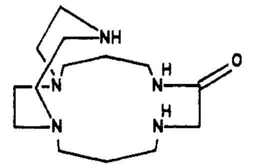

10

contained 14 lines, including a carbonyl carbon at 172 ppm (see Figure 3), as expected from the asymmetry of the ligand. The two signals around 25 ppm were due to the two central carbon atoms of the trimethylene groups. The mass spectrum is also in agreement with the proposed structure.

Conclusions

Complete reduction to the macrobicyclic complex $Cu(L3)^{2+}$ results in an ion of exceptional stability. There is no tendency toward hydrolysis even after 14 days in 4 M $HClO_4$. Indeed, the only method of removal of the metal ion is to react with Na_2S in a manner similar to that used in the preparation of the uncoordinated amide.

Investigations of this type are important in that examples are provided of the influence that metal-ion coordination can exert on the nature of the products isolated from a reaction sequence involving a series of finely tuned equilibria. Further study of the base-catalyzed hydrolysis of the imine-carbinolamine intermediate is underway since this represents a useful route to the synthesis of monooxo macrocyclic ligands.

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Supplementary Material Available: Tables S1-S13, containing anisotropic temperature parameters, selected intermolecular distances, hydrogen atom fractional atomic coordinates and isotropic temperature parameters, interatomic distances and bond angles involving the hydrogen atoms, mean plane calculations, fractional atomic coordinates and temperature parameters, and experimental crystallographic data for both complexes and hydrogen bonds for $[Cu(L2)](ClO_4)_2$ (14 pages); Tables S14 and S15, listing calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

Alternate Coordination Modes of $(CF_3)_2C(OH)_2$: Synthesis and Structure of Five-Coordinate Ni^{2+} and Cu^{2+} Complexes Derived from a Chelating *gem*-Diol[1]

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Abstract: Two modes of coordination of hexafluoropropane-2,2-diol to transition-metal ions (Ni^{2+}, Cu^{2+}, Mn^{2+}, Co^{3+}, Pd^{2+}, Pt^{2+}) have been found. The diionized *gem*-diol can form a four-membered chelate ring with amine or phosphine coligands to give neutral complexes $L_n\overline{MOC(CF_3)_2O}$. Alternatively, two molecules of the diol may condense to give a six-membered chelate ring $L_n\overline{MOC(CF_3)_2OC(CF_3)_2O}$. By suitable choice of coligands L, the central metal ion may be four-, five-, or six-coordinate. The two types of ring system are not in equilibrium, and the formation of the four-membered ring is favored by bulkier coligands. It is suggested that the six-membered chelate ring is formed by template condensation between two alkoxide ligands on the metal. A complete structural determination has been made on the Ni^{2+} and Cu^{2+} complexes with the tridentate macrocycle 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene as coligand. Both contain a four-membered chelate ring and are formulated as the five-coordinate species $(\overline{NNN})\overline{MOC(CF_3)_2O}$ (**5**, M = Cu; **6**, M = Ni). The crystals are both isomorphic and isostructural, and they have orthorhombic symmetry in space group *Pbca* with $Z = 8$. Cell dimensions are as follows: **5**, $a = 20.520$ (3) Å, $b = 15.760$ (5) Å, $c = 14.380$ (5) Å, $V = 4650$ (3) Å^3; **6**, $a = 20.462$ (4) Å, $b = 15.759$ (3) Å, $c = 14.398$ (3) Å, $V = 4643$ (3) Å^3. Full-matrix least-squares refinement on F of 205 variables with 2176 and 2112 unique observations converged at conventional agreement factors of 0.043 and 0.047 for **5** and **6**, respectively. In each crystal, a pair of complex molecules linked by pairs of water molecules sits on a crystallographic center of symmetry. One alkoxide oxygen atom is hydrogen bonded to the two water molecules, and the other to an ethanol molecule of solvation. The metal atom is in approximate square-pyramidal coordination; the axial bond in **5** is lengthened by a Jahn-Teller distortion. The chelating *gem*-diol ligand in **5** and **6** forms almost planar rings, with bite angles of 68.4 (1)° and 67.1 (1)°, respectively.

Only in a limited number of cases is a *gem*-diol stable with respect to elimination of water, and there are even fewer reported cases of metal alkoxides formed from such systems. Aldehydes RCHO add water to give $RCH(OH)_2$ where R is H or an electronegative group, such as CF_3 or CCl_3. In an unusual example of a stable alkoxide of $CH_2(OH)_2$, Day et al. have determined the structure of the polyoxomolybdate cluster $[(CH_2O_2)Mo_4O_{13}H]^{3-}$; the $CH_2O_2^{2-}$ unit is situated above four coplanar molybdenum atoms with each alkoxide bridging between two metal atoms at a Mo-O distance of 2.194 (5) Å.[2] They note that $CH_3CH(OH)_2$, $C_6H_5CH(OH)_2$, and $CF_3CH(OH)_2$ form similar adducts, but $(CF_3)_2C(OH)_2$ does not. A brief report has been made of the platinum complex $(Ph_3P)_2\overline{PtOC(CH_3)_2O}$; it is of limited stability and has not been fully characterized.[3]

For trichloroacetaldehyde, the hydrate $CCl_3CH(OH)_2$ is familiar, but there is little reported work on its metal complexes.

(1) Presented in part at the 3rd North American Chemical Congress, Toronto, June 1988, and in part at the XXVI ICCC, Porto, Aug 1988.

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A germanium derivative $(CH_3)_2GeOCH(CCl_3)O$ is of limited stability, readily eliminating CCl_3CHO.[4]

There have been several reports of complexes of 2,2′-bipyridyl ketone in which hydration of the carbonyl group occurs on coordination to metals such as Ni^{2+},[5,6] Cu^{2+},[6] Pd^{2+}, or Pt^{2+}.[7] The ligand remains neutral, coordinating through nitrogen with, in some cases, weak interaction between the metal and one hydroxyl group, and it appears that the diol is stabilized through steric requirements imposed by chelation.

It has long been known that hexafluoroacetone (HFA) adds water to give the stable hydrate, hexafluoro-2,2-propanediol, $(CF_3)_2C(OH)_2$.[8] In view of the established tendency of highly fluorinated alcohols to form stable alkoxides, this diol would be expected to form a range of derivatives, but few studies have been reported. It has a pK_a of 6.58, and monosalts of the group I metals, $M^+[HOC(CF_3)_2CO^-]$, may be isolated from aqueous solution;[9] pyrolysis of the Li^+ salt gives the dianion in $[Li^+]_2[(CF_3)_2CO_2^{2-}]$.[10] With a large cation, salts such as $[Ph_4P^+]_2[H_2\{OC(CF_3)_2OH\}_4^{2-}]$ may be isolated; the four diol residues in the anion are held together by extensive hydrogen bonding.[11]

The diol bridges between gold(I) atoms in the dinuclear complex $(R_3P)AuOC(CF_3)_2OAu(PR_3)$.[12] A chelating mode of attachment appears to be present in the complex $(PPh_3)_2PtOC(CF_3)_2O$, made indirectly by the reduction of the peroxy complex $(PPh_3)_2PtOC(CF_3)_2OO$;[13] the same route is used to prepare the unfluorinated analogue.[3] A similar structure is suggested in the nickel complex $(^tBuNC)_2NiOC(CF_3)_2O$,[14] but no structural determination has been made in either system.

Modinos and Woodward found a different mode of coordination in the complex $(PR_3)_2PtOC(CF_3)_2OC(CF_3)_2O$, where condensation of two molecules of the diol has produced a six-membered ring.[15] This was made by the reaction of a platinum aza diene complex with HFA containing small amounts of the hydrate.

These studies do not establish the conditions under which complexes of $(CF_3)_2C(OH)_2$ can be prepared in solution, nor do they show whether four- or six-membered chelate rings are favored. In order to resolve these points, and in view of the intrinsic interest of chelating *gem*-diols, we have studied the interaction of $(CF_3)_2C(OH)_2$ with some transition-metal ions in the presence of amine and phosphine coligands.

Experimental Section

General Materials. All chemicals were reagent-grade, commercial samples used without further purification. Microanalyses were performed by Malissa-Reuter Analytische Laboratorien, Germany, and by Guelph Chemical Laboratories, Guelph, ON. The compound numbering scheme is given in Table I.

Hexafluoroacetone Hemiacetal. Hexafluoroacetone (0.1 mol) was dissolved in ethanol (0.33 mol) in a sealed tube, and the resulting ethanolic solution of the hemiacetal was used for preparation of complexes.

Complex Preparation. In many cases, different ratios of reactants, different solvents, or other changes in reaction conditions were studied in an attempt to influence the nature of the product. Unless otherwise indicated, these changes did not lead to different identifiable products and are not described. The KOH required for neutralization in the reactions was added dropwise as a solution in EtOH (0.25 M). Melting points are uncorrected; in most cases, melting was accompanied by decomposition.

Table I. Metal[a] Complexes of $(CF_3)_2(OH)_2$

coligand	compound (no.)
Complexes Containing Four-Membered Chelate Rings	
phenanthroline	(phen)Cu(OCO) (**1**), (phen)Ni(OCO) (**2**), $(phen)_2Mn(OCO)\cdot 2H_2O$ (**3**)
$Me_2NCH_2CH_2NH_2$	$(Me_2NCH_2CH_2NH_2)Cu(OCO)$ (**4**)
mac[b]	(mac)Cu(OCO) (**5**), (mac)Ni(OCO) (**6**)
Ph_3P	$(Ph_3P)_2Pd(OCO)$ (**7a**), $(Ph_3P)_2Pt(OCO)$ (**7b**)
diphos[c]	(diphos)Ni(OCO) (**8**)
Complexes Containing Six-Membered Chelate Rings	
en	$(en)_2Cu(OCOCO)$ (**9**), $(en)_2Co(OCOCO)(OH)$ (**10**)
$Me_2NCH_2CH_2NMe_2$	(tmed)Cu(OCOCO) (**11**), (tmed)Ni(OCOCO) (**12**)
trien[d]	$(trien)Cu(OCOCO)\cdot 2H_2O$ (**13**)
α,α′-bipyridine	(bpy)Cu(OCOCO) (**14**), (bpy)Ni(OCOCO) (**15**), $(bpy)_2Cu(OCOCO)$ (**16**), $(bpy)_2Ni(OCOCO)$ (**17**)
phenanthroline	(phen)Cu(OCOCO) (**18**), $(phen)_2Mn(OCOCO)\cdot 2H_2O$ (**19**)
mac[b]	$(mac)Co(OCOCO)(OH)\cdot 2H_2O$ (**20**)
Ph_3P	$(Ph_3P)_2Ni(OCOCO)$ (**21**)
$MePPh_2$	$(MePPh_2)_2Ni(OCOCO)$ (**22**)

[a] Divalent metals except **10** and **20**, Co^{3+} complexes. [b] Mac is the tridentate macrocycle 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene. [c] Diphos = 1,2-bis(diphenylphosphino)ethane. [d] Trien = triethylenetetramine, $NH_2(CH_2CH_2NH)_2CH_2CH_2NH_2$.

Complexes with Phenanthroline Coligand. Addition of phenanthroline (2 mmol) to $CuCl_2\cdot 2H_2O$ (1 mmol) in EtOH (15 mL) gave a turquoise precipitate. Hemiacetal (2 mmol) was added, followed by KOH (2 mmol), giving a green solution. After the solution was stirred for 2 h, KCl was removed and solvent evaporated to give complex **1**: blue-green crystals from $(CH_3)_2CO$; mp 175 °C.

When the same procedure was carried with $CuCl_2$ and only 1 mmol of phenanthroline, the product was complex **18**: purple crystals from CH_2Cl_2; mp 150 °C.

The nickel complex was prepared in a manner similar to that of **1**, but with 3 mmol of phenanthroline. The product was an oil that deposited red crystals of **2** on slow evaporation from CH_2Cl_2; mp 167 °C.

The starting material for complex **3** was $(phen)_2MnCl_2$[15] (1 mmol) suspended in 1:4 $MeOH/H_2O$, which was added dropwise to hemiacetal (2 mmol) neutralized with KOH (2 mmol) in EtOH. The precipitate was recrystallized from MeOH containing additional phenanthroline (without which decomposition occurs) to give **3** as bright yellow needles, mp 214 °C. Analysis showed that the ratio of phenanthroline to metal in the product was 3:1.

Complex **19** was made from $(phen)MnCl_2$[16] (1 mmol) suspended in DMF. The salt $K[OC(CF_3)_2OH]$ (2 mmol, prepared by evaporation of the neutralized hemiacetal) was added in DMF solution, causing the manganese complex to dissolve. After removal of precipitated KCl, the solvent was removed in vacuo and the residual oil dissolved in $CH_2Cl_2/(CH_3)_2CO$. Ether was added to the cloud point, and **19** precipitated as golden crystals on standing; mp 179–183 °C. Analysis corresponded to a dihydrate.

Complex with *N,N*-Dimethylethylenediamine Coligand. To $CuCl_2\cdot 2H_2O$ (1 mmol) in EtOH (15 mL) was added an excess of $Me_2NCH_2CH_2NH_2$ (ca. 5 mmol) followed by hemiacetal (2 mmol) and KOH (2 mmol). Workup as for **1** gave **4**: purple crystals from CH_2Cl_2; mp 168 °C.

Complexes with Macrocyclic Coligand. The macrocycle 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene, as the bridged hydroxy complexes $[(mac)M(\mu\text{-}OH)_2M(mac)](ClO_4)_2$ (M = Cu, Ni), was made by published procedures.[18] Each complex (1 mmol) was dissolved in EtOH (25 mL), and an excess of the hemiacetal was added with stirring. KOH (2 mmol) was added, and the reaction mixture was stirred for ca. 1 h; then $KClO_4$ and the solvent were removed. The residue was recrystallized from CH_2Cl_2 and then EtOH to give the pure products **5** (mp 120 °C) and **6** (mp 142 °C), respectively. Analytical data and complete structural determinations showed each to contain one water and one ethanol of crystallization per mole of complex.

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Table II. Visible Spectral Data of Complexes

complex	no.	solvent[a]	λ_{max}, nm (ϵ)
(phen)Cu(OCO)	**1**	A	701 (20)
(phen)Ni(OCO)	**2**	A	520 (4.0)
$(Me_2NCH_2CH_2NH_2)Cu(OCO)$	**4**	E	542 (58)
(mac)Cu(OCO)·H_2O·EtOH	**5**	A	628 (93)
(mac)Ni(OCO)·H_2O·EtOH	**6**	E	362 (114), 400 (27), 610 (34)
(diphos)Ni(OCO)	**8**	A	402 (617)
$(en)_2Cu(OCOCO)$	**9**	E	577 (62)
$(en)_2Co(OCOCO)(OH)$	**10**	E	575 (91), 372 (97)
(tmed)Cu(OCOCO)	**11**	A	556 (103)
(tmed)Ni(OCOCO)	**12**	A	503 (103)
(trien)Cu(OCOCO)	**13**	E	638 (117)
(bpy)Cu(OCOCO)	**14**	E	595 (91)
(bpy)Ni(OCOCO)	**15**	E	515 (5.2)
$(bpy)_2Cu(OCOCO)$	**16**	E	606 (63)
(phen)Cu(OCOCO)	**18**	E	600 (69)
(mac)Co(OCOCO)(OH)	**20**	E	524 (67)
$(Ph_3P)_2Ni(OCOCO)$	**21**	B	490 (94)

[a] Key: A = acetone; E = ethanol; B = benzene.

The same method with the cobalt(III) complex $[(mac)(OH)Co(\mu\text{-}OH)_2Co(OH)(mac)](ClO_4)_2$[18] gave **20**: red crystals from MeOH/$CHCl_3$; mp 163 °C. Analysis corresponded to a dihydrate.

Complexes with Ethylenediamine Coligand. To $CuCl_2 \cdot 2H_2O$ (1 mmol) in EtOH was added excess ethylenediamine (ca. 5 mmol), hemiacetal (2 mmol), and KOH (2 mmol). Workup as before gave **9**: purple crystals from CH_2Cl_2/Et_2O; mp 132–133 °C. Analysis corresponded to a dihydrate.

The cobalt(III) complex *trans*-$[Co(en)_2Cl_2]Cl$ was prepared by standard methods[19] and converted to $[Co(en)_2Cl_2][BPh_4]$ by reaction with aqueous $NaBPh_4$. The tetraphenylborate (1 mmol) was dissolved in EtOH, and hemiacetal (2 mmol) and KOH (2 mmol) were added. After the solution was stirred for 1 h, $KBPh_4$ was removed, the solution evaporated to a purple oil, dissolved in CH_2Cl_2, and Et_2O added to the cloud point. Purple crystals of **10** formed on standing; mp 118 °C.

Complexes with *N,N,N',N'*-Tetramethylethylenediamine Coligand. To the anhydrous metal chloride (1 mmol) dissolved in ethanol with excess TMED (ca. 1 mmol) and excess hemiacetal was added KOH (2 mmol). Removal of KCl and workup as before gave the copper complex **11** [purple crystals from $CHCl_3$; mp 193–195 °C] and the nickel complex **12** [red crystals from CH_2Cl_2; mp 143–145 °C].

Complexes with Diethylenetriamine Coligand. The copper and nickel complexes were prepared by the same route as **11**, with excess of the triamine, to give **24a** [blue crystals from EtOH; mp 120 °C] and **24b** [purple crystals from $MeOH/CH_2Cl_2$; mp 160 °C].

Complex with Triethylenetetramine Coligand. The copper complex was prepared similarly from $CuCl_2$ and excess tetramine to give **13**: purple crystals from EtOH/2-PrOH; mp 128 °C. Analysis corresponded to a dihydrate.

Complexes with α,α'-Bipyridine Coligand. The same method as for **11**, but with bipyridine in a 1:1 ratio, gave the copper complex **14**: deep purple crystals from CH_2Cl_2; mp 215 °C. Use of excess bipyridine in the synthesis gave **16**: blue crystals from EtOH; mp 129 °C. This compound could also be made by reaction of excess bipyridine with **14**. The same procedure, but with a 2:1 excess of bipyridine, gave the nickel complex **15**: orange crystals from Me_2CO/Et_2O; mp 117–120 °C. Recrystallization of **15** from EtOH in the presence of excess bipyridine gave **17**: pink crystals; mp 220 °C.

Complexes with Phosphine Coligands. To $(Ph_3P)_2PtCl_2$ (1 mmol), dissolved in $CHCl_3$/hexanes, were added hemiacetal (2 mmol) and KOH (2 mmol). After the solution was stirred for 1 h, removal of KCl and solvent gave **7**: yellow-green crystals from $CHCl_3$/hexanes; mp 230 °C (lit.[12] mp 221–223 °C).

For nickel complexes of monodentate phosphines, $(PR_3)_2NiCl_2$ (1 mmol) was dissolved in CH_2Cl_2 and the resultant mixture added dropwise to a solution of $K[OC(CF_3)_2OH]$ (2 mmol) in CH_2Cl_2. After the solution was stirred for 1 h, KCl was removed and the solution volume reduced until the products precipitated as the yellow solids **21** (mp 95 °C) and **22** (mp 111–114 °C). These complexes could not be recrystallized without decomposition occurring.

With the bidentate phosphine, $NiCl_2 \cdot 2H_2O$ (1 mmol) was added to diphos (1 mmol) in EtOH. To the resulting suspension were added hemiacetal (2 mmol) and KOH (2 mmol). After the solution was stirred for 2 h, solids were removed and the solution was evaporated to give **8**: yellow crystals from $(CH_3)_2CO$; mp 238–241 °C.

Reaction with Me_3SnCl. Ethanolic KOH (2 mmol) was added to excess hemiacetal in EtOH and a solution of Me_3SnCl (2 mmol) in CH_2Cl_2 added dropwise, causing precipitation of KCl. Additional KOH was added to pH 7.5 and the stirred suspension kept at 50 °C for 1 h. Workup gave $Me_3SnOC(CF_3)_2OSnMe_3$ (**23**) white plates from Et_2O/hexanes: mp 78–82 °C; IR strong ν(C–O) at 945 cm^{-1}; ^1H NMR 0.45 ppm (s, $^{117}Sn/^{119}Sn$ satellites (unresolved), $^2J(Sn,H)$ = 58 Hz); ^{19}F NMR −81.66 ppm (s).

Salts of $(CF_3)_2C(OH)_2$. When the quaternary hydroxide in EtOH was added to the hemiacetal, a precipitate formed at a 1:2 ratio (that is, at the half-equivalence point). Recrystallization from hot EtOH gave the salts $[R_4M^+]_2[H_2\{OC(CF_3)_2OH\}_4]^{2-}$ as colorless crystals from EtOH. Melting points were as follows: Ph_4P^+, 105–107; Et_4N^+, 101–103; Ph_4As^+, 142–145 °C.

Characterization. All new compounds were characterized by elemental analysis (Table S-I, supplementary material). Infrared spectra of all the above complexes were consistent with their expected structures, showing strong C–F absorptions in the region 1100–1300 cm^{-1} and C–O–M absorptions near 955 cm^{-1}. Because of the presence of several C–F deformation modes, it was not possible to make an unambiguous assignment of absorptions distinguishing the four- and six-membered chelate rings. Complexes **5** and **6** showed absorptions at 1655 cm^{-1} associated with the C=N bond of the macrocyclic ligand.

Visible spectra of the complexes are given in Table II.

X-ray Structure Determinations

Data Collection and Reduction. Deep blue, multifaceted crystals with equant habit of **5** (M = Cu) and multifaceted turquoise blocks of **6** (M = Ni) were grown by slow evaporation of ethanolic solutions at room temperature. A preliminary photographic examination showed Laue symmetry *mmm*, and a careful examination of the films showed that **5** and **6** were isomorphic and isostructural. The systematic absences observed uniquely determine the space group as *Pbca*, No. 61.[20a] Crystal densities were determined by the neutral buoyancy method in mixtures of 1,2-$C_2H_4Br_2$ and *n*-pentane and confirmed the presence of the water and ethanol solvent molecules. With 8 formula units per cell, no crystallographic site symmetry is imposed. Crystal data for **5** and **6** are given in Table III.

The structure of **6** was undertaken first. Cell constants and an orientation matrix were refined with the angular settings for carefully centered, high-angle reflections.[21] ω-Scans of intense, low-angle reflections indicated satisfactory crystal quality. Intensity data were recorded at variable scan speeds so chosen as to optimize counting statistics within a maximum time per datum of 60 s. Background estimates were made by extending the scan by 25% on each side. Standard reflections were monitored regularly and showed a small increase in intensity. No correction was applied. The crystal faces were indexed by optical goniometry in preparation for an absorption correction. The data were processed with the Enraf-Nonius structure determination package, version 3.0,[22] running on a PDP 11/23+ computer. Standard deviations were assigned on the basis of counting statistics, a value was chosen for p of 0.06,[23] and an absorption correction was applied.[24] After equivalent reflections were averaged, 3849 unique data with $I > 0$ remained for solution and refinement of the structure.

The same procedure was followed for the Cu structure **5**. There was only random variation in the standard intensities, a value of 0.06 was chosen for p, and an absorption correction was applied. There were 3861 unique data with $I > 0$ for solution and refinement. Full details for both studies are presented in Table III.

Solution and Refinement of the Structures. The structure of **6** was solved by direct-methods techniques[25] and refined by full-matrix least-squares techniques on F,[22] minimizing the function

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Table III. Summary of X-ray Structure Determinations

	compound **6**	compound **5**
	Crystal Data	
compd, fw	$C_{17}H_{33}F_6N_6NiO_4$, 516.2	$C_{17}H_{33}CuF_6N_3O_4$, 521.0
cryst syst, space grp	orthorhombic, *Pbca* (No. 61)	
syst abs	$0kl$, k odd; $h0l$, l odd; $hk0$, h odd	
cell dimens (Å) (21 °C)	a = 20.462 (4)	a = 20.520 (3)
	b = 15.759 (3)	b = 15.760 (5)
	c = 14.398 (3)	c = 14.380 (5)
V (Å^3), Z	4643 (3), 8	4650 (3), 8
density (g cm^{-3}): obsd, calcd	1.53 (2), 1.488	1.51 (2), 1.477
	Experimental Details	
diffractometer, monochromator	Enraf-Nonius CAD4F, graphite	
radiation, λ (Å)	Mo Kα, 0.71073	
cryst detec (mm), toa (deg)	205, 2.5	
aperture (mm): vert, horiz	4.0, 5.0 + 0.35 tan θ	
centering reflcns, θ range	20, 25.0 < 2θ < 33.0	20, 25.0 < 2θ < 33.2
	Data Collection	
approx cryst dimens (mm)	0.17 × 0.55 × 0.50	0.22 × 0.48 × 0.46
cryst vol (mm^3), no. of faces	2.55 × 10^{-2}, 16	2.12 × 10^{-2}, 16
face indices	{100}, {001}, {210}	{100}, {001}, {210}, {210}
	122, $\bar{1}\bar{2}\bar{2}$, $11\bar{1}$, $\bar{1}\bar{1}1$,	
	$1\bar{1}1$, $\bar{1}1\bar{1}$, $1\bar{1}\bar{1}$, $\bar{1}11$	
ω-scan width: before, after	0.11, 0.14	0.14, 0.15
scan mode, width (deg)	ω–2θ, 0.75 + 0.35 tan θ	ω–2θ, 0.80 + 0.35 tan θ
index; θ range (deg)	$-1 \leqslant h \leqslant 24$, $0 \leqslant k \leqslant 18$, $0 \leqslant l \leqslant 17$; $0 \leqslant \theta \leqslant 25.0$	
scan speed (deg min^{-1})	1.4–4.0	1.5–4.0
max time/datum, total time	60 s, 51 h	60 s, 67 h
std reflcns	022, 040, 002, 210	040, 002, 210
monitor freq, % var	180m, +2.0	180m, 0.0
no. of data, std collected	4347, 112	4314, 78
	Data Processing	
corrections	Lorentz, polarization, and monochromator polarization	
decay, abs corrections	none, Gaussian	
abs coeff (cm^{-1}), grid size	9.10, 8 × 16 × 14	10.12, 8 × 16 × 16
transmissn: max, min	0.846, 0.488	0.815, 0.757
$R(F)$ for av: before, after	0.011, 0.010	0.012, 0.012
no. of unique data, signif	3849 > 0	3861 > 0
	Structure Refinement	
no. of observns, variables	2112, 205	2176, 205
final model: R_1, R_2	0.047, 0.060	0.043, 0.057
top residual (e Å^{-3}); coord	0.54 (7); 0.172, 0.443, 0.121	0.39 (7); 0.367, 0.152, 0.127
largest shift/error, param	0.31, z of O(4)	0.09, z of C(17)
goodness-of-fit (e)	1.44	1.35

$\sum w(||F_o| - |F_c||)^2$, where F_o and F_c are the observed and calculated structure amplitudes and the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$. With all non-hydrogen atoms included, and anisotropic thermal parameters assigned to Ni, F, N, and O atoms in the complex only, refinement of **6** converged at agreement factors $R_1 = \sum(||F_o| - |F_c||)/\sum(|F_o|) = 0.086$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.115$. Scattering factors for neutral, non-hydrogen atoms were taken from ref 20b, and the real components of the anomalous dispersion corrections were included for all atoms.[20b]

Of the 33 hydrogen atoms, 32 appeared in the top 40 peaks of a difference Fourier synthesis at peak heights ranging from 0.6 (1) to 0.2 (1) e Å^{-3}. All were included in idealized positions (C–H = 0.95 Å, N–H = 0.90 Å; sp^3 hybridization) with fixed isotropic thermal parameters 110% those of the atoms to which they are bonded. Methyl group positions were optimized by a least-squares routine. The scattering factor values were taken from Stewart et al.[26] With all non-hydrogen atoms except the carbon atoms of the complex assigned anisotropic thermal parameters and hydrogen atom positions recalculated to maintain ideal geometries, refinement of 205 variables converged at $R_1 = 0.047$ and $R_2 = 0.060$, with 2112 observations with $F_o > 2\sigma(F_o)$.

The final non-hydrogen atom coordinates of **6** were used as the starting point for the refinement of the Cu structure. All 33 hydrogen atoms were included in optimized positions, but their parameters were not refined. Clear evidence for 31 appeared in the top 38 peaks of a difference Fourier synthesis at peak heights ranging from 0.5 (1) to 0.2 (1) e Å^{-3}. The analysis converged at $R_1 = 0.047$ and $R_2 = 0.060$, for 205 variables and 2176 observations with $F_o > 2\sigma(F_o)$.

(26) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

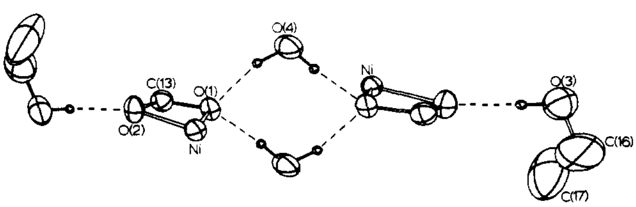

Figure 1. Hydrogen-bonding scheme in **6**.

Total difference Fourier synthesis for both structures showed no peaks with any chemical significance, and analyses of variance showed no unusual trends. Positional and U(equiv) thermal parameters are given for the refined atoms of both structures in Table SIX (supplementary material). Tables of hydrogen atom parameters, anisotropic thermal parameters, and structure amplitudes have been deposited as supplementary material. A summary of both refinements is presented in Table III.

Structure Descriptions. The formula unit of the crystals contains one molecule of complex, an ethanol, and a water molecule linked together in a strong hydrogen-bonding network (Figure 1). The molecule of ethanol forms a single hydrogen bond O(3)–HO3···O(2) to one of the chelating alkoxide atoms, O(2). The second alkoxide atom O(1) is hydrogen-bonded to the water molecule through O(1)···H1O4–O(4). A pair of these units is formed,

Table IV. Selected Interatomic Dimensions (Distances, Å; Angles, deg) for **5** (M = Cu) and **6** (M = Ni)

bond	6	5	bond	6	5
M-O(1)	2.037 (3)	1.977 (3)	M-O(2)	2.039 (4)	1.999 (4)
M-N(1)	2.023 (4)	1.989 (4)	M-N(2)	2.043 (5)	2.226 (4)
M-N(3)	2.051 (4)	2.018 (4)	O(1)-C(13)	1.378 (6)	1.380 (6)
O(2)-C(13)	1.363 (6)	1.359 (6)	O(3)-C(16)	1.523 (12)	1.445 (11)
N(1)-C(1)	1.480 (8)	1.494 (7)	N(1)-C(11)	1.276 (7)	1.270 (6)
N(2)-C(3)	1.491 (8)	1.498 (8)	N(2)-C(4)	1.489 (8)	1.470 (7)
N(3)-C(6)	1.502 (7)	1.496 (7)	N(3)-C(7)	1.505 (7)	1.506 (6)
C(1)-C(2)	1.513 (9)	1.513 (8)	C(2)-C(3)	1.515 (9)	1.505 (9)
C(4)-C(5)	1.518 (9)	1.512 (8)	C(5)-C(6)	1.512 (8)	1.534 (8)
C(7)-C(8)	1.535 (9)	1.551 (8)	C(7)-C(9)	1.536 (8)	1.522 (8)
C(7)-C(10)	1.528 (8)	1.516 (7)	C(10)-C(11)	1.511 (8)	1.525 (7)
C(11)-C(12)	1.518 (9)	1.487 (8)	C(13)-C(14)	1.548 (8)	1.529 (8)
C(13)-C(15)	1.531 (8)	1.553 (8)	C(16)-C(17)	1.465 (16)	1.480 (14)
angle	**6**	**5**	**angle**	**6**	**5**
O(1)-M-O(2)	67.1 (1)	68.4 (1)	O(1)-M-N(1)	163.9 (2)	166.1 (2)
O(1)-M-N(2)	100.5 (2)	99.7 (1)	O(1)-M-N(3)	96.6 (2)	96.5 (1)
O(2)-M-N(1)	100.3 (2)	100.0 (2)	O(2)-M-N(2)	101.6 (2)	100.4 (2)
O(2)-M-N(3)	154.6 (2)	156.5 (2)	N(1)-M-N(2)	91.9 (2)	89.8 (2)
N(1)-M-N(3)	91.4 (2)	91.8 (2)	N(2)-M-N(3)	100.5 (2)	100.0 (2)
M-O(1)-C(13)	91.1 (3)	91.2 (3)	M-O(2)-C(13)	91.4 (3)	90.9 (3)
M-N(1)-C(1)	109.5 (3)	109.9 (3)	M-N(1)-C(11)	128.6 (4)	128.9 (3)
C(1)-N(1)-C(11)	121.5 (5)	120.6 (4)	M-N(2)-C(3)	111.7 (4)	112.0 (3)
M-N(2)-C(4)	116.6 (4)	114.9 (3)	C(3)-N(2)-C(4)	112.3 (5)	113.0 (4)
M-N(3)-C(6)	118.3 (3)	117.3 (3)	M-N(3)-C(7)	107.8 (3)	108.4 (3)
C(6)-N(3)-C(7)	114.1 (4)	113.4 (4)	N(1)-C(1)-C(2)	109.9 (5)	110.7 (5)
C(1)-C(2)-C(3)	116.2 (5)	116.9 (5)	N(2)-C(3)-C(2)	113.2 (5)	112.7 (5)
N(2)-C(4)-C(5)	112.0 (5)	111.5 (5)	C(4)-C(5)-C(6)	114.6 (5)	114.6 (5)
N(3)-C(6)-C(5)	111.8 (5)	113.6 (4)	N(3)-C(7)-C(8)	110.6 (5)	110.2 (4)
N(3)-C(7)-C(9)	106.6 (4)	106.9 (4)	N(3)-C(7)-C(10)	111.2 (4)	111.4 (4)
C(8)-C(7)-C(9)	109.0 (5)	108.4 (4)	C(8)-C(7)-C(10)	108.3 (5)	108.8 (4)
C(9)-C(7)-C(10)	111.1 (5)	111.1 (4)	C(7)-C(10)-C(11)	120.3 (5)	120.2 (4)
N(1)-C(11)-C(10)	122.7 (5)	122.2 (4)	N(1)-C(11)-C(12)	125.1 (5)	126.5 (5)
C(10)-C(11)-C(12)	112.3 (5)	111.3 (4)	O(1)-C(13)-O(2)	110.6 (4)	109.5 (4)
O(1)-C(13)-C(14)	109.2 (4)	110.0 (4)	O(1)-C(13)-C(15)	108.5 (4)	107.6 (4)
O(2)-C(13)-C(14)	109.5 (4)	110.4 (4)	O(2)-C(13)-C(15)	110.3 (4)	109.8 (4)
C(14)-C(13)-C(15)	108.8 (5)	109.6 (4)	O(3)-C(16)-C(17)	118.6 (9)	116.6 (8)

positioned on a crystallographic center of symmetry, by a second hydrogen bond, O(1)···H2O4′-O(4)′, from the alkoxide atom, O(1), giving this atom a pseudo-four-coordinate geometry. The O(1)···O(4) distances of 2.785 (5) and 2.746 (5) Å in **6** and 2.792 (5) and 2.779 (5) Å in **5** are close to that of 2.75 Å found in the accurate neutron diffraction study of D_2O, ice 1 h, at 123 K.[27]

The geometry about the metal atom is best described as a distorted square pyramid with N(2) in the apical position (Figure 2). The small bite angle of the chelating alkoxide (67.1 (1)° for **6** and 68.4 (1)° for **5**) is the main source of distortion. The M-O-C-O ring of the chelating alkoxide is essentially planar, since the deviation of C(13) from the plane formed by the metal atom, O(1), and O(2) is 0.021 (5) Å for **5** and only 0.012 (5) Å for **6**. As a result, the CF_3 groups are evenly disposed above and below the plane (Table SVI (supplementary material)).

The two structures are very similar. Conformation and bond lengths in the macrocycle systems are similar to those previously found for the isothiocyanato complex $(mac)Ni(NCS)_2$.[18]

The major difference (29σ) between **6** and **5** is in the M-N(2) distance, which is 2.043 (5) Å for **6** and 2.226 (4) Å for **5**. The longer axial bond for the copper complex is expected from Jahn-Teller distortion. All other bonds involving the metal atom are also significantly shorter for the copper complex, values ranging from 6 to 14σ, consistent with its smaller atomic radius.

Previous structural studies on fluorinated alkoxides of nickel(II) have found values of 1.852 (4),[28] 1.840 (8),[29] and 1.842 (3) Å[30] for r(Ni-O) in four-coordinate Ni^{2+}, but 2.033 (3) Å when the metal is six-coordinate.[31] The two Ni-O bonds in the five-coordinate complex **6** average 2.038 (1) Å, close to those in the latter. The Cu-O bond lengths in **5** are significantly different (4σ), the values of 1.977 (3) and 1.999 (4) Å being significantly greater than those of 1.846 (9),[32] 1.895 (3),[33] and 1.920 (11) Å[34] found previously in fluorinated alkoxides of four-coordinate Cu^{2+}.

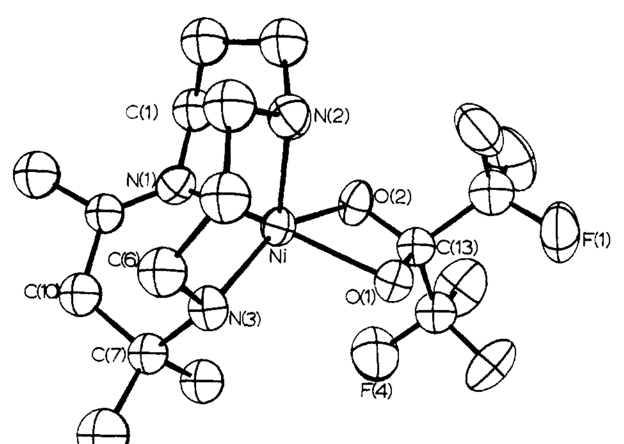

Figure 2. View of the complex $(\overline{NNN})M\overline{OC(CF_3)_2O}$ (**6**, M = Ni), showing the atom-numbering scheme. Atoms are drawn as 50% probability thermal ellipsoids.

Within the metal-alkoxide rings, the C-O bond distances vary from 1.359 (5) to 1.380 (5) Å, values typical of fluorinated alk-

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oxides of first-row transition metals.[35] The CF_3 groups experience less thermal motion than has been observed previously and consequently were better behaved during refinement. For **5** and **6**, the weighted mean C–F distances are 1.330 (3) and 1.336 (3) Å, and F–C–F angles are 105.9 (2) and 105.5 (2)°, respectively. C–C–F angles are more variable, ranging from 110.7 (5) to 115.0 (5)° in **5** and from 110.1 (5) to 115.1 (5)° in **6**.

Complexes **5** and **6** appear to be the first structurally characterized metal derivatives of a chelating *gem*-diol, and they may be compared with complexes of carbonate or carboxylate. The structure of the dinuclear (μ-carbonato)copper complex $[(mac)Cu(\mu\text{-}CO_3)Cu(mac)](ClO_4)_2$ has been determined by Davis and Einstein;[36] it has a macrocyclic ligand very similar to ours coordinated to the five-coordinate Cu^{2+} ion. The geometry around the metal closely resembles that found in **5**, with a bite angle of 65.3 (3)° for bidentate CO_3^{2-}. However, the Cu–O bonds are significantly (>4σ) longer at 2.028 (5) and 2.041 (1) Å, the C–O bond lengths in CO_3^{2-} are significantly (>3σ) shorter at 1.27 (1) and 1.32 (1) Å, and the O–C–O angle of 116.1 (6)° is much larger, consistent with sp^2 hybridization at carbon. Other chelating carbonates show similar structures.[37,38]

Comparison with a chelating carboxylate is complicated by the tendency of $RCOO^-$ to coordinate unsymmetrically. Only in copper complex **5** do we observe this, and there the difference in Cu–O bond lengths is marginal. For four-coordinate copper(I),[39] and for both five-[40] and six-coordinate[41] copper(II), acetate ligands chelate with Cu–O bonds of unequal length, although in the last case this has been associated with pseudo-Jahn–Teller distortion.[41,42] On average, bidentate acetate groups on copper typically show *longer* Cu–O bonds (mean 2.2–2.3 Å), *shorter* C–O bonds (~1.26 Å), a *larger* angle at carbon (120–122°), and a *smaller* bite angle at copper (52–55°) than those found with $[OC(CF_3)_2O]^{2-}$ or the carbonato complexes. A similar trend is found when acetate coordinates to six-coordinate nickel(II): The Ni–O bond lengths are nearly equal at 2.103 (9) and 2.116 (9) Å, C–O bonds are 1.25 (2) Å, and the bite angle is 62.4 (3)°.[43]

These differences are consistent with the nature of $[OC(CF_3)_2O]^{2-}$ as a bidentate, *dinegative*, ligand bonding to the metal ion more strongly than carboxylate. Equivalent, shorter metal–oxygen bonds, in conjunction with longer C–O bonds, change the geometry of the four-membered chelate ring to give a larger bite angle and consequently more effective overlap of ligand orbitals with orbitals on the metal. Metal–oxygen distances are comparable to those found in the oxides (2.09 Å for NiO and 1.95 Å for CuO). The fluorinated diol unambiguously occupies two coordination sites on the metal, whereas carboxylate is often intermediate between monodentate and bidentate modes of coordination.

Results and Discussion

We find that complexes containing either four- or six-membered chelate rings may be formed by reaction in solution. The former represent the first reported examples of chelated dialkoxides formed by direct reaction of a metal ion with the parent diol. In all cases, suitable amine or phosphine coligands are present to stabilize a four-, five-, or six-coordinate, neutral complex. Metal ions investigated include Cu^{2+}, Ni^{2+}, Mn^{2+}, Co^{3+}, Pd^{2+}, and Pt^{2+}. Table I summarizes representative complexes prepared. The four-membered ring $\overline{MOC(CF_3)_2O}$ is abbreviated M(OCO) and the six-membered ring $\overline{MOC(CF_3)_2OC(CF_3)_2O}$ M(OCOCO).

In most cases, a specific combination of metal and coligand produces only one type of complex, having either a four- or a six-membered chelate ring. Since complexes were isolated by crystallization from solution, it is possible that differential solubilities may favor the isolation of a particular complex. However, there was little evidence for the formation of mixtures of complexes of the two types. Only in the case of Cu^{2+} and Mn^{2+} with phenanthroline as coligand were we able to isolate products containing both types of chelate ring. Once formed, the chelate rings were very stable. In no case did a six-membered ring eliminate HFA nor was it possible to carry out a ring-expansion reaction in which a four-membered ring was converted to six-membered by reaction with an excess of ligand. With bipyridine as coligand, both four-coordinate complexes (bpy)M(OCOCO) and six-coordinate complexes $(bpy)_2M(OCOCO)$ could be isolated for M = Cu or Ni.

In order to confirm the assigned structures, and because of the novelty of the chelated dialkoxides derived from a *gem*-diol, we have carried out structural determinations on complexes containing both types of ring system. Strutures of the similar, five-coordinate, Cu^{2+} and Ni^{2+} complexes (mac)M(OCO), **5** and **6**, are reported here, and the structures of the complexes (tmed)Cu(OCOCO) (**11**) and $(Ph_3P)_2Pt(OCO)$ (**7b**) will be reported elsewhere.[44]

Properties of the Ligands. The properties of the chelating fluorinated alkoxides would be expected to be comparable to those of perfluoropinacolato (PFP^{2-}), which has the same donor set in a five-membered ring, and we find this to be the case. Where a comparison is possible in similar complexes, visible spectra of five- and six-membered rings are very similar. Some λ_{max} values are as follows: (tmed)Ni(OCOCO), 503 nm; (tmed)Ni(PFP), 500 nm;[45] (tmed)Cu(OCOCO), 556 nm; (tmed)Cu(PFP), 559 nm;[45] $(PPh_3)_2Ni(OCOCO)$, 490 nm; $(PPh_3)_2Ni(PFP)$, 476 nm.[45] With the strained four-membered ring, there is a slight shift to lower energy in similar complexes: (mac)Cu(OCO), 628 nm; (mac)Cu(PFP), 662 nm;[46] (diphos)Ni(OCO), 402 nm; (diphos)Ni(PFP), 444 nm.[45]

In pyridine, the complex (tmed)Ni(OCOCO) undergoes solvation to a green species, presumably five-coordinate. We have previously found that (tmed)Ni(PFP) is not solvated in pyridine, an effect attributed to the bulk of the two highly substituted ligands.[45] It appears that the additional flexibility of the six-membered ring allows coordination of a solvent molecule. However, the complexes of π-acceptor ligands (bpy)Ni(OCOCO) and (phen)Ni(OCOCO) do not interact with pyridine, presumably for electronic rather than steric reasons.

In the platinum complex $(PPh_3)_2Pt(OCO)$ (**7b**), $^1J(Pt,P)$ = 3577 Hz, slightly less than the values found in $(PPh_3)_2Pt(PFP)$ (3669 Hz),[47] in the carbonato complex $(Ph_3P)_2Pt(CO_3)$ (3697 Hz),[48] or in cis-$(Ph_3P)_2PtCl_2$ (3678 Hz),[49] indicating a fairly strong trans influence for the chelating diol.

Mechanism of Complex Formation

These results throw some light on the process by which condensation of two diol molecules occurs in solution.

It is well established that nucleophilic attack on HFA may lead to formation of an additional C–O–C linkage. This may occur by reaction of an alkoxide ion in solution, e.g.[50]

$$H^- + (CF_3)_2C{=}O \rightarrow HC(CF_3)_2O^- \xrightarrow{HFA} HC(CF_3)_2OC(CF_3)_2O^-$$

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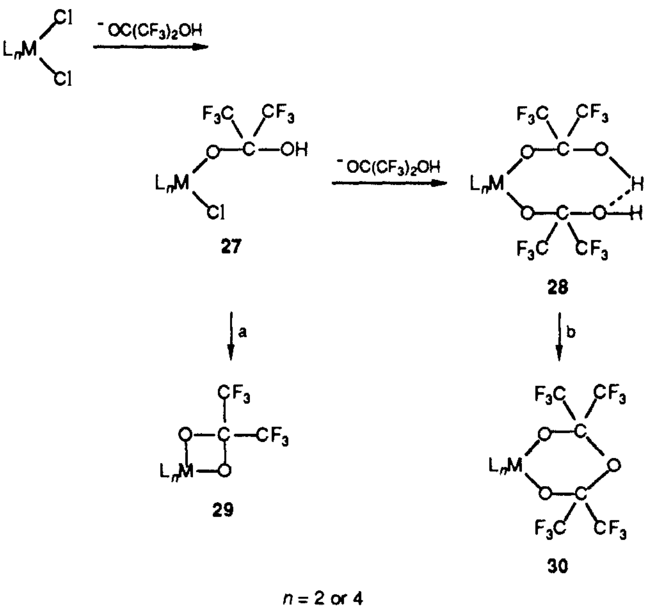
Scheme I



This type of reaction may have occurred during the isolation of the complexes $(PR_3)_2\overline{PtOC(CF_3)_2OC(CF_3)_2O}$ described by Modinos and Woodward,[15] since this was carried out with a mixture of diol and free ketone. However, we consider it very unlikely that free HFA is involved in reactions described here. All of our syntheses were carried out in ethanolic solution with no attempt made to exclude water. Guthrie[51] has shown that the equilibrium constants for the addition of methanol or water to HFA are 3.0×10^3 and 1.2×10^6, respectively, so the concentration of free ketone dissolved in ethanol/water mixtures would be negligible. The condensation of two molecules of the diol to form an ether linkage

$$HOC(CF_3)_2OH + HOC(CF_3)_2OH \rightarrow HOC(CF_3)_2OC(CF_3)_2OH + H_2O$$

would normally be expected to occur only under acidic conditions, not in the basic solution we used.

We therefore suggest that the initial step in the reaction is coordination of one alkoxide ion to the metal, giving intermediate **27**. Reaction may then follow one of two pathways: ring closure (a) to give the four-membered ring in complex **29** or coordination of a second alkoxide ligand to give **28**. The six-membered ring is then formed by a template condensation process (b) between the two coordinated ligand ions in **28**. Once formed, the six-membered chelate ring in **30** is stable (Scheme I).

In the intermediate **28**, where two alkoxides are coordinated to the same metal ion, the species will be stabilized (and the elimination of water facilitated) by intramolecular hydrogen-bonding. Clearly, amounts of the two types of product, **29** and **30**, will be determined by the relative rates of the cyclization step (a) and the condensation (b). In general, the system shows a preference for one or the other ring size; only in two cases could complexes containing both types of ring be isolated.

While electronic effects may be significant in some cases, the determining factor seems to be the steric bulk of the coligand(s), L. Since the formation of the six-membered ring involves the coordination of a second bulky alkoxide ligand, it would be expected to be disfavored by the presence of other sterically demanding ligands, and the observed reactions may be rationalized on this basis.

Where M = Cu and L_2 = phen, where either size of ring can be produced, the four-membered ring is formed when an excess of coligand is present, while a 1:1 phenanthroline to Cu^{2+} ratio produces (phen)Cu(OCOCO) (**18**). Presumably the excess coligand is coordinated to the metal during the reaction, giving the hindered intermediate $(phen)_2CuCl\{OC(CF_3)_2OH\}$, which cyclizes and loses phen to give the observed product (phen)Cu(OCO) (**1**) and the Ni^{2+} analogue **2**. When excess coligand is not present, the intermediate is the four-coordinate $(phen)CuCl\{OC(CF_3)_2OH\}$, where a second alkoxide ligand may be introduced. In the case of the smaller, more flexible, bipyridine ligand and Cu^{2+} or Ni^{2+}, coordination of the second alkoxide ligand is possible, and a six-membered ring is produced when reaction is carried out with either a 1:1 ratio (**14** and **15**) or an excess of coligand. Consistent with this, we were able to prepare six-coordinate complexes of Cu^{2+} and Ni^{2+} containing two diamine molecules with bipyridine, **16** and **17**, but not with phenanthroline.

With phenanthroline and Mn^{2+}, where six-coordination is more common, the use of the six-coordinate reagent $(phen)_2MnCl_2$ leads to the expected product $(phen)_2Mn(OCO)$ (**3**). Use of the four-coordinate complex $(phen)MnCl_2$ leads to the formation of a six-membered ring through the four-coordinate intermediate $(phen)Mn\{OC(CF_3)_2OH\}_2$, but through subsequent transfer of coligand the final product is $(phen)_2Mn(OCOCO)$ (**19**). Other workers have noted the ease with which phenanthroline is transferred between four- and six-coordinate complexes of Mn^{2+}.[17]

The same effect is shown with the Cu^{2+} complexes of ethylenediamine and substituted ethylenediamines. The bulkiest amine coligand, $Me_2NCH_2CH_2NMe_2$, forms a six-membered ring in **11**, the intermediate being four-coordinate. With the less hindered coligand $Me_2CH_2CH_2NH_2$, the intermediate is the six-coordinate $(Me_2NCH_2CH_2NH_2)_2CuCl\{OC(CF_3)_2OH\}$, which cyclizes to **4**. With unsubstituted ethylenediamine, the intermediate is again six-coordinate, but steric hindrance is reduced to the point where a second alkoxide is coordinated and a six-membered ring is formed in **9** and **10**. The tetradentate amine triethylenetetramine behaves similarly to bis(ethylenediamine), and the product is (trien)Cu(OCOCO) (**13**).

With the bulky tridentate macrocycle as coligand, Cu^{2+} and Ni^{2+} form the five-coordinate complexes (mac)M(OCO) (**5** and **6**). The starting materials for these reactions are the bridged dinuclear complexes $[(mac)M(\mu\text{-}OH)_2M(mac)](ClO_4)_2$.[18] Intermediates are the sterically hindered five-coordinate species $(mac)M(OH)\{OC(CF_3)_2OH\}$, and ready cyclization occurs, giving a four-membered ring. With Co^{3+}, the reagent is $[(mac)Co(OH)(\mu\text{-}OH)_2Co(OH)(mac)](ClO_4)_2$, in which the metal is six-coordinate. It appears that the terminal OH^- ligands are replaced first, followed by bridge cleavage as a second alkoxide ion attacks the more electrophilic 3+ metal ion, leading to the formation of a six-membered ring in **20**.

The formation of complexes of Ni^{2+} with phosphines as coligands follows the same pattern. With $(diphos)NiCl_2$, alkoxide and Cl^- are required to be cis in the intermediate, leading to (diphos)Ni(OCO) (**8**). Using unidentate phosphines gives $(R_3P)_2Ni(OCOCO)$ (**21** and **22**), because the intermediate is trans (or tetrahedral) and cyclization is disfavored. With the Pd^{2+} or Pt^{2+} ion, the antisymbiotic effect produces a cis disposition of ligands in the intermediate. Ring closure is rapid, and $(PPh_3)_2Pd(OCO)$ and $(PPh_3)_2Pt(OCO)$ (**7a** and **7b**) are formed. The fact that these are different from the complexes $(R_3P)_2Pt(OCOCO)$ prepared previously[15] supports the suggestion that the latter were formed by reactions involving free HFA.

As additional confirmation of the suggested mechanism, the ligand was reacted with Me_3SnCl under the conditions used to prepare the complexes. Replacement of Cl^- introduces only one ligand ion in the intermediate $Me_3SnOC(CF_3)_2OH$; neither ring closure nor template condensation is possible, and the only product is $Me_3SnOC(CF_3)_2OSnMe_3$ (**23**). (The silicon analogue has been prepared by the reaction of Me_3SiCl with the dilithium salt $Li_2[O(CF_3)_2CO]$ in acetone.[10]) Compounds with two HFA residues, such as $Me_3Sn\{OC(CF_3)_2\}_2H$, are known to form readily when trimethyltin derivatives react with free HFA.[50]

Reaction with the tridentate ligand $NH_2CH_2CH_2NHCH_2CH_2NH_2$ (dien) gives a different type of product. With both Ni^{2+} (**23**) and Cu^{2+} (**24**), the stoichiometry and visible spectrum of the

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product indicate the composition $[M(dien)_2]^{2+}[HOC(CF_3)_2O^-]_2$, in which the metal is complexed by two triamine ligands to give a large, stable dication with octahedral coordination. The structure of the fluorinated anion is unclear; it is different from that reported previously by Roesky et al. where the complex dianion $[H_2\{OC(CF_3)_2OH\}^{2-}]$ contains *four* diol residues.[11] Since the latter had been made by the hydrolysis of the anion $[(CF_3)_2C{=}NC(CF_3)_2O^-]$, we repeated the synthesis by the direct reaction of aqueous $(CF_3)_2C(OH)_2$ with base in the presence of large cations (Et_4N^+, Ph_4P^+, Ph_4As^+); in each case, the product isolated contained the same $[H_2\{OC(CF_3)_2OH\}_4{}^{2-}]$ dianion. It seems likely that the structure of the loosely bonded free anion formed from the diol is easily influenced by the nature of the counterion present, and investigation of this point is continuing.

Conclusions

These results clearly establish the preferred modes of coordination of hexafluoropropane-2,2-diol. In the diionized form, it chelates to a variety of metal ions, with bridging found only with ions such as Au^+, where the formation of small rings is disfavored. The reduction of basicity of the alkoxides accompanying fluorination causes them to coordinate to one metal center only; it is not surprising this ligand does not form a polyoxomolybdate cluster complex analogous to that derived from $CH_2(OH)_2$.[2] The formation of complexes containing six-membered rings results from the increased stability of the ethereal linkage found in fluorinated systems and the ease with which it is formed by a template condensation reaction.

We conclude that the ready availability and unique properties of $(CF_3)_2C(OH)_2$ make it particularly suitable for reaction with a large variety of metal ions to produce stable complexes.

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Supplementary Material Available: Tables of analytical data, hydrogen atom parameters, anisotropic thermal parameters, additional intramolecular dimensions, selected torsion angles, a weighted least-squares plane, and atomic and thermal parameters (12 pages); listings of calculated and observed structure factors (38 pages). Ordering information is available on any current masthead page.

Subsite-Differentiated Analogues of Native $[4Fe-4S]^{2+}$ Clusters: Preparation of Clusters with Five- and Six-Coordinate Subsites and Modulation of Redox Potentials and Charge Distributions

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Abstract: The subsite-differentiated cluster $[Fe_4S_4(LS_3)Cl]^{2-}$ (1, LS_3 = 1,3,5-tris((4,6-dimethyl-3-mercaptophenyl)thio)-2,4,6-tris(*p*-tolylthio)benzene(3−)) in Me_2SO solution reacts with a variety of bidentate and tridentate ligands to afford the substituted clusters $[Fe_4S_4(LS_3)L']^{z-}$. Some ten clusters of this type were prepared in order to examine the effects of cluster charge and coordination number at the unique subsite on relative stabilities of oxidation states and charge distributions as sensed by ^{57}Fe isomer shifts. This is the first comprehensive study of such effects with Fe_4S_4 clusters. Clusters prepared include those with L′ = PhS^- (**4**), $Me_2NCS_2^-$ (**5**), pyridine-2-thiolate (**6**), 1,4,7-triazacyclononane (**8**), hydrotris(1-pyrazolyl)borate (**9**), and 1,2-disubstituted benzenes such as benzene-1,2-dithiolate (**11**). Cluster formation is detected by ^1H NMR isotropic shifts of the LS_3 ligand, which are highly sensitive to L′. A tabulation of shifts is presented. All clusters have effective trigonal symmetry in solution. Among the more significant properties of the substituted clusters are the following: (i) chemically reversible $[Fe_4S_4]^{3+/2+}$ redox couples at potentials ca. 300–700 mV more negative than that of reference cluster **4**; (ii) negative shifts of the potentials of the $[Fe_4S_4]^{3+/2+}$ and $[Fe_4S_4]^{2+/+}$ couples on mononegative cluster **8** vs **1** and **4**; and (iii) skewing of electron distribution at the unique subsites toward "ferric-like" (**5**, **6**, **11**) and "ferrous-like" (**8**, **9**) character vs symmetrically delocalized **4**. Other matters considered include the source of stability of certain substituted clusters and the effects of cluster charge and core charge density on redox potentials. The data presented approximate the intrinsic effects of various potential ligand sets at a single subsite in native clusters. The possible biological implications of this work are illustrated with the P-clusters of nitrogenase, whose terminal ligation may depart from that of the now-classical native clusters $Fe_4S_4(S{\cdot}Cys)_4$.

We have pointed out recently that certain native Fe_4S_4 clusters exhibit structural and reactivity features localized at a specific Fe subsite.[2] Examples include the covalently bridged, magnetically coupled cluster–siroheme active site of *E. coli* sulfite reductase,[3,4] the $Fe_3S_4 \rightleftarrows Fe_4S_4$ cluster interconversion in aconitase where the same subsite is occupied and voided in the two processes,[5-8] and the incorporation of Fe^{2+}, Co^{2+}, and Zn^{2+} ions in the Fe_3S_4 cluster of *Desulfovibrio gigas* ferredoxin II.[9-11] Sub-

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