ethylenebis(salicylideneaminato))(methanol)iron(III)]

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Received February 16, 1989

Three iron(III) complexes of formulas $[Fe_2(salen)_2ox]\cdot H_2O$ (**1**), $[Fe_2(salen)_2dhbq]\cdot 1.5H_2O$ (**2**), and $[Fe_2(salen)_2(CH_3OH)_2sq]$ (**3**), where salen = N,N'-ethylenebis(salicylideneaminate) ($C_{16}H_{14}N_2O_2^{2-}$), ox = oxalate ($C_2O_4^{2-}$), dhbq = the dianion of 2,5-dihydroxy-1,4-benzoquinone ($C_6H_2O_4^{2-}$), and sq = the dianion of 3,4-dihydroxy-3-cyclobutene-1,2-dione ($C_4O_4^{2-}$), have been prepared. The crystal structure of **3** has been solved at room temperature. It crystallizes in the monoclinic system, space group $P2_1/a$, with a = 13.278 (3) Å, b = 14.464 (3) Å, c = 9.574 (2) Å, β = 96.24 (2)°, and Z = 2. The structure consists of μ-1,3-squarato-bridged $[Fe^{III}(salen)CH_3OH)]$ binuclear units. The iron(III) is hexacoordinate, with the four donor atoms of salen and two oxygen atoms, one of a methanol molecule and the other of the squarate bridge, building a distorted octahedron around the metal ion. The magnetic behavior of all three complexes has been studied in the 4.2–300 K temperature range. The HDVV, ($\hat{H} = -J\hat{S}_1\cdot\hat{S}_2$), $S_1 = S_2 = {}^5/_2$ spin-exchange model applied to the measured magnetic susceptibilities vs temperature yields J values of −7.1, −0.92, and −0.39 cm^{-1} for **1**–**3**, respectively. A discussion about the pathway of exchange interaction in this series is presented.

Introduction

It is now well-known that magnetic interactions between paramagnetic centers can be propagated not only by single-atom but also by multiatom bridges.[2] The distance dependence of the magnetic coupling is of continuing interest[3] although, up to now, most of the reported results have dealt with binuclear copper(II) complexes with intramolecular copper–copper distances in the range 5–8 Å; relatively strong interactions were observed with bridging ligands such as end-to-end azide,[4] oxalate,[5] oxamate and oxamide,[3,6] dithiooxalate,[7] tetrathiooxalate,[8] derivatives of the dianion of 2,5-dihydroxy-1,4-benzoquinone,[9] and 2,2′-bipyrimidine.[10]

Intramolecular copper–copper distances greater than 10 Å were achieved with bridging ligands such as terephthalate[11] and 4,4′-bipyridine,[12] and weak antiferromagnetic interactions were observed in both cases. In fact, it is most likely that in the former case the interaction is intermolecular instead of intramolecular, whereas in the latter the observed antiferromagnetic coupling cannot be attributed to intermolecular interaction only. These two examples illustrate the difficulties involved in the determination of the limit of intramolecular exchange interaction through extended bridges. The distance-dependent limit to exchange coupling was raised by Coffman and Buettner.[13] The question

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