

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 HClO₄. Indeed, the only method of removal of the metal ion is to react with Na₂S 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)](ClO₄)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 Ni²⁺ and Cu²⁺ Complexes Derived from a Chelating gem-Diol¹

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Abstract: Two modes of coordination of hexafluoropropane-2,2-diol to transition-metal ions (Ni²⁺, Cu²⁺, Mn²⁺, Co³⁺, Pd²⁺, Pt²⁺) have been found. The diionized gem-diol can form a four-membered chelate ring with amine or phosphine coligands to give neutral complexes $L_n MOC(CF_3)_2O$. Alternatively, two molecules of the diol may condense to give a six-membered chelate ring $L_n MOC(CF_3)_2 OC(CF_3)_2 O$. 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 $(NNN)MOC(CF_3)_2O(5, M = Cu; 6, M = Ni)$. 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) Å³; 6, a = 20.462 (4) Å, b = 15.759(3) Å, c = 14.398 (3) Å, V = 4643 (3) Å³. 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 CCI_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 CH₃CH(OH)₂, C₆H₅CH(OH)₂, and CF₃CH(OH)₂ form similar adducts, but $(CF_3)_2C(OH)_2$ does not. A brief report has been made of the platinum complex (Ph₃P)₂PtOC(CH₃)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 (CH₃)₂GeOCH(CCl₃)O is of limited stability, readily eliminating CCl₃CHO.⁴

There have been several reports of complexes of 2,2'-bipyridyl ketone in which hydration of the carbonyl group occurs on co-ordination 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, $M^{+}[HOC(CF_{3})_{2}CO^{-}]$, may be isolated from aqueous solution;⁹ pyrolysis of the Li⁺ salt gives the dianion in [Li⁺]₂[(CF₃)₂CO₂²⁻].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 (PPh₃)₂PtOC(CF₃)₂O, made indirectly by the reduction of the peroxy complex $(PPh_3)_2$ $PtOC(CF_3)_2OO_3^{-13}$ the same route is used to prepare the unfluorinated analogue.³ A similar structure is suggested in the nickel complex $({}^{t}BuNC)_{2}\dot{N}iOC(CF_{3})_{2}\dot{O}$,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

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Table I.	Metal ^a	Complexes	of	$(CF_{3})_{2}(OH)_{2}$
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coligand	compound (no.)
Complexes Co	ntaining Four-Membered Chelate Rings
phenanthroline	(phen)Cu(OCO) (1), (phen)Ni(OCO) (2),
	$(\text{phen})_2 \text{Mn}(\text{OCO}) \cdot 2H_2 O(3)$
Me ₂ NCH ₂ CH ₂ NH ₂	$(Me_2NCH_2CH_2NH_2)Cu(OCO)$ (4)
mac ^b	(mac)Cu(OCO) (5), $(mac)Ni(OCO)$ (6)
₽h₃P	$(Ph_3P)_2Pd(OCO)$ (7a), $(Ph_3P)_2Pt(OCO)$ (7b)
diphos ^c	(diphos)Ni(OCO) (8)
Complexes C	ontaining Six-Membered Chelate Rings
en	$(en)_2Cu(OCOCO)$ (9),
	$(en)_2Co(OCOCO)(OH)$ (10)
Me ₂ NCH ₂ CH ₂ NMe 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),
	$(\text{phen})_2 \text{Mn}(\text{OCOCO}) \cdot 2H_2 O$ (19)
mac ^b	$(mac)Co(OCOCO)(OH) \cdot 2H_2O$ (20)
Ph ₃ P	$(Ph_3P)_2Ni(OCOCO)$ (21)
MePPh ₂	$(MePPh_2)_2Ni(OCOCO)$ (22)

^a Divalent metals except 10 and 20, Co³⁺ 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, NH₂(CH₂CH₂NH)₂CH₂CH₂NH₂.

points are uncorrected; in most cases, melting was accompanied by decomposition.

Complexes with Phenanthroline Coligand. Addition of phenanthroline (2 mmol) to CuCl₂·2H₂O (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 (CH₃)₂CO; mp 175 °C.

When the same procedure was carried with CuCl₂ 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 CH₂Cl₂; mp 167 °C.

The starting material for complex 3 was (phen)₂MnCl₂¹⁵ (1 mmol) suspended in 1:4 MeOH/H₂O, 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)MnCl₂¹⁶ (1 mmol) suspended in DMF. The salt K[OC(CF₃)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 CuCl₂. 2H₂O (1 mmol) in EtOH (15 mL) was added an excess of Me₂NCH₂CH₂NH₂ (ca. 5 mmol) followed by hemiacetal (2 mmol) and KOH (2 mmol). Workup as for 1 gave 4: purple crystals from CH₂Cl₂; mp 168 °C.

Complexes with Macrocyclic Coligand. The macrocycle 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene, as the bridged hydroxy complexes $[(mac)M(\mu-OH)_2M(mac)](ClO_4)_2$ (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 KClO₄ and the solvent were removed. The residue was recrystallized from CH₂Cl₂ 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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Trans. 1978, 68.

Lable II. Thislete Operation Data of Completion	Table	II.	Visible	Spectral	Data of	Complexes
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complex	no.	solvent ^a	$\lambda_{max}, nm(\epsilon)$
(phen)Cu(OCO)	1	A	701 (20)
(phen)Ni(OCO)	2	Α	520 (4.0)
$(Me_2NCH_2CH_2NH_2)Cu(OCO)$	4	E	542 (58)
(mac)Cu(OCO)·H ₂ O·EtOH	5	Α	628 (93)
(mac)Ni(OCO) H ₂ O·EtOH	6	Ε	362 (114), 400 (27),
· · · · ·			610 (34)
(diphos)Ni(OCO)	8	Α	402 (617)
(en) ₂ Cu(OCOCO)	9	E	577 (62)
$(en)_2Co(OCOCO)(OH)$	10	E	575 (91), 372 (97)
(tmed)Cu(OCOCO)	11	Α	556 (103)
(tmed)Ni(OCOCO)	12	Α	503 (103)
(trien)Cu(OCOCO)	13	Ē	638 (117)
(bpy)Cu(OCOCO)	14	Ε	595 (91)
(bpy)Ni(OCOCO)	15	E	515 (5.2)
(bpy) ₂ Cu(OCOCO)	16	E	606 (63)
(phen)Cu(OCOCO)	18	E	600 (69)
(mac)Co(OCOCO)(OH)	20	E	524 (67)
(Ph ₃ P) ₂ Ni(OCOCO)	21	В	490 (94)

^{*a*}Key: A = acetone; E = ethanol; B = benzene.

The same method with the cobalt(III) complex [(mac)(OH)Co(μ -OH)₂Co(OH)(mac)](ClO₄)₂¹⁸ gave 20: red crystals from MeOH/CHCl₂; mp 163 °C. Analysis corresponded to a dihydrate.

Complexes with Ethylenediamine Coligand. To $CuCl_2 \cdot 2H_2O(1 \text{ mmol})$ 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 methods¹⁹ and converted to $[Co(en)_2Cl_2][BPh_4]$ by reaction with aqueous NaBPh₄. 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, KBPh₄ was removed, the solution evaporated to a purple oil, dissolved in CH₂Cl₂, and Et₂O 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 CHCl₃; mp 193–195 °C] and the nickel complex 12 [red crystals from CH₂Cl₂; 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/CH₂Cl₂; 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 CH₂Cl₂; 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 Me₂CO/Et₂O; 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 CHCl₃/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 CHCl₃/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(CF₃)_2OH] (2 mmol) in CH₂Cl₂. 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, NiCl₂·2H₂O (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 Me₃SnCl. Ethanolic KOH (2 mmol) was added to

excess hemiacetal in EtOH and a solution of Me₃SnCl (2 mmol) in CH₂Cl₂ 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 Me₃SnOC(CF₃)₂OSnMe₃ (23) white plates from Et₂O/hexanes: mp 78-82 °C; IR strong ν (C-O) at 945 cm⁻¹; ¹H NMR 0.45 ppm (s, ¹¹⁷Sn/¹¹⁹Sn satellites (unresolved), ²J(Sn,H) = 58 Hz); ¹⁹F 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 $1100-1300 \text{ cm}^{-1}$ 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-C₂H₄Br₂ 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 techniques²⁵ 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	$C_{17}H_{22}F_6N_6N_1O_4$, 516.2	$C_{17}H_{22}CuF_2N_2O_4$, 521.0	
cryst syst, space grp	orthorhombic, P	bca (No. 61)	
syst abs	0kl, k odd; h0l, l d	dd: 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 CA	D4F, graphite	
radiation, λ (Å)	Μο Κα, 0.	71073	
cryst detec (mm), toa (deg)	205, 2	.5	
aperture (mm): vert, horiz	$4.0, 5.0 \pm 0.$	35 tan θ	
centering reflens, θ range	$20, 25.0 < 2\theta < 33.0$	$20, 25.0 < 2\theta < 33.2$	
	Data Callestian		
	Data Collection		
approx cryst dimens (mm)	$0.17 \times 0.55 \times 0.50$	$0.22 \times 0.48 \times 0.40$	
cryst vol (min ²), no. of faces	2.52×10^{-1} , 10	2.12×10^{-1} , 10	
face indices	$\{100\}, \{001\}, \{210\}$	{100}, {001}, {210}, {210}	
	122, 122, 111, 111, 111, 171, 171, 171,		
		0.14.0.15	
ω -scan width: before, after	0.11, 0.14	0.14, 0.15	
scan mode, width (deg)	$\omega = 2\theta$, 0.75 + 0.35 tan θ	$\omega = 2\theta$, 0.80 + 0.35 tan θ	
index; θ range (deg)	$-1 \le h \le 24, 0 \le k \le 18, 0$	$\leq l \leq 1/; 0 \leq \theta \leq 25.0$	
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 reficns	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 i	monochromator polarization	
decay abs corrections	none (aussian	
abs coeff (cm^{-1}) , grid size	9 10. 8 × 16 × 14	$10.12.8 \times 16 \times 16$	
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	
no. or unique utit, signi	5017 - 0		
	Structure Refinement		
no. of observns, variables	2112, 205	2176, 205	
final model: R_{12} , 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	

 $\sum w(||F_0| - |F_c||)^2$, where F_0 and F_c are the observed and calculated structure amplitudes and the weight w is defined as $4F_0^2/\sigma^2(F_0^2)$. 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 $R_1 = \sum (||F_0| - |F_c||)/\sum (|F_0|) = 0.086$ and $R_2 = (\sum w(|F_0| - |F_c|)^2 / \sum wF_0^2)^{1/2}$ = 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; sp³ 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



Figure 1. Hydrogen-bonding scheme in 6.

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 $F_o > 2\sigma(F_o)$.

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- $\cdot \cdot O(2)$ 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)- $\cdot \cdot H1O4-O(4)$. A pair of these units is formed,

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Fable IV.	Selected Interatom	ic Dimensions	(Distances, .	Å; .	Angles,	deg)	for	5	(M	= (Cu) a	nd 6	(M	=]	Ni)	
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bond	6	5	bond	6	5
	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 CF₃ 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) Å³⁰ for r(Ni-O) in four-coordinate Ni²⁺, but 2.033 (3) Å when the metal is six-coordinate.³¹ The two Ni-O bonds in the five-co-



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

ordinate 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) Å³⁴ found previously in fluorinated alkoxides of four-coordinate Cu²⁺.

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 CF₃ 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 $[(mac)Cu(\mu-CO_3)Cu(mac)](ClO_4)_2$ has been determined by Davis and Einstein;³⁶ it has a macrocyclic ligand very similar to ours coordinated to the five-coordinate Cu2+ 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 (>4 σ) longer at 2.028 (5) and 2.041 (1) Å, the C–O bond lengths in CO_3^{2-} are significantly (>3 σ) 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 sp² 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-coordinate41 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 $(\sim 1.26 \text{ Å})$, a larger angle at carbon (120–122°), and a smaller bite angle at copper (52-55°) than those found with [OC- $(CF_3)_2 \tilde{O}]^{2-}$ 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 metaloxygen 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

Trans. 1970, 1956.

ions investigated include Cu2+, Ni2+, Mn2+, Co3+, Pd2+, and Pt2+. Table I summarizes representative complexes prepared. The four-membered ring MOC(CF₃)₂O is abbreviated M(OCO) and the six-membered ring $MOC(CF_3)_2OC(CF_3)_2OM(OCOCO)$.

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 sixmembered 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, Cu²⁺ and Ni²⁺ complexes (mac)M(OCO), 5 and 6, are reported here, and the structures of the complexes (tmed)Cu(OCOCO) (11) and (Ph₃P)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 (PFP²⁻), 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 (PPh₃)₂Ni(OCOCO), 490 nm; (PPh₃)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 sixmembered 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 (PPh₃)₂Pt(PFP) (3669 Hz),⁴⁷ in the carbonato complex (Ph₃P)₂Pt(CO₃) (3697 Hz),48 or in cis-(Ph₃P)₂PtCl₂ (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⁻ + (CF₃)₂C=O → HC(CF₃)₂O⁻
$$\xrightarrow{\text{HFA}}$$

HC(CF₃)₂OC(CF₃)₂O⁻

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This type of reaction may have occurred during the isolation

of the complexes $(PR_3)_2PtOC(CF_3)_2OC(CF_3)_2O$ 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. Guthrie⁵¹ 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 sixmembered 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 hydrogenbonding. 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 Cu²⁺ 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(CF₃)₂OH}, which cyclizes and loses phen to give the observed product (phen)Cu(OCO) (1) and the Ni²⁺ analogue 2. When excess coligand is not present, the intermediate is the four-coordinate (phen)CuCl{OC(CF₃)₂OH}, where a second alkoxide ligand may be introduced. In the case of the smaller, more flexible, bipyridine ligand and Cu²⁺ or Ni²⁺, 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 Cu²⁺ and Ni²⁺ 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)₂MnCl₂ leads to the expected product (phen)₂Mn(OCO) (3). Use of the four-coordinate complex (phen)MnCl₂ leads to the formation of a six-membered ring through the four-coordinate intermediate (phen)Mn{OC(CF₃)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 Ni²⁺ form the five-coordinate complexes (mac)M(OCO) (5 and 6). The starting materials for these reactions are the bridged dinuclear complexes [(mac)M(μ -OH)₂M(mac)](ClO₄)₂.¹⁸ Intermediates are the sterically hindered five-coordinate species (mac)M(OH){OC(CF₃)₂OH}, and ready cyclization occurs, giving a four-membered ring. With Co³⁺, the reagent is [(mac)Co-(OH)(μ -OH)₂Co(OH)(mac)](ClO₄)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 Ni²⁺ with phosphines as coligands follows the same pattern. With (diphos)NiCl₂, alkoxide and Cl⁻ are required to be cis in the intermediate, leading to (diphos)Ni(OCO) (8). Using unidentate phosphines gives (R₃P)₂Ni(OCOCO) (21 and 22), because the intermediate is trans (or tetrahedral) and cyclization is disfavored. With the Pd²⁺ or Pt²⁺ ion, the antisymbiotic effect produces a cis disposition of ligands in the intermediate. Ring closure is rapid, and (PPh₃)₂Pd(OCO) and (PPh₃)₂Pt(OCO) (7a and 7b) are formed. The fact that these are different from the complexes (R₃P)₂Pt-(OCOCO) prepared previously¹⁵ 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 Me₃SnCl under the conditions used to prepare the complexes. Replacement of Cl⁻ introduces only one ligand ion in the intermediate Me₃SnOC(CF₃)₂OH; neither ring closure nor template condensation is possible, and the only product is Me₃SnOC(CF₃)₂OSnMe₃ (23). (The silicon analogue has been prepared by the reaction of Me₃SiCl with the dilithium salt Li₂[O(CF₃)₂CO] in acetone.¹⁰) Compounds with two HFA residues, such as Me₃Sn{OC(CF₃)₂]₂H, are known to form readily when trimethyltin derivatives react with free HFA.⁵⁰

Reaction with the tridentate ligand $NH_2CH_2CH_2NHCH_2C-H_2NH_2$ (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 [H₂|OC-(CF₃)₂OH²⁻] contains four diol residues.¹¹ Since the latter had been made by the hydrolysis of the anion $[(CF_3)_2C=NC(C-1)]$ $F_{3}_{2}O^{-}$, 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 Me₂SO solution reacts with a variety of bidentate and tridentate ligands to afford the substituted clusters $[Fe_4S_4(LS_3)L']^{2-}$. 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 ⁵⁷Fe isomer shifts. This is the first comprehensive study of such effects with Fe₄S₄ 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 LS3 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 $Fe_3S_4 \rightleftharpoons Fe_4S_4$ cluster interconversion in aconitase

where the same subsite is occupied and voided in the two processes, 5-8 and the incorporation of Fe²⁺, Co²⁺, and Zn²⁺ ions in the Fe₃S₄ cluster of *Desulfovibrio gigas* ferredoxin II.⁹⁻¹¹ Sub-

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