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Coordination Modes of Polydentate Ligands. 1. Template Synthesis of Complexes of Ni^{2+}, Cu^{2+}, and Co^{2+} with Pentadentate and Hexadentate Ligands: Structure of a Highly Distorted Six-Coordinate Co^{2+} Complex[1]

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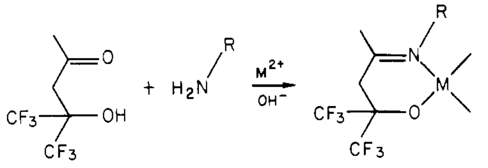
A number of new, polyfunctional ligands and their metal complexes have been synthesized by the template condensation of diamines with 5,5,5-trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone, $HOC(CF_3)_2CH_2COCH_3$, in the presence of Ni^{2+}, Cu^{2+}, or Co^{2+}. The manner of coordination of the ligand depends on the size of potential chelate rings in the complex, the nature of donor atoms present, and the identity of the metal. Specifically, condensation using $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ and Ni^{2+} gives $Ni[(OC(CF_3)_2CH_2C(CH_3){=}N(CH_2)_3NHCH_2{-})_2]$. Use of $NH_2(CH_2)_2O(CH_2)_2NH_2$ gives $M[(OC(CF_3)_2CH_2C(CH_3){=}N(CH_2)_2)_2O]$ (M = Ni, Cu, or Co) while use of $NH_2(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$ gives $M[(OC(CF_3)_2CH_2C(CH_3){=}N(CH_2)_2OCH_2{-})_2]$ (M = Ni, Cu, or Co). For the last ligand, a structure involving trans-bridged, four-coordinate geometry is suggested for the Ni^{2+} complex, while a complete structural determination has been carried out for the Co^{2+} analogue. Crystals are triclinic, space group $P\bar{1}$, with unit cell dimensions $a = 10.144$ (3) Å, $b = 15.740$ (6) Å, $c = 15.579$ (6) Å, $\alpha = 102.56$ (3)°, $\beta = 92.03$ (3)°, $\gamma = 96.58$ (3)°, $V = 2407$ Å^3, and $Z = 4$. Data were collected for 4470 reflections, giving $R = 0.0498$ and $R_w = 0.0577$. The structure shows the complex to be mononuclear with six-coordinate Co^{2+} in highly distorted octahedral geometry. Two alkoxy oxygen atoms in the ligand (Co–O, 1.93–1.96 Å) make an O–Co–O angle of 122°; two imino nitrogen atoms (Co–N, 2.13–2.14 Å) are trans collinear about Co, while the two ethereal oxygen atoms (Co–O, 2.32–2.34 Å) in the chain make an unusually small (69–70°) bite angle at Co. Hydrogenation of iminoalkoxy ligand complexes using $LiAlH_4$ gives the corresponding aminoalkoxy ligands, which give complexes with Ni^{2+}, Cu^{2+}, and Co^{2+} or Co^{3+}. Different structures observed in the corresponding complexes after hydrogenation are discussed in terms of increased ring flexibility.

Introduction

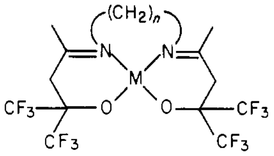
We have previously reported[3-6] that the fluorinated keto alcohol 5,5,5-trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone (hexafluorodiacetone alcohol, HFDA) readily undergoes template condensation reactions with primary amines in the presence of a metal ion, the products being iminoalkoxy complexes of the metal. (We describe these as "template condensations" because reaction of amines with HFDA will not occur in the absence of the metal ion.)



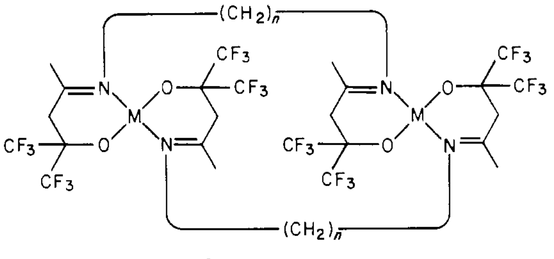
HFDA

1, M = Cu, Ni, etc.

The structure of the metal complex is dependent on the nature of the group R. When R is alkyl, the resulting iminoalkoxy ligand is uninegative and bidentate, and two such ligands coordinate to Cu^{2+} in a trans square-planar configuration to give a neutral complex.[6] With diamines, $H_2N(CH_2)_nNH_2$, template condensation with two molecules of HFDA occurs readily, giving a dinegative, tetradentate ligand, and coordination to Cu^{2+} or Ni^{2+} then gives neutral square-planar complexes. However, the overall structure of the product depends on the chain length of the diamine, with short chains (n = 2 or 3) giving mononuclear[7] units[3] (**2**). The donor atoms around the metal are, of necessity, in a cis configuration in this type of complex. A similar arrangement is found when two such tetradentate ligands are coordinated to Ce^{4+} to give a neutral complex in which the metal is eight-coordinate.[5] In contrast, the use of longer chain diamines leads to the formation of dinuclear complexes in which the metal is four-coordinate in a trans square-planar configuration (**3**). We have confirmed coordination of type **3** by complete structural determinations for compounds where M = Ni, n = 6[8] and where M = Cu, n = 5,[9] and the general properties of related compounds lead us to conclude that dinuclear structures are found for long-chain diamine condensations up to n = 12.



2, M = Cu or Ni, n = 2 or 3



3, M = Cu or Ni

In our initial studies on these systems,[3] we found that the incorporation of a secondary amino donor site into the chain

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[2] (a) The University of Western Ontario. (b) The University of Windsor.

[3] Martin, J. W. L.; Willis, C. J. *Can. J. Chem.* **1977**, *55*, 2459.

[4] Martin, J. W. L.; Willis, C. J. *Can. J. Chem.* **1978**, *56*, 2966.

[5] Timmons, J. H.; Martin, J. W. L.; Martell, A. E.; Rudolf, P.; Clearfield, A.; Arner, J. H.; Loeb, S. J.; Willis, C. J. *Inorg. Chem.* **1980**, *19*, 3553.

[6] Loeb, S. J.; Richardson, J. R.; Willis, C. J. *Inorg. Chem.* **1983**, *22*, 2736.

[7] We use the terms mononuclear and dinuclear with reference to the number of metal atoms in one unit of the complex.

[8] Martin, J. W. L.; Payne, N. C.; Willis, C. J. *Inorg. Chem.* **1978**, *17*, 3478.

[9] Barber, D. L.; Loeb, S. J.; Martin, J. W. L.; Payne, N. C.; Willis, C. J. *Inorg. Chem.* **1981**, *20*, 272.

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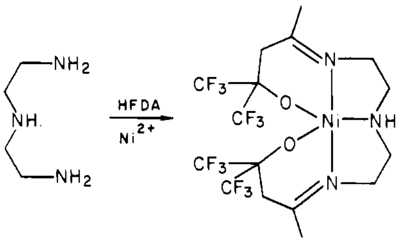
Table I. Analytical Data, Magnetic Moments, and Mass Spectra

compd	formula	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	magnetic moment (300 K), μ_B	mass spectra parent ion,[a] *m/e*
Ni(i-ONNNNO)[b] (**5**)	$C_{20}H_{28}F_{12}N_4O_2Ni$	37.35	37.51	4.39	4.38	8.71	8.84	3.61	642
a-HONNNNOH[c] (**6**)	$C_{20}H_{38}Cl_4F_{12}N_4O_2$	32.62	31.85	5.20	4.98	7.61	7.58		589
Ni(a-ONNNNO) (**7**)	$C_{20}H_{32}F_{12}N_4O_2Ni$	37.12	36.16	4.98	4.79	8.66	8.55	3.31	646
Co(a-ONNNNO)PF$_6$ (**8**)	$C_{20}H_{32}F_{18}N_4O_2PCo$	30.31	28.01	4.07	4.05	7.06	6.38	0.99	648
Ni(i-ONONO) (**9**)	$C_{16}H_{18}F_{12}N_2O_3Ni$	33.54	33.50	3.17	3.28	4.89	4.82	diamag	572/1143
Cu(i-ONONO) (**10**)	$C_{16}H_{18}F_{12}N_2O_3Cu$	33.26	33.31	3.14	3.20	4.85	4.65	1.76	577/1153
Co(i-ONONO) (**11**)	$C_{16}H_{18}F_{12}N_2O_3Co$	33.53	33.55	3.16	2.84	4.89	4.83	4.82	573
Ni(a-ONONO) (**14**)	$C_{16}H_{22}F_{12}N_2O_3Ni$	33.30	33.27	3.84	3.91	4.85	4.57	3.22	576
Cu(a-ONONO) (**12**)	$C_{16}H_{22}F_{12}N_2O_3Cu$	33.03	32.92	3.81	3.95	4.81	4.69	1.75	581
Co(a-ONONO) (**15**)	$C_{16}H_{22}F_{12}N_2O_3Co$	33.29	33.28	3.84	3.85	4.85	4.65	4.27	577
Ni(i-ONOONO) (**17**)	$C_{18}H_{22}F_{12}N_2O_4Ni$	35.04	35.73	3.59	3.63	4.54	4.47	diamag	616
Cu(i-ONOONO) (**19**)	$C_{18}H_{22}F_{12}N_2O_4Cu$	34.76	34.96	3.57	3.66	4.50	4.55	1.77	621
Co(i-ONOONO) (**20**)	$C_{18}H_{22}F_{12}N_2O_4Co$	35.02	35.04	3.59	3.63	4.54	4.55	4.54	617
a-HONOONOH[c] (**21**)	$C_{18}H_{28}Cl_2F_{12}N_2O_4$	33.92	33.73	4.40	4.60	4.75	4.65		565
Ni(a-ONOONO) (**22**)	$C_{18}H_{26}F_{12}N_2O_4Ni$	34.81	34.58	4.22	4.53	4.51	4.39	diamag	620
Cu(a-ONOONO) (**23**)	$C_{18}H_{26}F_{12}N_2O_4Cu$	34.54	34.60	4.19	4.39	4.48	4.37	1.77	625
Co(a-ONOONO) (**24**)	$C_{18}H_{26}F_{12}N_2O_4Co$	34.80	34.75	4.22	3.75	4.51	4.68	4.57	621
Ni(i-ONOONO)·CH$_3$OH (**18**)	$C_{19}H_{26}F_{12}N_2O_5Ni$	35.16	35.05	4.04	3.91	4.32	4.56	3.18	620

[a] For the species containing ^{58}Ni, ^{63}Cu, or ^{59}Co. [b] Letters in parentheses represent the sequence of potential donor atoms in the ligands: a = aminoalkoxy ligand; i = iminoalkoxy ligand. [c] Free aminoalkoxy ligands were analyzed as hydrochlorides.

connecting the two amino groups produced a mononuclear complex of five-coordinate nickel, **4**. In the present paper,



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we report an extension of these studies to ligands derived from α,ω-diamines in which the chain connecting the two $-NH_2$ groups contains one or two additional donor sites, either secondary amino or ethereal oxygen. After template condensation, the resulting iminoalkoxy ligands are potentially penta- or hexadentate, and the properties of the complexes demonstrate the manner of their interaction with the metal ion. A complete structural determination has been made for a Co^{2+} complex of a hexadentate ligand.

Experimental Section

General Information. Volatile compounds were manipulated on a conventional vacuum manifold. Infrared spectra were recorded on a Beckman 4250 spectrometer, visible–UV spectra on a Cary 118 spectrometer, and mass spectra on a Varian MAT 311A instrument. Microanalysis was performed by Guelph Analytical Laboratories, Guelph, Ontario, Canada; all analytical data are in Table I. Magnetic susceptibilities were determined by the Gouy method at 300 K.

5,5,5-Trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone (HFDA) was prepared by the condensation of hexafluoroacetone with acetone as described previously.[3]

Condensation with $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$. The tetraamine was a commercial sample (BASF) which was purified by recrystallization of the tetrahydrochloride from ethanol (mp 295 °C). The amine hydrochloride (2.57 g, 8.29 mmol), HFDA (3.58 g, 16.0 mmol), and anhydrous $NiCl_2$ (1.00 g, 7.7 mmol) were dissolved in ethanol (50 mL), and KOH (3.23 g, 57.7 mmol) in ethanol (50 mL) was added dropwise with constant stirring. The color of the solution changed from yellow to pale blue; it was stirred 24 h at 25 °C and then filtered to remove KCl. Concentration by evaporation yielded the nickel complex **5**, recrystallized from ethanol as pale blue crystals, mp 235–237 °C.

The reaction was repeated with use of anhydrous $CuCl_2$. It was apparent from color changes that some condensation was occurring, but no solid product could be characterized. The same result was obtained when $NiCl_2$ was used in a reaction with triethylenetetramine, $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, the product appearing as a blue oil, which could not be crystallized. Attempts to prepare iminoalkoxy complexes of cobalt using either of the above tetraamines in condensation reactions were unsuccessful. It was apparent that condensation was occurring, and the resulting solutions were easily air-oxidized, but neither Co^{2+} nor Co^{3+} complexes could be isolated as solids.

Hydrogenation. The nickel complex **5** (8.40 g, 13.1 mmol) was dissolved in anhydrous ether (100 mL) and $LiAlH_4$ (2.70 g, 71 mmol) in ether added with stirring. The reaction was quenched with ethanol after 1.5 h and the solution filtered and acidified with concentrated aqueous HCl. On cooling, the aminoalkoxy ligand **6** as the tetrahydrochloride separated as white crystals, mp 290–292 °C.

The ligand hydrochloride (1.14 g, 1.58 mmol) and $NiCl_2·6H_2O$ (0.38 g, 1.58 mmol) were dissolved in ethanol, and KOH (0.53 g, 9.5 mmol) in ethanol was added, causing an immediate color change from green through red to violet. Evaporation gave the aminoalkoxy Ni^{2+} complex **7** as light blue crystals from methanol, mp 225 °C dec.

Attempts to isolate the analogous complexes of Cu^{2+} and Co^{2+} were unsuccessful, giving only oily products. In the latter case, the solution of the complex darkened on exposure to air and oxidation to Co^{3+} was carried out with use of an excess of I_2 in ethanol. Filtration and evaporation gave a red-brown solid, purified by CH_2Cl_2 extraction, which was redissolved in ethanol and an excess of NH_4PF_6 added. Evaporation followed by CH_2Cl_2 extraction gave the Co^{3+} aminoalkoxy complex as the PF_6^- salt, **8**, as fine brown crystals shown by analysis and magnetic moment to be slightly impure. Attempts to convert the iodide into salts of other anions (ClO_4^-, BF_4^-) did not lead to characterizable compounds.

Condensations with $NH_2(CH_2)_2O(CH_2)_2NH_2$. Bis(2-aminoethyl) ether was prepared from bis(2-hydroxyethyl) ether by the azide route as described by Kulstad and Malmsten;[10] like these authors, we find the Gabriel synthesis used previously[11] to be unsatisfactory for compounds of this type. The diamine (1.00 g, 9.55 mmol), HFDA (4.28 g, 19.0 mmol), and anhydrous $NiCl_2$ (1.24 g, 9.56 mmol) were dissolved in ethanol (100 mL), and KOH (1.07 g, 19.1 mmol) in ethanol was added. After it was stirred 12 h at 25 °C, the solution was filtered and evaporated to give the Ni^{2+} complex **9** as red-purple crystals from ethanol.

The Cu^{2+} complex, **10**, was prepared similarly from $CuCl_2$, giving pale blue crystals from ethanol. By the use of $CoCl_2·6H_2O$ in a similar reaction the Co^{2+} complex, **11**, was isolated as lavender crystals from ether.

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[10] Kulstad, S.; Malmsten, L. A. *Acta Chem. Scand., Ser. B* **1979**, *B33*, 469.

[11] Dietrich, B.; Lehn, J.-M.; Sauvage, J. P. *Tetrahedron Lett.* **1969**, 2885.

Hydrogenation. The Cu^{2+} complex **10** (5.5 g, 9.5 mmol) was dissolved in anhydrous THF (100 mL) and added dropwise to a slurry of $LiAlH_4$ (3.62 g, 96 mmol) in THF. After it was stirred 2 h at 25 °C, the solution was quenched with ethanol and a rapid current of air passed during 12 h to oxidize Cu^+ to Cu^{2+}. The resulting blue suspension was filtered and solvent removed by rotoevaporation to yield a blue oil. Extraction with pentane followed by concentration gave the aminoalkoxy Cu^{2+} complex **12** as blue crystals.

The above Cu^{2+} complex was dissolved in dilute aqueous HCl and gaseous H_2S passed until the solution was colorless above a black precipitate of CuS. Removal of the latter followed by concentration of the solution failed to yield the free ligand hydrochloride in a crystalline form, with only oils remaining, and a solution of the aminoalkoxy ligand was therefore used for the preparation of the Ni^{2+} and Co^{2+} complexes. Assuming quantitative decomposition of the aminoalkoxy Cu^{2+} complex, a solution of the ligand hydrochloride in ethanol was added to the stoichiometric amount of $NiCl_2{\cdot}6H_2O$ in ethanol, and the solution was neutralized (KOH), filtered, evaporated to dryness, and extracted with CH_2Cl_2, followed by crystallization from hexane to give the Ni^{2+} complex, **14**, as very pale green crystals.

The Co^{2+} complex, **15**, was prepared similarly, giving pink crystals from ether.

Condensations with $NH_2(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$. 1,2-Bis(2-aminoethoxy)ethane was prepared from 1,2-bis(2-hydroxyethoxy)ethane by the azide route.[10] The diamine (1.00 g, 6.75 mmol), HFDA (3.02 g, 13.5 mmol), and anhydrous $NiCl_2$ (0.88 g, 6.75 mmol) were dissolved in ethanol (50 mL), and KOH (0.76 g, 13.5 mmol) in ethanol was added. When it was refluxed for 12 h, the solution changed from green to red, and filtration followed by evaporation gave a red oil, which yielded the Ni^{2+} complex, **17**, as red crystals from $CHCl_3$–C_5H_{12}.

Similar reaction using $CuCl_2$ gave the Cu^{2+} complex, **19**, as dark blue crystals from ethanol. In the case of the analogous Co^{2+} complex (with use of $CoCl_2{\cdot}6H_2O$), heating was not necessary, and the initially deep blue solution turned a dull red-violet during the addition of base. The Co^{2+} complex, **20**, was isolated after stirring the reaction mixture 24 h at 25 °C, giving deep red-brown crystals from ether.

Hydrogenation. The Cu^{2+} complex **19** (7.5 g, 28 mmol) in anhydrous ether (200 mL) was added dropwise to $LiAlH_4$ (3.0 g, 79 mmol) in ether with stirring. After 1.5 h, the mixture was quenched with ethanol and air-oxidized as before. After filtration and removal of most of the solvent the blue residue was dissolved in dilute aqueous NaOH (100 mL) and extracted with CH_2Cl_2. Evaporation of the dried CH_2Cl_2 yielded the aminoalkoxy Cu^{2+} complex, **23**, as dark blue crystals from ethanol.

The above Cu^{2+} complex was dissolved in ether and gaseous HCl passed through, causing the color to change from blue to yellow. Evaporation gave a yellow oil, which was dissolved in water, followed by addition of aqueous K_2S to remove Cu^{2+} as CuS. Removal of the latter by filtration, followed by evaporation, yielded a white solid from which the aminoalkoxy ligand, **21**, was isolated (as the dihydrochloride) by extraction with ethanol.

The above ligand hydrochloride (1.00 g, 1.57 mmol) and $NiCl_2{\cdot}6H_2O$ (0.373 g, 1.57 mmol) were dissolved in ethanol, and KOH (0.18 g, 3.14 mmol) in ethanol was added. After filtration and evaporation, the Ni^{2+} aminoalkoxy complex, **22**, was isolated as red crystals from pentane. Slow recrystallization from methanol gave the stable methanol solvate as green crystals, reverting to red on heating.

A similar procedure using $CoCl_2{\cdot}6H_2O$ gave the Co^{2+} aminoalkoxy complex, **24**, as pale purple crystals from ether.

Characterization. All new compounds were characterized by elemental analysis (Table I) and mass spectral analysis; in each case, peaks corresponding to the expected parent ions were observed. Visible spectra are recorded in Table II. All compounds had infrared spectra consistent with their expected structures, showing C═N absorptions at 1660–1680 cm^{-1} (iminoalkoxy complexes) or N—H absorptions at 3240–3300 cm^{-1} (aminoalkoxy complexes), together with strong C—F absorptions at 1160–1190 cm^{-1}.

X-ray Data Collection and Reduction. Crystallization performed by slow evaporation from a diethyl ether solution yielded red-brown prisms of $Co[(OC(CF_3)_2CH_2C(CH_3)N(CH_2)_2OCH_2-)_2]$ (**20**). Diffraction experiments were performed on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo $K\bar{\alpha}$ radiation. The initial orientation matrix was obtained from 15 machine-centered reflections selected from a rotation photograph. Twelve high-angle reflections ($20 < 2\theta < 25°$) were located from a rapid-scan data collection. Fifteen reflections (including these 12 high-angle reflections) were employed to determine that the crystal system was triclinic. Partial rotation photographs around each axis showed no symmetry. These reflections were used to obtain the final lattice parameters and the orientation matrix. Machine parameters, crystal data, and data collection parameters are summarized in Table III. The space group was consistent with $P1$ or $P\bar{1}$; $P\bar{1}$ was confirmed by solution and refinement of the structure. $+h,\pm k,\pm l$ data were collected in two shells (4.5–35, 35–45°). Three standard reflections were recorded every 97 reflections; their intensities showed no statistically significant change over the duration of data collection. The data were processed with use of the SHELX-76 program package on the computing facilities at the University of Windsor. A total of 4470 reflections with $F_o^2 > 3\sigma(F_o^2)$ were collected.

Table II. Visible Absorption Spectra

compd	solvent	ν_{max}, cm^{-1} (ϵ)
Ni(i-ONNNO) (**5**)	CH_2Cl_2	12 700 (6.2), 16 700 (15)
Ni(a-ONNNO) (**7**)	CH_2Cl_2	12 800 (2.8), 16 300 (8.8), 26 000 (16)
$Co(a\text{-}ONNNO)^+$ (**8**)	CH_2Cl_2	16 700 (105), 19 000 (175), 27 800 (8400)
Ni(i-ONONO) (**9**)	CH_2Cl_2	19 800 (52), 23 000 (51)
Cu(i-ONONO) (**10**)	$(CH_3)_2CO$	16 800 (104)
Co(i-ONONO) (**11**)	CH_2Cl_2	20 600 (81)
Ni(a-ONONO) (**14**)	CH_2Cl_2	14 900 (22), 20 200 (25), 25 000 (58)
Cu(a-ONONO) (**12**)	$(CH_3)_2CO$	16 100 (161)
Co(a-ONONO) (**15**)	CH_2Cl_2	17 400 (16), 21 500 (42)
Ni(i-ONOONO) (**17**)	CH_2Cl_2	18 900 (52), 24 100 (22)
	CH_3OH	15 500 (28), 22 200 (22), 25 300 (49)
Cu(i-ONOONO) (**19**)	CH_2Cl_2	16 700 (91)
Co(i-ONOONO) (**20**)	CH_2Cl_2	18 300 (25), 22 200 (29)
Ni(a-ONOONO) (**22**)	CH_2Cl_2	18 200 (43), 25 000 (25)
	CH_3OH	15 000 (26), 21 700 (20), 24 700 (43)
Cu(a-ONOONO) (**23**)	CH_2Cl_2	16 100 (75), 18 700 (68)
Co(a-ONOONO) (**24**)	CH_2Cl_2	18 200 (59), 21 700 (61)

Table III. Summary of Crystal Data, Intensity Collection, and Structure Refinement of $Co[(OC(CF_3)_2CH_2C(CH_3)N(CH_2)_2OCH_2-)_2]$

formula (mol wt)	$CoF_{12}O_4N_2C_{18}H_{22}$ (617.35)
a, Å	10.144 (3)
b, Å	15.740 (6)
c, Å	15.579 (6)
α, deg	102.56 (3)
β, deg	92.03 (3)
γ, deg	96.58 (3)
cryst syst	triclinic
space group	$P\bar{1}$
V, $Å^3$	2407 (1)
d_{calcd}, g/cm^3	1.70
Z	4
cryst dimens, mm	0.42 × 0.18 × 0.15
cryst faces	(100), (001), (010), $[\bar{1}10]$
μ, abs coeff, cm^{-1}	7.68
radiation	Mo $K\alpha$ ($\lambda = 0.71069$ Å)
scan speed, deg/min	2.0–5.0 ($\theta/2\theta$ scan)
scan range, deg	1.05 below $K\alpha_1$ to 1.10 above $K\alpha_2$
bkgd/scan time ratio	0.5
data collected	2θ of 4.5–45°, $+h,\pm k,\pm l$
unique data ($F_o^2 > 3\sigma(F_o^2)$)	4470
no. of variables	488 (2 equal blocks)
data variable ratio	9.2
% R	4.98
% R_w	5.77

Structure Solution and Refinement. The two Co atom positions in the asymmetric unit were located from a Patterson map synthesis. The remaining 72 non-hydrogen atoms were located from a series of difference Fourier map calculations. Four cycles of block-diagonal least-squares refinement with all the non-hydrogen atoms described isotropically gave $R = 11.85\%$. In subsequent cycles Co, F, and N atoms were described anisotropically, yielding $R = 6.39\%$. An

Table IV. Positional Parameters[a]

molecule 1				molecule 2			
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co(1)	792 (1)	3546 (1)	7366 (1)	Co(2)	6367 (1)	1777 (1)	2272 (1)
F(1)	3235 (6)	4354 (4)	401 (3)	F(13)	5375 (6)	−992 (3)	3613 (3)
F(2)	2108 (5)	3097 (3)	−7 (3)	F(14)	6516 (5)	−772 (3)	2551 (3)
F(3)	1237 (5)	4220 (4)	9849 (3)	F(15)	4408 (5)	−1062 (3)	2359 (3)
F(4)	3981 (5)	2550 (3)	8917 (3)	F(16)	3835 (4)	1369 (3)	3802 (3)
F(5)	4543 (4)	3271 (3)	7964 (3)	F(17)	3706 (5)	168 (4)	4240 (3)
F(6)	5126 (5)	3805 (3)	9318 (4)	F(18)	2925 (4)	187 (3)	2970 (3)
F(7)	4205 (5)	4088 (3)	6213 (4)	F(19)	504 (4)	1242 (3)	418 (3)
F(8)	4052 (5)	3465 (3)	4859 (3)	F(20)	590 (4)	2426 (3)	1413 (3)
F(9)	3272 (5)	4690 (3)	5299 (3)	F(21)	9020 (4)	2099 (3)	412 (3)
F(10)	768 (7)	4014 (4)	4685 (4)	F(22)	355 (5)	181 (3)	1547 (3)
F(11)	20 (6)	2766 (4)	4910 (4)	F(23)	9068 (5)	434 (4)	2584 (3)
F(12)	1665 (7)	2896 (5)	4109 (3)	F(24)	727 (5)	1362 (3)	2524 (4)
O(1)	1908 (4)	3243 (2)	8256 (3)	O(5)	5373 (4)	687 (2)	2427 (2)
O(2)	−1193 (4)	4048 (3)	7058 (3)	O(6)	6593 (4)	3307 (3)	2497 (3)
O(3)	−945 (4)	2868 (3)	8025 (3)	O(7)	4349 (5)	2259 (3)	1942 (3)
O(4)	1537 (4)	3928 (2)	6354 (3)	O(8)	8275 (4)	1873 (3)	2085 (3)
N(1)	1036 (5)	4888 (3)	8072 (3)	N(3)	6752 (5)	2249 (3)	3663 (3)
N(2)	584 (5)	2201 (3)	6691 (3)	N(4)	6007 (5)	1306 (3)	887 (3)
C(1)	2831 (6)	3779 (4)	8835 (4)	C(19)	5299 (6)	376 (4)	3168 (4)
C(2)	2361 (8)	3849 (5)	9781 (5)	C(20)	5384 (7)	−613 (5)	2913 (5)
C(3)	4114 (8)	3354 (5)	8771 (5)	C(21)	3944 (7)	520 (5)	3546 (5)
C(4)	3139 (6)	4708 (4)	8657 (4)	C(22)	6410 (6)	777 (4)	3885 (4)
C(5)	1995 (6)	5209 (4)	8638 (4)	C(23)	6623 (6)	1759 (4)	4211 (4)
C(6)	2031 (7)	6089 (5)	9274 (5)	C(24)	6746 (8)	2100 (5)	5194 (5)
C(7)	−77 (6)	5394 (4)	7981 (4)	C(25)	7121 (7)	3210 (4)	3997 (4)
C(8)	−846 (7)	4967 (4)	7118 (4)	C(26)	7546 (7)	3589 (4)	3228 (4)
C(9)	−2260 (8)	3852 (5)	7611 (5)	C(27)	5361 (8)	3658 (5)	2650 (5)
C(10)	−2238 (7)	2934 (5)	7681 (5)	C(28)	4435 (9)	3193 (5)	1959 (6)
C(11)	−672 (7)	1986 (4)	7942 (4)	C(29)	3825 (7)	1722 (5)	1128 (5)
C(12)	−394 (7)	1587 (4)	6996 (4)	C(30)	4871 (7)	1600 (5)	460 (4)
C(13)	1256 (7)	1928 (4)	6045 (4)	C(31)	6846 (6)	893 (4)	420 (4)
C(14)	1072 (9)	1003 (6)	5490 (6)	C(32)	6790 (8)	745 (5)	−571 (5)
C(15)	2394 (7)	2530 (4)	5809 (4)	C(33)	7891 (6)	547 (4)	896 (4)
C(16)	2061 (6)	3421 (4)	5676 (4)	C(34)	8869 (6)	1279 (4)	1514 (4)
C(17)	3399 (8)	3912 (5)	5489 (5)	C(35)	9781 (7)	1763 (5)	951 (5)
C(18)	1139 (10)	3271 (6)	4839 (6)	C(36)	9772 (9)	814 (5)	2033 (5)

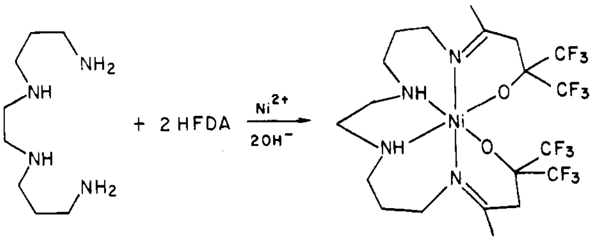
[a] Multiplied by 10^4.

analytical absorption correction was applied, the average correction being 1.129 50. Methylene hydrogen atom positions were calculated, and methyl hydrogens were located from a difference Fourier synthesis. C–H bond lengths were fixed at 1.08 Å, and hydrogen atoms were assigned temperature factors 1.2 times the isotropic temperature factors of the bonded atom. In the final cycle of block-diagonal least-squares refinement, in which hydrogen atom contributions were included, the maximum shift/σ on a parameter was 0.009. A final difference Fourier showed no peaks of chemical significance, the largest peak being 0.5 electron associated with the methyl group at C(14). Final R factors are included in Table III. The following results for $Co[(OC(CF_3)_2CH_2C(CH_3)NC_2H_4OCH_2-)_2]$ are tabulated: positional parameters (Table IV), interatomic distances and angles (Table V), and temperature factors, hydrogen atom coordinates, angles and distances associated with the CF_3 groups, and values of $10|F_o|$ and $10|F_c|$ (supplementary material).

Results and Discussion

In view of the strong interaction between donor nitrogen atoms and first-row transition-metal ions, it seemed probable that template condensation of an α,ω-diamine containing two secondary amino donor sites in the chain would lead to complexes in which the central metal ion was six-coordinate. However, the exact correspondence between the steric preferences of the metal and the ligand required for the formation of a mononuclear complex may not necessarily be achieved in every case. Where this compatibility is not found, the ligand may bridge between two metal ions, rather than chelate, leading to polymeric products and increasing the difficulty of purification and characterization.

We find the cleanest reaction among tetraamines investigated to occur with *N*,*N*′-bis(3-aminopropyl)diaminoethane, $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$, on Ni^{2+}. This condensation occurs at 25 °C (whereas many similar reactions require heating) to give the neutral, mononuclear compound **5**.



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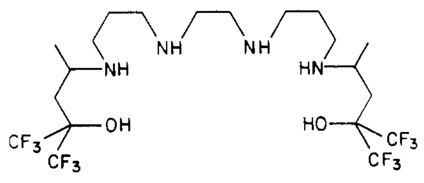
The product was characterized as containing six-coordinate Ni^{2+} from its visible spectrum, and the parent ion corresponding to the mononuclear species appeared in the mass spectrum. We have previously shown[4] that iminoalkoxy ligands of this type can be hydrogenated with $LiAlH_4$ to the corresponding amino alcohols, which may be isolated and used to prepare further metal complexes. In the present case, reduction gave the amino alcohol **6**, which coordinated to Ni^{2+} (as the dianion) to give the further neutral, mononuclear complex **7** containing six-coordinate Ni^{2+}.

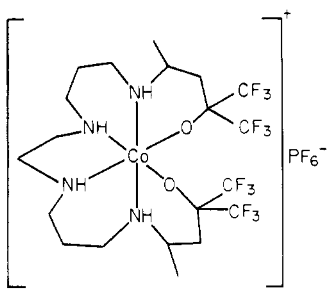
Attempts to repeat this reaction sequence with other metals were less successful. With Cu^{2+}, condensation appeared to occur, but a pure product analogous to **5** could not be isolated. Reaction of ligand **6** with Cu^{2+} gave a mixture of products, apparently associated, among which the Cu^{2+} analogue of **7**



6

was identified in a mass spectrum. We attribute the failure to isolate a mononuclear complex to the more labile nature of Cu^{2+} species and their lower tendency to six-coordination.

In the case of cobalt, the system is further complicated by the possibility of oxidation of Co^{2+} to Co^{3+}. We have previously shown[4] that the five-coordinate Co^{2+} aminoalkoxy analogue of **4** is very resistant to oxidation, as is the case with other five-coordinate Co^{2+} complexes.[12] Introduction of an additional donor site, giving a six-coordinate ligand with N_4O_2 donor atoms, would be expected to favor oxidation to Co^{3+}, and this we find to be the case. Oxidation of Co^{2+}, by either air or common oxidizing agents (H_2O_2, halogens), occurred readily in both the template condensation reaction and the coordination of ligand **6**, and from the latter we isolated a cationic Co^{3+} complex, **8**, as the PF_6^- salt.



8

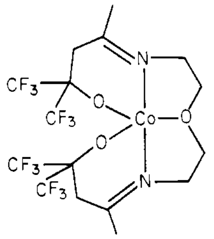
The latter could not be isolated in a high state of purity, and its magnetic moment of 0.99 μ_B may indicate some residual Co^{2+} species, although a moment of the order of 0.5 μ_B would be expected from temperature-independent paramagnetism in low-spin cobalt(III).[13]

Complexes **5**, **7**, and **8** contain five linked chelate rings: four six-membered and the fifth five-membered. That this arrangement is favorable for the isolation of mononuclear, six-coordinate metal complexes is shown by our failure to isolate any analogous product with use of triethylenetetramine, $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, as starting amine. While it was clear that condensation reactions occurred with this tetraamine when HFDA and metal ions were used, the products were invariably oils or glasses of clearly polymeric nature.

Having shown that, under suitable conditions, coordination could occur from one or two amino groups in a long chain, we then investigated analogous systems in which ethereal oxygen atoms are incorporated into α,ω-diamines. Since oxygen is a generally weaker coordinating atom than nitrogen, it would be expected that some differences in structural preferences of metal ions would be seen, and this proved to be the case.

When condensation of HFDA with bis(2-aminoethyl) ether, $NH_2(CH_2)_2O(CH_2)_2NH_2$, was attempted on Ni^{2+}, the product, **9**, was red and diamagnetic, clearly demonstrating four-coordinate, square-planar geometry. Extinction coefficients in the visible region in solution were about 50, which we have previously shown[8] to be characteristic of trans coordination of the N_2O_2 donor atoms in complexes of this type. (With cis geometry, values of ϵ are in the range 140–250.) The mass spectrum showed a peak corresponding to a dinuclear complex, and it is clear that the oxygen atom in the chain is uncoordinated, giving a type **3** structure in which two coordinated metal ions are held together by two five-membered $-(CH_2)_2O(CH_2)_2-$ chains. The Cu^{2+} complex **10** appears to be similar, with a mass spectrum containing a peak for a dinuclear species.

With the Co^{2+} analogue, **11**, the situation is less clear. The absence of a peak in the mass spectrum for the dinuclear unit suggests a mononuclear structure, and the magnetic moment (4.82 μ_B) and visible spectrum are consistent with high-spin, five-coordinate Co^{2+} and eliminate the possibility of either tetrahedral or square-planar geometry. There was no apparent tendency to solvation to six-coordinate Co^{2+} in donor solvents, an effect we have noted before[4] and attributed to the steric effects of the bulky fluorinated alkoxy group. It appears, therefore, that the ethereal oxygen is coordinated in complex **11**, giving four linked chelate rings, two six- and two five-membered:



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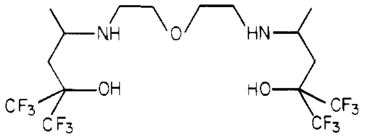
Hydrogenation of the iminoalkoxy Cu^{2+} complex **10** using $LiAlH_4$ gave the corresponding aminoalkoxy compound **12**, from which the free ligand, **13**, could be isolated by removal of the metal. When this ligand was used to prepare a Ni^{2+} complex, **14**, the product was green, monomeric, and paramagnetic, showing that, in contrast to the iminoalkoxy analogue, the ethereal oxygen atom was coordinated to the metal ion in a five-coordinate structure. This difference may be ascribed to the greater flexibility of the reduced ligand, allowing the formation of the two five-membered and two six-membered chelate rings. The hydrogenated Cu^{2+} complex, **12**, was also monomeric, but the coordination geometry at the metal could not be established from spectral and magnetic properties as can be done for Ni^{2+}. In the case of Co^{2+}, the hydrogenated complex, **15**, (from ligand **13** and Co^{2+}) was monomeric and probably five-coordinate. None of the five-coordinate species showed any tendency to solvation to six-coordinate compounds.



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There are clearly three factors influencing the geometry of metal complexes of these dinegative, potentially pentadentate ligands: the donor strength of the fifth donor site in the chain, the flexibility of the chelate rings, and the steric preferences of the central metal ion. For the strongly coordinating amino group, the complexes are generally five-coordinate, but when the weaker ethereal oxygen donor is combined with the less flexible iminoalkoxy chelate ring, the complexes are four-coordinate with metal ions in cases where this is usually a stable arrangement (Ni^{2+}, d^8; Cu^{2+}, d^9) and five-coordinate only with Co^{2+}, where steric preferences of the d^7 metal ion are less significant. The increase in ring flexibility accompanying

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(12) Morassi, R.; Mani, F.; Sacconi, L. *Inorg. Chem.* **1973**, *12*, 1246.

(13) Figgis, B. N.; Lewis, J. In "Modern Coordination Chemistry"; Lewis, J., Wilkins, R. G., Eds.; Interscience: New York, 1960; p 422.

Table V. Selected Interatomic Distances and Angles

Distances (Å)

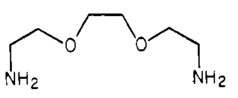
molecule 1		molecule 2		molecule 1		molecule 2	
Co(1)-O(1)	1.933 (4)	Co(2)-O(5)	1.954 (4)	C(7)-C(8)	1.511 (8)	C(25)-C(26)	1.51 (1)
Co(1)-O(2)	2.317 (4)	Co(2)-O(6)	2.339 (4)	C(8)-O(2)	1.430 (8)	C(26)-O(6)	1.426 (8)
Co(1)-O(3)	2.339 (4)	Co(2)-O(7)	2.341 (5)	O(2)-C(9)	1.455 (9)	O(6)-C(27)	1.431 (9)
Co(1)-O(4)	1.952 (4)	Co(2)-O(8)	1.961 (4)	C(9)-C(10)	1.48 (1)	C(27)-C(28)	1.42 (1)
Co(1)-N(1)	2.141 (4)	Co(2)-N(3)	2.138 (4)	C(10)-O(3)	1.423 (9)	C(28)-O(7)	1.46 (1)
Co(1)-N(2)	2.132 (4)	Co(2)-N(4)	2.127 (5)	O(3)-C(11)	1.427 (9)	O(7)-C(29)	1.410 (8)
O(1)-C(1)	1.353 (6)	O(5)-C(19)	1.349 (7)	C(11)-C(12)	1.520 (9)	C(29)-C(30)	1.51 (1)
C(9)-C(2)	1.55 (1)	C(19)-C(20)	1.534 (9)	C(12)-N(2)	1.469 (9)	C(30)-N(4)	1.478 (9)
C(2)-C(3)	1.53 (1)	C(19)-C(21)	1.535 (9)	N(2)-C(13)	1.260 (8)	N(4)-C(31)	1.281 (8)
C(3)-C(4)	1.546 (9)	C(19)-C(22)	1.535 (8)	C(13)-C(14)	1.51 (1)	C(31)-C(32)	1.51 (1)
C(4)-C(5)	1.480 (9)	C(22)-C(23)	1.505 (8)	C(13)-C(15)	1.516 (9)	C(33)-C(34)	1.557 (8)
C(5)-C(6)	1.514 (9)	C(23)-C(24)	1.504 (9)	C(16)-C(17)	1.55 (1)	C(34)-C(35)	1.55 (1)
C(5)-N(1)	1.270 (7)	C(23)-N(3)	1.270 (8)	C(16)-C(18)	1.54 (1)	C(34)-C(36)	1.55 (1)
N(1)-C(7)	1.475 (9)	N(3)-C(25)	1.487 (7)	C(16)-O(4)	1.343 (7)	C(34)-O(8)	1.354 (7)

Angles (deg)

molecule 1		molecule 2		molecule 1		molecule 2	
O(1)-Co(1)-O(2)	145.8 (2)	O(5)-Co(2)-O(6)	149.5 (2)	C(7)-N(1)-Co(1)	116.7 (3)	C(25)-N(3)-Co(2)	117.5 (4)
O(1)-Co(1)-O(3)	84.2 (2)	O(5)-Co(2)-O(7)	88.9 (2)	C(5)-N(1)-C(7)	120.1 (5)	C(23)-N(3)-C(25)	119.1 (5)
O(1)-Co(1)-O(4)	121.6 (2)	O(5)-Co(2)-O(8)	121.9 (2)	C(13)-N(2)-Co(1)	122.3 (4)	C(31)-N(4)-Co(2)	121.4 (4)
O(1)-Co(1)-N(1)	90.6 (2)	O(5)-Co(2)-N(3)	91.9 (2)	C(12)-N(2)-Co(1)	117.7 (4)	C(30)-N(4)-Co(2)	117.4 (4)
O(1)-Co(1)-N(2)	87.8 (2)	O(5)-Co(2)-N(4)	88.3 (2)	C(12)-N(2)-C(13)	120.0 (5)	C(30)-N(4)-C(31)	120.4 (5)
O(2)-Co(1)-O(3)	69.7 (2)	O(6)-Co(2)-O(7)	69.0 (2)	O(1)-C(1)-C(2)	109.0 (5)	O(5)-C(19)-C(20)	107.7 (5)
O(2)-Co(1)-O(4)	89.8 (2)	O(6)-Co(2)-O(8)	86.4 (2)	O(1)-C(1)-C(3)	107.5 (5)	O(5)-C(19)-C(21)	108.6 (5)
O(2)-Co(1)-N(1)	75.7 (2)	O(6)-Co(2)-N(3)	75.0 (2)	O(1)-C(1)-C(4)	114.1 (5)	O(5)-C(19)-C(22)	115.2 (5)
O(2)-Co(1)-N(2)	105.6 (2)	O(6)-Co(2)-N(4)	105.1 (2)	C(1)-C(4)-C(5)	116.3 (5)	C(19)-C(22)-C(23)	118.3 (5)
O(3)-Co(1)-O(4)	151.3 (2)	O(7)-Co(2)-O(8)	144.7 (2)	C(4)-C(5)-C(6)	118.9 (5)	C(22)-C(23)-C(24)	116.5 (6)
O(3)-Co(1)-N(1)	104.6 (2)	O(7)-Co(2)-N(3)	105.3 (2)	C(4)-C(5)-N(1)	118.2 (5)	C(22)-C(23)-N(3)	119.8 (5)
O(3)-Co(1)-N(2)	75.3 (2)	O(7)-Co(2)-N(4)	75.3 (2)	C(6)-C(5)-N(1)	122.9 (6)	C(24)-C(23)-N(3)	123.6 (5)
O(4)-Co(1)-N(1)	88.8 (2)	O(8)-Co(2)-N(3)	91.4 (2)	N(1)-C(7)-C(8)	107.6 (5)	N(3)-C(25)-C(26)	107.5 (5)
O(4)-Co(1)-N(2)	92.1 (2)	O(8)-Co(2)-N(4)	87.9 (2)	C(7)-C(8)-O(2)	110.6 (6)	C(25)-C(26)-O(6)	111.3 (5)
N(1)-Co(1)-N(2)	178.4 (2)	N(3)-Co(2)-N(4)	179.4 (2)	O(2)-C(9)-C(10)	106.7 (6)	O(6)-C(27)-C(28)	107.1 (6)
Co(1)-O(1)-C(1)	127.9 (4)	Co(2)-O(5)-C(19)	127.9 (3)	C(9)-C(10)-O(3)	107.1 (6)	C(27)-C(28)-O(7)	108.9 (7)
Co(1)-O(2)-C(8)	104.6 (4)	Co(2)-O(6)-C(26)	103.2 (4)	O(3)-C(11)-C(12)	110.4 (6)	O(7)-C(29)-C(30)	111.8 (6)
Co(1)-O(2)-C(9)	114.8 (4)	Co(2)-O(6)-C(27)	112.9 (4)	C(11)-C(12)-N(2)	108.7 (5)	C(29)-C(30)-N(4)	106.7 (6)
C(8)-O(2)-C(9)	113.4 (5)	C(26)-O(6)-C(27)	113.3 (5)	N(2)-C(13)-C(14)	124.9 (6)	N(4)-C(31)-C(32)	117.2 (5)
C(10)-O(3)-Co(1)	114.5 (4)	C(28)-O(7)-Co(2)	114.7 (4)	C(13)-C(15)-C(16)	116.2 (6)	C(31)-C(33)-C(34)	113.5 (5)
C(11)-O(3)-Co(1)	105.3 (4)	C(29)-O(7)-Co(2)	106.9 (4)	C(15)-C(16)-C(17)	105.3 (6)	C(33)-C(34)-C(35)	106.9 (5)
C(10)-O(3)-C(11)	113.5 (5)	C(28)-O(7)-C(29)	113.3 (6)	C(15)-C(16)-C(18)	108.8 (5)	C(33)-C(34)-C(36)	109.5 (5)
Co(1)-O(4)-C(16)	126.0 (4)	Co(2)-O(8)-C(34)	124.8 (3)	C(15)-C(16)-O(4)	116.5 (5)	C(33)-C(34)-O(8)	114.7 (5)
C(5)-N(1)-Co(1)	122.4 (3)	C(23)-N(3)-Co(2)	123.4 (3)				

hydrogenation of the C=N bond is then sufficient to change the balance of stability in favor of five-coordination in each case.

When the chain connecting the two amino groups was extended to include two ethereal oxygen atoms, somewhat different trends were observed. The diamine studied was 1,2-bis(2-aminoethoxy)ethane (**16**), and this condensed readily



16

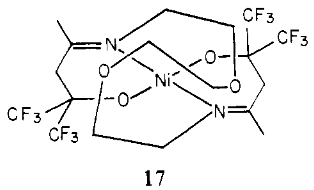
with HFDA in the presence of Ni^{2+}, Cu^{2+}, or Co^{2+}, giving neutral complexes for which, in each case, only the mononuclear species could be detected in the mass spectrum.

The Ni^{2+} complex, **17**, was red in the solid state or in solution in noncoordinating solvent and diamagnetic, showing four-coordinate, square-planar geometry at the metal atom. Extinction coefficients in the visible region were in the range 20–50, again indicating a trans arrangement of the N_2O_4 donor group.

However, the solution behavior of **17** was unusual in that it solvated readily in methanol solution, giving a green solution having a spectrum typical of five-coordinate Ni^{2+}. Evaporation gave a green solvate, **18**, stable at 25 °C in air, which gave an analysis for a 1:1 adduct with methanol and reverted to the red, unsolvated complex **17** on slight heating. Solutions in dichloromethane–methanol mixtures showed isosbestic points at 16 700 and 23 500 cm^{-1}. With pyridine, solvation of **17** did not occur.

This solvation behavior is completely different from that of Ni^{2+} complexes which we have previously studied.[8] The iminoalkoxy Ni^{2+} complexes formed by template condensations using long-chain diamines $NH_2(CH_2)_nNH_2$ (n = 6, 8, or 12), which are four-coordinate and dinuclear with type 3 structures, remain completely unsolvated in methanol solution and are partially solvated to five-coordination by pyridine. If the $-(CH_2)_2O(CH_2)_2O(CH_2)_2-$ units in diamine **16** were behaving after condensation as inert, eight-atom chains, one would expect behavior in solution similar to that when the $-(CH_2)_8-$ chains are present, and the differences found, together with the monomeric nature of **17**, suggest a different type of structure.

We suggest that these observations are consistent with a trans-chelating mode of coordination by the diamine residue:



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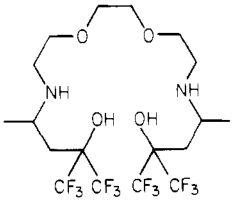
The bridging between trans coordination sites of a long-chain chelating ligand is now well-recognized in a number of compounds,[14] and its occurrence is generally attributed to steric interactions between bulky trans substituents. In the present case, the bulky fluorinated alkoxy groups will prefer a trans arrangement, which we have found in every case except those where cis geometry is imposed by short chain lengths in some diamines, giving type **2** structures.

There is a clear resemblance between the postulated structure of **16** and that found for its Co^{2+} analogue (discussed below), with the notable difference that the ethereal oxygen atoms in the Ni^{2+} complex are not coordinated to the metal ion, because of the preference of the d^8 species for four-coordination. However, the difference in structure between **17** and the complexes derived from long-chain diamines $NH_2(CH_2)_nNH_2$, where no donor sites are present in the chain, is probably due to kinetic effects in the template condensation reaction. Weak interactions between ethereal oxygen atoms and the metal ion during condensation would tend to encourage chelation of diamine **16** to one metal ion and the subsequent formation of a mononuclear complex. In contrast, a diamine in which two amino groups are connected by a long, inert hydrocarbon chain would tend to bridge two metal ions, rather than chelate, resulting in the observed dinuclear complexes.

The unusual solvation behavior of the nickel complex **17** is presumably steric in origin, associated with a distortion of the coordination plane of the metal ion resulting from the trans-bridging ligand. It is not clear why this should result in preferential coordination by methanol, rather than pyridine, and further studies are in progress on this system.

The Cu^{2+} iminoalkoxy complex **19**, analogous to **17**, was apparently similar in structure but showed no tendency to solvation. Hydrogenation gave the aminoalkoxy Cu^{2+} complex **23**, from which the free amino alcohol ligand, **21**, could be isolated.



21

This ligand readily coordinated (as the dianion) to give neutral complexes of Ni^{2+} (**22**) and Co^{2+} (**24**). Each metal complex, **22**, **23**, and **24**, appeared from its mass spectrum to be mononuclear. The Ni^{2+} complex was red and diamagnetic and gave solution behavior very similar to that of the iminoalkoxy analogue **17**. Extinction coefficients in solution in noncoordinating solvents were low (20–50), consistent with a trans square-planar arrangement of the N_2O_4 donor atoms, and solvation occurred readily with methanol to give a solution spectrum typical of five-coordinate Ni^{2+}; again, pyridine did not solvate.

It would appear that, in this case, the hydrogenation of C=N bonds in the ligand has made little difference to its mode of coordination to the metal, which is still trans bridged in a four-coordinate structure. This contrasts with the Ni^{2+} complex of ligand **13**, where the ethereal oxygen atom became coordinated on hydrogenation. The difference may be accounted for in terms of the greater chain length in ligand **21**, which permits formation of the preferred trans-bridged structure. With ligand **13**, trans bridging is not possible, and the cis bridging imposed on the mononuclear complex favors coordination from the ethereal oxygen atom.

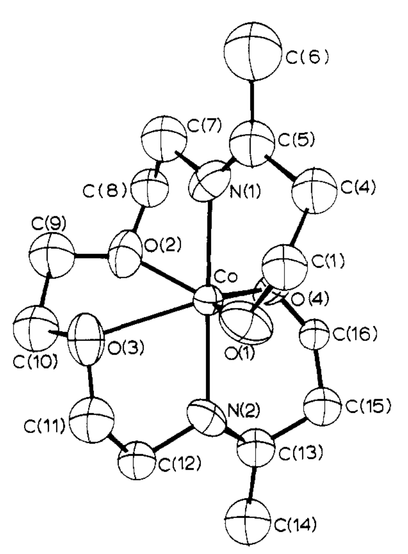


Figure 1. The structure of **20**, showing the arrangement of the five chelate rings. Trifluoromethyl groups are omitted.

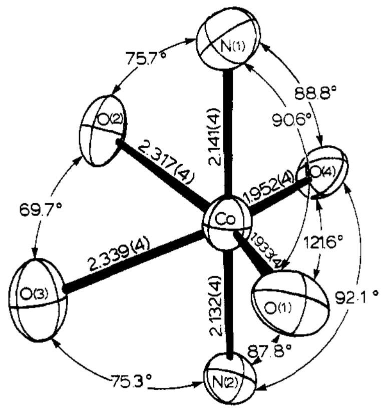


Figure 2. Detail of the structure showing the coordination around cobalt.

Structure of a Hexacoordinate Cobalt(II) Complex. As mentioned above, diamine **16** readily underwent template condensation with HFDA in the presence of Co^{2+}, giving a neutral complex, **20**. In contrast to the two complexes derived from the tetraamines studied, this compound showed no tendency for oxidation to Co^{3+}, either in air or with common oxidizing agents (H_2O_2, halogens). Clearly, this is a result of the weaker ligand field strength of the N_2O_4 donor set, which destabilizes the higher oxidation state.

Complex **20** formed deep red-brown crystals with a magnetic moment of 4.54 μ_B. Since the coordination geometry of the metal ion could not be deduced from these properties, a complete structural investigation was carried out, showing the Co^{2+} ion to be six-coordinate in highly distorted octahedral geometry. Figure 1 shows the arrangement of the five chelate rings (the two CF_3 groups on C(1) and on C(16) are omitted for clarity), while Figure 2 shows the detailed geometry at the central Co^{2+} ion. (The crystal contains two molecules in nonequivalent positions; small differences in dimensions, shown in Table V, are not of any chemical significance. Data in the figures refer to molecule 1.) The following points may be noted:

(i) Bond lengths from Co^{2+} to the alkoxy oxygen atoms, O(1) and O(4), are in the range 1.93–1.96 Å, considerably shorter than those to the ethereal oxygen atoms, O(2) and O(3) (2.32–2.34 Å). The former may be compared with metal–oxygen bond lengths that we have determined previously in

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[14] Hill, W. E.; Taylor, J. G.; McAuliffe, C. A.; Muir, K. W.; Manojlovic-Muir, L. *J. Chem. Soc., Dalton Trans.* **1982**, 833 and references therein.

type **3** complexes of Ni^{2+} (1.84 Å)[8] and Cu^{2+} (1.86–1.87 Å).[9] The longer bond lengths from Co^{2+} to ethereal oxygen atoms, indicating, as expected, a weaker interaction, are consistent with those found previously (2.17, 2.33 Å) in an octahedral Co^{2+} complex of a neutral, macrocyclic ligand.[15]

(ii) Bond lengths to the two imino nitrogen atoms are 2.13–2.14 Å, significantly shorter than those to ethereal oxygen atoms but slightly longer than metal–nitrogen distances that we have found in four-coordinate complexes of Ni^{2+} (1.90 Å)[8] or Cu^{2+} (2.00–2.03 Å).[9]

(iii) The two nitrogen atoms are in essentially linear coordination to Co^{2+} (178–179°) with the two alkoxy oxygen atoms in positions very close to the plane perpendicular to the N–Co–N axis; O–Co–N angles are in the range 88–92°. However, the O–Co–O angle *within* this plane is no less than 121.6°, a gross departure from octahedral geometry. In fact, this side of the molecule is better described in terms of trigonal-bipyramidal geometry around Co^{2+}, with the nitrogen atoms occupying axial sites and the alkoxy oxygen atoms on two equatorial sites.

(iv) The two ethereal oxygen atoms, O(2) and O(3), are approximately 0.6 Å above and below the plane defined by the alkoxy oxygens and Co^{2+}. The O–Co–O bite angle in the central five-membered ring is unusually low at 69–70°; more usual values in systems of this type are 75.5° on Co^{2+},[15] 78.7° on Ni^{2+},[16] and 73° on Mn^{2+}.[17]

It appears that the steric requirements of the multiply chelated ligand, in conjunction with the weak interactions between the metal ion and the ethereal oxygen atoms, have distorted the geometry around Co^{2+} to the point where it is intermediate between octahedral six-coordination and a five-coordinate structure where O(2) and O(3) share one corner of a trigonal-bipyramidal arrangement. The relationship of this structure to the postulated trans-bridged square-planar geometry of **17** may easily be seen; it is only necessary to increase the O(1)–Co–O(4) angle to approximate linearity, while removing O(2) and O(3) to nonbonding distances, in order to produce a four-coordinate structure.

Conclusions

This work has shown that the template condensation of the fluorinated keto alcohol HOC(CF$_3$)$_2$CH$_2$C(O)CH$_3$ with the amino group is of general applicability in the preparation of metal complexes of potentially polydentate, iminoalkoxy, Schiff-base type ligands. However, the actual mode of coordination of the ligand and geometry of the resulting metal complex are influenced by small differences in the donor strength of the potentially coordinating atoms, the chain length and geometry of the ligand molecule, and the steric preferences of the metal ion. In the case of Co^{2+}, where the steric requirements of the d^7 metal ion are not strongly defined, the geometry of a six-coordinate complex is dominated by the need to accommodate a set of five linked chelate rings. In other instances, some potential donor sites remain uncoordinated in the ultimate complex, but there is evidence that their presence has influenced the course of the condensation reaction.

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Registry No. **5**, 88412-35-5; **6**, 88412-36-6; **7**, 88412-37-7; **8**, 88412-39-9; **9**, 88425-08-5; **10**, 88412-40-2; **11**, 88412-41-3; **12**, 88412-43-5; **14**, 88412-42-4; **15**, 88412-44-6; **16**, 929-59-9; **17**, 88412-45-7; **18**, 88425-09-6; **19**, 88412-46-8; **20**, 88412-47-9; **21**, 88412-48-0; **22**, 88412-49-1; **23**, 88412-50-4; **24**, 88412-51-5; NH$_2$(CH$_2$)$_3$NH(CH$_2$)$_2$NH(CH$_2$)$_3$NH$_2$·4HCl, 13493-17-9; NH$_2$(CH$_2$)$_2$O(CH$_2$)$_2$NH$_2$, 2752-17-2; HFDA, 10487-10-2; 1,2-bis(2-hydroxyethoxy)ethane, 112-27-6.

Supplementary Material Available: Tables of temperature factors, hydrogen atom coordinates, bond angles and distances associated with the CF$_3$ groups, and values of $10|F_o|$ and $10|F_c|$ (35 pages). Ordering information is given on any masthead page.

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Steric Effects in Electron-Transfer Reactions. 1. Trends in Homogeneous Rate Constants for Reactions between Members of Structurally Related Redox Series

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Three series of structurally related inorganic complexes based on Ru(NH$_3$)$_5$(py)$^{3+,2+}$, Co(1,10-phen)$_3$$^{3+,2+}$, and Cu(H$_{-2}$-triglycine)$^{0,-}$ have been prepared. The remaining members of each series contain organic substituents, methyl, cyclohexyl, bis(hydroxymethyl)methyl, or tris(hydroxymethyl)methyl, in place of hydrogens located on the periphery of the ligands. Each complex displays a one-electron redox couple that involves the III and II oxidation states of the metal. Formal reduction potentials are reported in 0.2 M NaCl. Electron-transfer reaction rate constants for all possible cross-reactions between the Ru(III) and Co(II) complexes and between the Cu(III) and Co(II) complexes are reported. The dependence of the magnitude of these rate constants on the free energy change for the reaction and on the size of the reactants is analyzed by using the concepts of Marcus' theory. For the Ru(III) + Co(II) reactions, large organic substituents result in a reduction in the rate constants with respect to values calculated with use of Marcus' theory, whereas for the Cu(III) + Co(II) reactions the steric effects are less predictable.

Introduction

During the last three to four decades, numerous theoretical and experimental studies have been directed toward understanding the factors that influence the rates of electron-transfer reactions in solution.[1-3] Reactions involving transition-metal complexes have played a key role in many of these studies because the orbital from which an electron originates and the orbital to which it is transferred are identified with single atoms. Furthermore, the wide variety of available ligands

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