Contribution from the Chemistry Department,
University of Western Ontario, London, Ontario, N6A 5B7, Canada

Fluorinated Alkoxides. 14. Template Synthesis of Some Large-Ring Iminoalkoxy Complexes of Ni^{2+} and Cu^{2+}. Structure of a Dinuclear Square-Planar Nickel(II) Complex

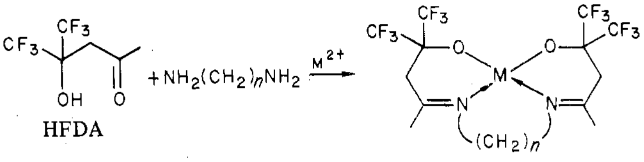
JOHN W. L. MARTIN, NICHOLAS C. PAYNE,* and CHRISTOPHER J. WILLIS*

Received May 25, 1978

The template condensation of 5,5,5-trifluoro-4-hydroxy-4-(trifluoromethyl)-2-pentanone, $(CF_3)_2C(OH)CH_2COCH_3$, with an α,ω-diamine $NH_2(CH_2)_nNH_2$ (n = 2, 3, 4, 5, 6, 8, or 12) in the presence of a metal ion (Cu^{2+}, Ni^{2+}) leads to a series of stable, neutral, iminoalkoxy metal complexes. An X-ray structural elucidation of the Ni complex with n = 6 has been completed, showing it to have a dinuclear composition. Crystals are monoclinic, space group $C2/c$, with unit cell dimensions a = 28.867 (5), Å, b = 9.982 (2) Å, c = 17.276 (3) Å, and β = 105.49 (1)°. Full-matrix least-squares refinement on F converged with a conventional agreement factor of 0.046. Each Ni atom is coordinated in square-planar geometry to trans N_2O_2 donor atoms in two ligand molecules whose $-(CH_2)_6-$ chains link the two metal coordination planes at an angle of 55°; there is no direct Ni–Ni interaction. Molar mass determinations (acetonitrile solution) on the nickel complexes (which are all red and diamagnetic) show a change from mononuclear to dinuclear aggregation at $n \geq 4$; evidence from the formation of five-coordinate adducts with pyridine suggests that the complexes with n = 5, 8, or 12 are similar in structure to the n = 6 complex but a different arrangement, tentatively assigned to a cis dinuclear geometry, is present for n = 4. The copper complexes appear to be exclusively mononuclear in solution. Reaction pathways by which such condensation products could arise are discussed.

Introduction

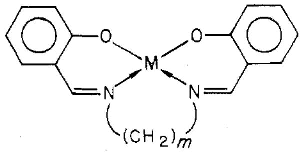
We have recently reported[1] the template synthesis of complexes of a new class of tetradentate fluorinated ligands by the condensation of 5,5,5-trifluoro-4-hydroxy-4-(trifluoromethyl)-2-pentanone (hexafluorodiacetone alcohol, HFDA) with short-chain diamines in the presence of a metal ion:



1, n = 2, 3; M = Ni, Cu

These complexes are diamagnetic and square planar with Ni^{2+} and assumed to be roughly square planar with Cu^{2+}. With the small ring size of chelate ligands derived from ethylenediamine or 1,2- or 1,3-diaminopropane, a cis geometry is clearly imposed on the metal atom. It was of interest, therefore, to extend this study to longer chain terminal diamines in the hope of preparing similar complexes and determining the influence of increasing ring size on their structures. In this paper, we report results on complexes having values of n up to 12.

There is an obvious resemblance between these complexes and the familiar aromatic tetradentate Schiff base systems.



2

For the latter, there has been considerable interest in the effect on the geometry at the metal atom of increasing the value of m above 3. For cobalt(II) complexes, Hariharin and Urbach,[2] using spectroscopic and magnetic data, found a highly flattened tetrahedral arrangement for m = 3, which became closer to tetrahedral as m was increased to 6. In all cases, mass spectra corresponded to monomeric species. Weigold and West[3] also suggested approximately tetrahedral geometry at large values of m (7–10).

For nickel(II) complexes, Hoyt and Everett[4] found that the m = 5 complex was diamagnetic and square planar, whereas some degree of paramagnetism was found when m = 6–10. For m = 11 or 12, isomeric diamagnetic and paramagnetic forms could be prepared. They ascribed the paramagnetism to the presence of oxygen bridging in the solid state. Other workers[5] have carried out molecular weight studies on nickel complexes in pyridine solution and found a trimer with m = 3 and lower degrees of association with m = 4–6; copper(II) complexes were similar.

The majority of these Schiff base complexes previously studied have had poor solubility characteristics, usually dissolving only in donor solvents, such as pyridine, where a strong interaction with the metal is probable. Reliable estimation of the degree of molecular association in the solid state is therefore difficult, and there is a lack of definite structural information.

Using the appropriate α,ω-diamine, we have carried out template condensation reactions with Ni^{2+} and Cu^{2+} to prepare complexes of type **1** with n = 4, 5, 6, 8, and 12. In all cases, the synthesis proceeded readily under mild conditions, in fact the diamines with larger values of n condensed more readily than did ethylenediamine. The nickel complexes were all red and diamagnetic in the solid state and red in solution in nondonor solvents, as would be expected for square-planar four-coordinate nickel(II). With both the nickel and copper complexes, the melting points decreased as the value of n increased (Table I) and volatility increased to a maximum at n = 12. All compounds sublimed unchanged in vacuo, and mass spectra showed strong parent ion peaks at the molecular mass values expected for structure **1**.

The complexes were generally soluble in common solvents, but attempts to determine solution molecular weights osmometrically gave variable results. Apparent association was found in chloroform and, more noticeably, in benzene, where concentration-dependent molecular weights up to that of a tetramer were found in some cases. In order to resolve the question of molecular association, and in view of the intrinsic interest of the conformation of a large chelate ring, a complete structural determination of the nickel complex with n = 6 was undertaken.

Experimental Section

General Information. Volatile compounds were manipulated in a conventional vacuum manifold. Infrared spectra were recorded on a Perkin-Elmer 621 instrument, visible–UV spectra on Cary 14 and 118 spectrometers, mass spectra on a Varian MAT 311A instrument,

Table I. Analytical Data and Magnetic Moments

		% C		% H		% N			
n	mol formula	calcd	found	calcd	found	calcd	found	μ_{eff}, μ_B (300 K)	mp, °C
				Nickel Complexes					
4	$C_{32}H_{36}F_{24}N_4Ni_2O_4$	34.5	34.6	3.25	3.22	5.03	5.06	a	300–302
5	$C_{34}H_{40}F_{24}N_4Ni_2O_4$	35.8	35.7	3.53	3.57	4.90	4.84	a	281–283
6	$C_{36}H_{44}F_{24}N_4Ni_2O_4$	36.9	37.0	3.79	3.79	4.79	4.78	a	214–216
8	$C_{40}H_{52}F_{24}N_4Ni_2O_4$	39.2	39.4	4.27	4.28	4.57	4.64	a	153–154
12	$C_{48}H_{68}F_{24}N_4Ni_2O_4$	43.1	43.2	5.12	5.07	4.18	4.13	a	139–141
				Copper Complexes					
3	$C_{15}H_{16}CuF_{12}N_2O_2$	32.9	32.7	2.94	2.85	5.11	5.09	1.85	255–257 (subl)
4	$C_{16}H_{18}CuF_{12}N_2O_2$	34.2	34.4	3.23	3.36	4.98	5.10	1.91	230 (subl)
5	$C_{17}H_{20}CuF_{12}N_2O_2$	35.5	35.3	3.50	3.48	4.86	4.77	1.77	188–189
6	$C_{18}H_{22}CuF_{12}N_2O_2$	36.6	36.7	3.76	3.71	4.75	4.68	1.76	158–160
8	$C_{20}H_{26}CuF_{12}N_2O_2$	38.9	39.0	4.24	4.33	4.53	4.70	1.75	152–153
12	$C_{24}H_{34}CuF_{12}N_2O_2$	42.8	42.9	5.08	5.08	4.15	4.15	1.74	71–73

[a] Diamagnetic.

and molecular weights on a Hewlett-Packard 301A vapor-pressure osmometer. Magnetic moments were determined by the Gouy method at 300 K. Microanalyses were performed by Malissa-Reuter Laboratories, West Germany; all analytical and magnetic data are in Table I.

5,5,5-Trifluoro-4-hydroxy-4-(trifluoromethyl)-2-pentanone (HFDA) was prepared from acetone and hexafluoroacetone as described previously.[1]

Diamines were commercial samples (Aldrich) used without further purification.

Preparation of Complexes. The preparation and characterization of nickel complexes for n = 2 or 3 and of the copper complex for n = 2 have been described previously.[1] Nickel complexes for n = 4, 5, 6, 8, and 12 were prepared by the following general route. Nickel(II) chloride hexahydrate (2.4 g, 10 mmol) in warm ethanol was added with stirring to a solution of the appropriate diamine (15 mmol) in ethanol, at which point a semigelatinous solid separated. HFDA (4.9 g, 22 mmol) was then added, followed by potassium hydroxide (1.15 g, 20.5 mmol) in ethanol. Upon cooling of the mixture, potassium chloride separated, sometimes accompanied by red crystals of the product. The solution was filtered and the filtrate evaporated to dryness and extracted with dichloromethane or chloroform to separate the product from potassium chloride. The crude complexes were recrystallized from dichloromethane, chloroform, or benzene, except where n = 4, for which refluxing in acetonitrile for 30–40 min was needed to dissolve the solid.

Copper complexes were prepared in similar fashion using anhydrous copper(II) chloride and the diamine in a 1:1.2 molar ratio. The products with n = 4 and n = 8 were recrystallized only after dissolving in refluxing acetonitrile.

Characterization. Infrared Spectra. For both nickel and copper complexes, infrared spectra showed the absence of any absorption bands corresponding to the primary amino, carbonyl, or hydroxy groups present in the starting materials. Instead, a strong band in the region 1644–1674 cm^{-1} was present, attributed to the ν(C=N) stretching mode characteristic of coordinated imino groups. The frequency of this band showed no systematic variation as the value of n was increased from 2 to 12 in either the copper or the nickel series, nor was there any significant difference between the mononuclear and dinuclear complexes. All complexes showed strong ν(C–F) absorptions in the region 1150–1250 cm^{-1}.

Mass Spectra. Initial mass-spectral runs showed strong parent-ion peaks corresponding to mononuclear molar masses for all complexes, including those previously prepared with n = 2 or 3. After the existence of dinuclear species had been definitely established, mass spectra were rerun up to mass values 3 times the mononuclear formula weight. Low-intensity (10% or less of mononuclear parent ion) peaks were present at or near the expected mass for dinuclear species for both nickel and copper species for n = 4, 5, and 6, whereas the spectra of those compounds with n = 2, 3, 8, and 12 were clear in this region.

Structural Determination. The crystals of the nickel complex (n = 6) used for the structural determination were prepared by slow crystallization from a solution in ethanol/(+)-α-phenethylamine [supplied by Norse Laboratories Inc.; $[\alpha]^{20}_D$ +38.1°]. This solution had been prepared for use in a study of optical activity in complexes of this type;[7] the presence of the asymmetric solvent did not appear to affect the crystal form of the unsolvated nickel complex precipitating.

Table II. Crystal Data

$C_{36}H_{44}F_{24}N_4Ni_2O_4$
a = 28.867(5) Å
b = 9.982(2) Å
c = 17.276(3) Å
β = 105.49(1)°
μ(Cu Kα) = 20.44 cm^{-1}

fw 1170.48
space group $C2/c$
Z = 4
cell volume 4978 Å^3
d(obsd)[a] = 1.624 (1) g cm^{-3}
d(calcd) = 1.620 g cm^{-3}

[a] By neutral buoyancy in CCl_4 and 1,2-dibromoethane.

Table III. Experimental Conditions for Data Collection

radiation: Cu Kα_1, Ni-foil prefilter (0.018 mm)
takeoff angle: 1.8° (for 90% of maximum Bragg intensity)
aperture: (0.5 × 0.5) mm^2, 32 cm from crystal
counter: 34 cm from crystal
data collected: $+h$, $k \leq 1$, $\pm l$ for $0 < 2\theta < 60°$; $+h$, $-k$, $\pm l$ for $60 < 2\theta < 131.3°$
scan: θ–2θ corrected for dispersion, range 1.2° (symmetric) for all data
scan speed: 2° min^{-1}
background: 10 s for $0 < 2\theta < 90°$; 20 s for $90 < 2\theta < 131.3°$; stationary crystal, stationary counter at scan limits
standards: six recorded every 200 reflections, $\bar{4}00$, 002, 400, $1\bar{1}1$, $0\bar{2}0$, $00\bar{2}$

From preliminary Weissenberg and precession photography the crystals were found to belong to the monoclinic system. Systematic absences of hkl for $h + k$ odd and $h0l$ for l odd were observed. The space group was thus determined to be either Cc or $C2/c$.[8]

A crystal of approximate dimensions 0.35 × 0.23 × 0.13 mm^3 was selected and measured using a microscope fitted with a filar eyepiece. An optical goniometry study assigned Miller indices to the 12 crystal faces; in point group $2/m$ (as was later confirmed) these are the forms {100}, {001}, {111}, and $\{11\bar{1}\}$. The crystal was mounted with the long dimension [010] offset by some 5° from the diffractometer ϕ axis. Crystal data are given in Table II.

Intensity data were collected using a Picker FACS-1 computer-controlled diffractometer. From a least-squares refinement of 30 intense, carefully centered reflections, with $31 < 2\theta < 63°$, cell constants and an orientation matrix were obtained. Prefiltered Cu Kα_1 radiation (λ 1.54056 Å) was used. Conditions of data collection are given in Table III.

The ω scans of several intense, low-angle reflections, recorded as a check on crystal mosaicity, had an average width at half-height of 0.06°. These ω scans were rerun following the data collection and indicated no appreciable increase in crystal mosaicity. The standard reflections showed only random fluctuations, and it was evident that no significant crystal decomposition had occurred.

The intensity data were processed with the value for p, the "ignorance" factor, taken as 0.04.[9] An absorption correction was applied[10] to the 4464 data for which $F^2 > 0$. Transmission coefficients varied between 0.625 and 0.788.

Structure Solution and Refinement. For the solution and refinement of the structure only the 3197 unique data with $F^2 > 3\sigma(F^2)$ were used. A Patterson synthesis could not be solved assuming space group

Table IV. Final Atomic Positional and Thermal Parameters[a]

atom	x	y	z	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	3826.8 (2)	2765 (1)	2235.9 (3)	527 (3)	563 (3)	402 (3)	5 (2)	129 (2)	−57 (2)
F(1)	3159 (1)	6357 (3)	588 (2)	1125 (19)	1061 (20)	945 (18)	398 (16)	61 (15)	225 (15)
F(2)	3044 (1)	4305 (3)	810 (2)	778 (15)	1209 (21)	987 (18)	−83 (15)	−51 (13)	77 (16)
F(3)	3461 (1)	4853 (3)	1 (1)	1157 (20)	1501 (25)	565 (13)	251 (18)	60 (13)	−54 (14)
F(4)	4590 (1)	6088 (3)	1859 (2)	943 (18)	1617 (28)	997 (19)	−483 (18)	169 (15)	−57 (19)
F(5)	4404 (1)	5481 (3)	648 (2)	1240 (20)	1132 (20)	935 (17)	−128 (16)	563 (16)	172 (16)
F(6)	4071 (1)	7221 (3)	987 (2)	1635 (29)	671 (17)	1775 (31)	−87 (17)	515 (24)	255 (19)
F(7)	3420 (1)	−1031 (3)	2646 (2)	2320 (38)	686 (17)	854 (18)	471 (19)	152 (21)	−52 (14)
F(8)	3593 (1)	−481 (3)	3865 (1)	1738 (27)	883 (18)	672 (14)	−11 (17)	38 (16)	221 (13)
F(9)	2856 (1)	−787 (3)	3218 (2)	1716 (31)	1177 (25)	1576 (30)	−680 (23)	381 (25)	285 (22)
F(10)	2998 (1)	3290 (3)	3279 (2)	1380 (24)	945 (20)	1212 (22)	216 (17)	579 (19)	−228 (17)
F(11)	2529 (1)	1699 (4)	3328 (2)	1112 (22)	2053 (35)	1649 (29)	−217 (24)	934 (22)	−390 (28)
F(12)	3205 (1)	1834 (3)	4210 (2)	1804 (29)	1345 (24)	717 (16)	−86 (21)	655 (18)	−171 (16)
O(1)	3990 (1)	3829 (2)	1478 (1)	653 (13)	566 (13)	470 (11)	42 (10)	180 (10)	−6 (10)
O(2)	3685 (1)	1689 (2)	3007 (1)	609 (13)	738 (15)	427 (11)	−48 (11)	127 (9)	6 (10)
N(1)	4124 (1)	4018 (3)	3041 (1)	572 (15)	620 (18)	427 (13)	42 (12)	136 (11)	−64 (12)
N(2)	3561 (1)	1474 (3)	1437 (1)	536 (14)	628 (17)	408 (12)	29 (13)	119 (11)	−65 (12)
C(1)	3830 (1)	5119 (3)	1405 (2)	662 (20)	591 (21)	546 (18)	81 (16)	150 (15)	38 (15)
C(2)	4222 (2)	5979 (4)	1222 (3)	1027 (31)	663 (27)	789 (26)	−102 (22)	201 (25)	53 (21)
C(3)	3370 (2)	5180 (5)	694 (2)	912 (29)	836 (30)	647 (24)	163 (25)	97 (20)	104 (21)
C(4)	3692 (1)	5681 (4)	2148 (2)	818 (24)	608 (21)	682 (22)	188 (18)	175 (18)	−42 (18)
C(5)	4040 (1)	5265 (4)	2930 (2)	736 (22)	600 (23)	575 (19)	65 (17)	187 (16)	−121 (16)
C(6)	4245 (2)	6345 (4)	3531 (3)	1241 (35)	711 (27)	795 (27)	80 (24)	85 (25)	−285 (22)
C(7)	4450 (1)	3486 (4)	3785 (2)	658 (19)	688 (22)	405 (15)	−8 (16)	95 (14)	−65 (15)
C(8)	4791 (1)	2464 (4)	3605 (2)	610 (18)	764 (25)	467 (16)	29 (16)	124 (14)	23 (15)
C(9)	4890 (1)	1860 (4)	642 (2)	640 (20)	992 (30)	518 (18)	−52 (19)	199 (15)	−192 (19)
C(10)	4671 (1)	526 (4)	780 (3)	699 (23)	923 (30)	890 (27)	1 (21)	274 (20)	−402 (24)
C(11)	4332 (1)	603 (4)	1312 (2)	726 (22)	571 (21)	737 (22)	5 (17)	254 (18)	−138 (18)
C(12)	3846 (1)	1166 (4)	867 (2)	664 (20)	807 (25)	512 (17)	−41 (18)	204 (15)	−201 (17)
C(13)	3165 (1)	873 (3)	1412 (2)	569 (18)	618 (20)	481 (16)	−21 (15)	52 (14)	−21 (15)
C(14)	2937 (2)	−173 (5)	815 (2)	939 (29)	1013 (33)	671 (23)	−312 (25)	105 (21)	−233 (22)
C(15)	2912 (1)	1278 (4)	2027 (2)	488 (17)	773 (23)	631 (19)	−41 (16)	142 (15)	2 (17)
C(16)	3237 (1)	1184 (3)	2900 (2)	648 (19)	587 (20)	538 (18)	−68 (16)	221 (15)	4 (15)
C(17)	3284 (2)	−280 (5)	3158 (3)	1155 (35)	739 (29)	682 (25)	−122 (25)	130 (24)	50 (22)
C(18)	2981 (2)	1991 (5)	3435 (3)	1037 (33)	1010 (39)	767 (27)	−218 (27)	494 (24)	−162 (25)

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. All parameters have been multiplied by 10^4. [b] $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)$ Å^2. The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Cc but was readily interpreted in space group *C*2/*c*, and positional parameters were determined for the Ni atom. Instead of the expected eight molecules in the unit cell, it soon became apparent that there were four dinuclear[23] units, each positioned on a crystallographic 2 axis, Wyckoff notation e. Solution of the structure therefore involved the location of an additional 34 nonhydrogen atoms, and these were found through a series of least-squares refinements and Fourier synthesis calculations. Refinement of atomic parameters was by full-matrix least-squares techniques on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where the weighting factor $w = 4F_o^2/\sigma^2(F_o)^2$ and $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The neutral-atom scattering factors for the nonhydrogen atoms were those of Cromer and Waber[11] and those for H atoms were from Stewart, Davidson, and Simpson.[12] The $\Delta f'$ and $\Delta f''$ components of anomalous dispersion given by Cromer and Liberman[13] were included in the calculations for the Ni atom. Refinement of all nonhydrogen atoms with anisotropic thermal parameters gave agreement factors $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.088$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.096$. The 16 methylene hydrogen atoms were located as well-defined peaks, and the six methyl-group hydrogen atoms were found in areas of appreciable electron density in a difference Fourier synthesis. These H atoms were in positions which compared favorably with idealized coordinates found by assuming sp^3 geometry about the C atoms and using an H–C bond distance of 1.00 Å. The H atoms were given isotropic thermal parameters and their contributions in calculated positions were included in subsequent refinement cycles, without attempting to refine their parameters.

After a series of refinement cycles, each followed by recalculation of the H atom parameters, refinements converged with values of R_1 of 0.046 and R_2 of 0.055. The largest shift in the final cycle was 0.036 esd, in the x coordinate of F(1). The highest peak in a difference Fourier synthesis was 0.40 (6) e Å^{-3}, lying close to a CF_3 group, and was of no chemical significance. Reflections $15,\bar{1},\bar{3}$, $1\bar{5}\bar{1}$, $21,\bar{1},\bar{2}$ and $2\bar{2}4$ were in error and were omitted from the final cycle. A statistical analysis of R_2 over various ranges of $|F_o|$, $\lambda^{-1} \sin\theta$, and diffractometer setting angles χ and ϕ indicated a suitable weighting scheme. The error in an observation of unit weight is 2.28 electrons. Final positional and thermal parameters for the nonhydrogen atoms are given in Table IV and those for the H atoms in Table V. The structure factor amplitudes are presented in Table VI.

Table V. Derived Hydrogen Atom Positional (×10^4) and Thermal Parameters

atom[a]	x	y	z	B, Å^2
H1C(4)	3694	6681	2124	6.15
H2C(4)	3368	5353	2149	6.15
H1C(7)	4644	4241	4093	5.10
H2C(7)	4259	3060	4120	5.10
H1C(8)	4595	1734	3272	5.37
H2C(8)	4993	2904	3291	5.37
H1C(9)	5080	1720	242	6.13
H2C(9)	4621	2505	409	6.13
H1C(10)	4484	169	237	7.08
H2C(10)	4934	−102	1023	7.08
H1C(11)	4281	−320	1499	5.77
H2C(11)	4476	1185	1780	5.77
H1C(12)	3674	502	465	5.66
H2C(12)	3899	2010	588	5.66
H1C(15)	2802	2226	1926	5.45
H2C(15)	2630	681	1980	5.45
H1C(14)	2583	−232	783	7.74
H2C(14)	2970	87	267	7.74
H3C(14)	3090	−1058	969	7.74
H1C(6)	4546	6007	3917	8.20
H2C(6)	4320	7156	3248	8.20
H3C(6)	4005	6586	3834	8.20

[a] H atoms are numbered according to the atom to which they are bonded; thus H1N(1) is bonded to N(1), etc.

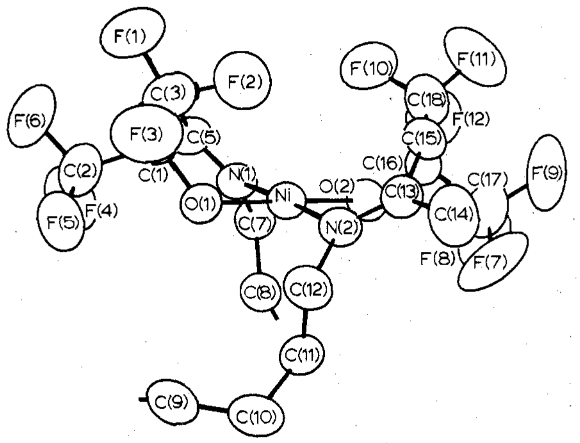


Figure 1. View of the half-molecular unit showing the atom numbering scheme.

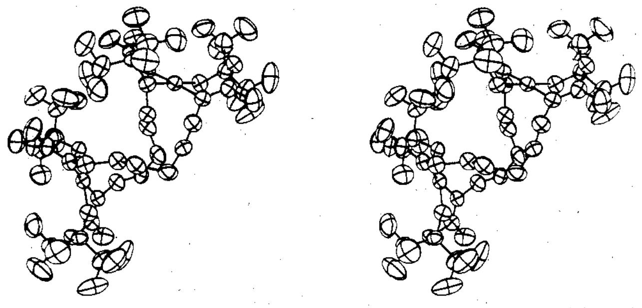
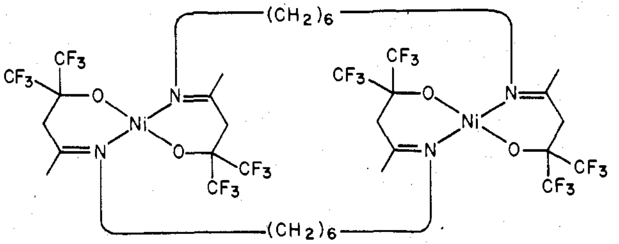


Figure 2. Stereoview of the dinuclear complex. Atoms are plotted with 50% probability thermal ellipsoids.

Structure Description

A perspective drawing, showing the atom-numbering scheme of the half-molecular unit for which the structure was solved, is given in Figure 1, and an ORTEP stereodiagram of the dinuclear molecule is shown in Figure 2. There is a crystallographic 2 axis, passing between the linking C atom chains, which imposes C_2 symmetry upon the structure, shown in a line drawing as 3.



3

Each Ni atom is coordinated in square-planar geometry to trans imino nitrogen and alkoxo oxygen donor atoms of separate, quadridentate, N_2O_2-donor ligands. The square planes about the two Ni atoms in the molecule are inclined at an angle of 55.4° to each other and are joined by chains of six carbon atoms linking the imino nitrogen atoms of the ligands, thus giving a central 18-membered ring, which is twisted in helical fashion. The six-membered iminoalkoxy chelate rings all have "half-boat" configurations.

Table VII. Selected Weighted Least-Squares Planes[a]

Plane 1: $A = 25.2, B = -4.64, C = -1.45, D = 8.02$[b]					
Ni	−0.006 (1)	O(1)	0.021 (2)	O(2)	0.026 (2)
N(1)	0.043 (3)	N(2)	0.041 (2)		
Plane 2: $A = 25.2, B = -4.64, C = -1.47, D = 8.06$					
Ni	−0.037	O(1)	−0.008 (2)	O(2)	−0.008 (2)
N(1)	0.011 (3)	N(2)	0.010 (2)		
Plane 3: $A = 26.2, B = 0.862, C = -11.0, D = 7.82$					
Ni	0.000 (1)	N(1)	0.003 (2)	C(7)	−0.003 (3)
C(5)	0.012 (3)	C(4)	−0.005 (4)	C(6)	−0.017 (5)
Plane 4: $A = 9.83, B = -7.18, C = 8.52, D = 3.68$					
Ni	0.000 (1)	N(2)	−0.015 (3)	C(12)	0.001 (4)
C(13)	0.006 (3)	C(14)	0.024 (5)	C(15)	−0.009 (4)
Plane 5: $A = 27.8, B = 2.56, C = -3.09, D = 11.6$					
N(1)	−0.041 (3)	C(5)	0.081 (4)	C(1)	−0.069 (4)
O(1)	0.023 (2)	Ni	−0.938	C(4)	−0.537
Plane 6: $A = 11.6, B = -9.02, C = 0.652, D = 2.92$					
N(2)	−0.029 (3)	C(13)	0.052 (3)	C(16)	−0.049 (3)
O(2)	0.023 (2)	Ni	−0.833	C(15)	−0.567

[a] Distances given are displacements from the plane in Å with those without esd's related to atoms not included in the calculations on the plane. [b] The form of the plane equation is $Ax + By + Cz - D = 0$.

Table VIII. Intramolecular Dimensions[a]

Bond Lengths, Å			
Ni-O(1)	1.843 (2)	C(8)-C(9)′	1.506 (5)
Ni-O(2)	1.841 (2)	C(9)-C(10)	1.520 (6)
Ni-N(1)	1.896 (3)	C(10)-C(11)	1.514 (5)
Ni-N(2)	1.896 (3)	C(11)-C(12)	1.515 (5)
O(1)-C(1)	1.362 (4)	C(12)-N(2)	1.476 (4)
C(1)-C(2)	1.520 (6)	N(2)-C(13)	1.280 (4)
C(1)-C(3)	1.551 (5)	C(13)-C(14)	1.491 (5)
C(1)-C(4)	1.547 (5)	C(13)-C(15)	1.498 (5)
C(4)-C(5)	1.510 (5)	C(15)-C(16)	1.551 (5)
C(5)-C(6)	1.504 (5)	O(2)-C(16)	1.354 (4)
N(1)-C(5)	1.273 (4)	C(16)-C(17)	1.524 (6)
N(1)-C(7)	1.475 (4)	C(16)-C(18)	1.552 (5)
C(7)-C(8)	1.505 (5)	mean C-F dist	1.327 (5)

Bond Angles, Deg			
O(1)-Ni-O(2)	178.1 (1)	C(7)-C(8)-C(9)′	112.1 (3)
N(1)-Ni-N(2)	177.1 (1)	C(8)′-C(9)-C(10)	113.6 (3)
O(1)-Ni-N(1)	89.4 (1)	C(9)-C(10)-C(11)	114.4 (3)
N(1)-Ni-O(2)	89.9 (1)	C(10)-C(11)-C(12)	111.8 (3)
O(2)-Ni-N(2)	90.3 (1)	C(11)-C(12)-N(2)	110.2 (3)
N(2)-Ni-O(1)	90.3 (1)	Ni-N(2)-C(12)	115.9 (2)
O(1)-C(1)-C(4)	115.0 (3)	Ni-N(2)-C(13)	121.8 (2)
O(1)-C(1)-C(2)	107.4 (3)	C(12)-N(2)-C(13)	122.2 (3)
O(1)-C(1)-C(3)	107.9 (3)	N(2)-C(13)-C(14)	125.2 (3)
C(2)-C(1)-C(3)	109.9 (3)	N(2)-C(13)-C(15)	116.7 (3)
C(2)-C(1)-C(4)	109.8 (3)	C(14)-C(13)-C(15)	118.0 (3)
C(3)-C(1)-C(4)	106.7 (3)	C(13)-C(15)-C(16)	113.0 (3)
C(1)-C(4)-C(5)	112.7 (3)	C(15)-C(16)-O(2)	114.7 (3)
C(4)-C(5)-C(6)	117.7 (3)	C(15)-C(16)-C(17)	109.0 (3)
C(4)-C(5)-N(1)	117.2 (3)	C(15)-C(16)-C(18)	106.7 (3)
C(6)-C(5)-N(1)	125.0 (3)	C(17)-C(16)-C(18)	110.1 (3)
Ni-N(1)-C(5)	120.3 (2)	O(2)-C(16)-C(17)	108.0 (3)
Ni-N(1)-C(7)	117.4 (2)	O(2)-C(16)-C(18)	108.3 (3)
C(5)-N(1)-C(7)	122.3 (3)	mean angles for CF_3 groups	
N(1)-C(7)-C(8)	111.4 (2)	C-C-F	112.1 (4)
		F-C-F	106.7 (4)

[a] C(*n*) and C(*n*)′ are atoms in the two halves of the dinuclear structure related by the C_2 axis.

The detailed geometry within the coordination plane is very close to square planar with angles in the "plane" ranging from 89.5 to 90.3°. A slight pyramidal distortion places the Ni atom slightly out from the O(1), N(1), O(2), N(2) plane and away from the central large ring, by 0.037 Å. Some weighted least-squares planes are given in Table VII. Intramolecular dimensions are summarized in Table VIII. The Ni–N bond lengths, mean 1.896 (3) Å, agree well with those observed for similar donors in square-planar Ni(II) complexes of a number of unsaturated tetraazamacrocyclic ligands[14] and are shorter than that observed (2.05 (1) Å) by Martin, Johnston, and Curtis[15] for the five-coordinate complex [NiL(NCS)$_2$], where L is the ligand 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene. The mean Ni–O distance, 1.842 (2) Å, is short compared to the normally observed range[16] (1.85–1.93 Å) for square-planar Ni(II) complexes, but no previous published structure has

Table IX. Torsional Angles (deg) for the Six-Membered Rings

Ring 1		Ring 2	
Ni-O(1)-C(1)-C(4)	21.1 (4)	Ni-O(2)-C(16)-C(15)	14.8 (4)
O(1)-C(1)-C(4)-C(5)	40.7 (4)	O(2)-C(16)-C(15)-C(13)	44.6 (4)
C(1)-C(4)-C(5)-N(1)	−53.5 (5)	C(16)-C(15)-C(13)-N(2)	−54.1 (4)
C(4)-C(5)-N(1)-Ni	1.1 (4)	C(15)-C(13)-N(2)-Ni	2.3 (4)
C(5)-N(1)-Ni-O(1)	46.8 (3)	C(13)-N(2)-Ni-O(2)	43.1 (3)
N(1)-Ni-O(1)-C(1)	−57.5 (2)	N(2)-Ni-O(2)-C(16)	−51.1 (2)

described the coordination of a perfluoroalkoxo group, $-(CF_3)_2CO^-$, to a first-row transition element.

The six-membered chelate rings formed by the coordinated, condensed hexafluorodiacetone alcohol residues are found to be in "half-boat" configurations. The ring incorporating Ni, O(1), C(1), C(4), C(5), and N(1) is similar, but not identical, to that of Ni, O(2), C(16), C(15), C(13), and N(2). Nearly planar geometry about the C=N bonds in these rings is shown by the least-squares plane through Ni, N(1), C(7), C(5), C(4), and C(6) and that through Ni, N(2), C(12), C(13), C(14) and C(15) respectively, Table VII.

Conformations of six-membered chelate rings containing a C=N bond have received some attention recently, especially by Hodgson and co-workers.[17-19] From the structures of a series of copper(II) complexes formed by the condensation of (2-aminoethyl)pyridine (or its N-substituted analogues), Hodgson has concluded that, when the bite angle of imino-nitrogen–Cu–amino-nitrogen is acute, the Cu atom will lie farther from the basal plane of the boat than does the central methylene carbon atom. When the bite angle is near 90°, Cu and C atoms are nearly equidistant from this plane, and when it is obtuse, the C atom is the more distant. However, this approach is limited by departures from the idealized "half-boat" structure. The basal plane is in some cases only approximate, and mean deviations can amount to as much as 0.14 Å.[18] An alternative approach is to examine torsion angles shown in Table IX. In this structure, the torsion angles of 21.1 (4)° between the Ni–O(1) and C(1)–C(4) vectors in one ring and that of 14.8 (4)° between Ni–O(2) and O(1)–C(2) of the other ring indicate a twist away from the strict "rigid boat" (for which this torsion angle would be zero) toward the "half-chair" conformation. The latter is by no means uncommon, having been observed in a number of nickel(II) and copper(II) complexes.[14,15,20-22]

There would appear to be little difference in energy between the half-boat and half-chair conformations, the strain being minimized by small torsional deformations, and the geometry adopted by the ring may be determined in many cases by intermolecular interactions within the crystal lattice.

The trifluoromethyl groups attached to the chelate rings in our structure are in either axial or equatorial conformations; the C–C bond lengths of the former (1.522 (6) Å mean) are comparable to those of the latter (1.552 (5) Å mean), considering a 3σ error and the considerable thermal motion of these groups.

The 18-membered central ring adopts a twisted helical conformation, with a mean C–C bond length of 1.512 (6) Å and a mean C–C–C angle of 113.0 (3)°. The Ni···Ni distance is 6.589 (2) Å.

Solution Studies: Structures of Other Complexes

Table X. Molecular Weights (Osmometric in Acetonitrile)

	mol wt of nickel complex		mol wt of copper complex	
value of *n*	calcd	found	calcd	found
2	530^a	527	535^a	530
2^d	543^a	547		
3	543^a	544	548^a	543
4	1114^b	1085	562^a	568
5	1142^b	1119	576^a	581
6	1170^b	1185	590^a	589
8	1226^b	1154	618^a	626
12		*c*	674^a	682

[a] Calculated for mononuclear complex. [b] Calculated for dinuclear complex. [c] Insufficiently soluble. [d] From $NH_2CH_2CH(CH_3)NH_2$.

Table XI. Visible Absorption Spectra of Nickel Complexes

value of *n*	maximum, cm^{-1} (ϵ)[a]	solvent[c]
2	20 500 (248)	a
	20 800 (249)	m
	20 600, 26 000	a/py
2^b	20 500 (246)	a
	20 700 (240)	m
3	19 350 (168)	a
	19 500 (157)	m
	19 400, 26 000	a/py
4	20 300 (138)	a
	20 800, 25 600	a/py
5	19 250 (70)	a
	19 200, 26 600	a/py
6	19 150 (76)	a
	19 300 (82)	c
	19 200, 26 300	a/py
8	19 150 (69)	a
	19 100, 27 000	a/py
12	19 300 (84)	c
	19 200 (68)	b

[a] For dinuclear complexes, ϵ is calculated per mole of nickel. [b] From $NH_2CH_2CH(CH_3)NH_2$. [c] Key: a = acetonitrile, m = methanol, c = chloroform, b = benzene.

We can now attempt to interpret available data on the other complexes prepared in this study. Osmometric molecular weight measurements showed apparent association, particularly in nonpolar solvents, and we attempted to reduce this by working in the more polar solvent acetonitrile. The results are shown in Table X, and, since they show the expected dinuclear structure for the known complex, we can have some confidence in the other figures. Since the change from mononuclear to dinuclear structure involves the detachment and transfer of two chelate rings on each metal atom, it is improbable that any change in structure occurs between the solid and the solution.

A clear trend in the molecular weight data is immediately apparent. Whereas all the copper complexes are, within experimental error, mononuclear, the nickel complexes change from a mononuclear to a dinuclear structure as *n* is increased from 3 to 4. In other words, the structure **1** is disfavored for nickel when the central chelate ring exceeds six members. However, a study of the solution spectra and solvation of the series shows that this change does *not* correspond to the change from the cis mononuclear structure **1** to the trans dinuclear structure **3**.

We have previously shown[1,6] that nickel complexes of this type, where bulky fluorinated ligands are incorporated into chelate rings, tend to form five-coordinate monosolvates only, rather than the more usual six-coordinate adducts. As Table XI shows, the present series continues this trend. The complexes all gave red solutions showing typical square-planar nickel(II) spectra in noncoordinating (chloroform, benzene) or weakly coordinating (methanol, acetonitrile) solvents, with extinction coefficients decreasing from 240–250 in the complexes with a central five-membered cis chelate ring (*n* = 2) to 168 with six-membered cis chelate ring (*n* = 3) and lower values (70–80) in the dinuclear complexes with *n* = 5–12. The addition of pyridine generally produced a green coloration and typical absorptions (e.g., at 26–27 000 cm^{-1}) associated with production of five-coordinate species. In the

Table XII. Visible Absorption Spectra of Copper Complexes[a]

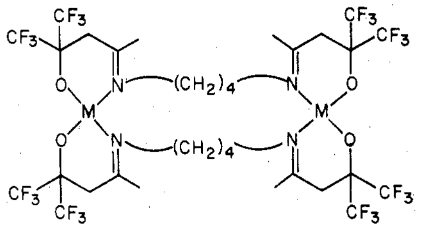
value of n	maximum, cm^{-1} (ϵ)	solvent
2	15 900 (156)	a
	15 800 (167)	d
	10 400 (sh), 15 000 (172)	py
3	15 400 (138), 19 200 (sh)	a
	15 200 (138), 18 300 (74)	d
	14 000 (sh), 15 000 (127)	py
4	14 900-16 700 (114) (br)	a
	16 800 (103), 18 000 (sh)	py
5	16 400 (sh), 18 000 (128)	a
	16 400 (sh), 17 700 (129)	d
	16 300 (sh), 17 500 (130)	py
6	15 900 (sh), 18 000 (128)	a
	16 400 (sh), 18 100 (127)	d
	17 100 (220)	py
8	16 600 (sh), 18 200 (118)	a
	16 400 (sh), 18 200 (113)	d
	16 800 (110), 17 900 (sh)	py
12	16 400 (sh), 18 100 (111)	a
	16 400 (sh), 18 200 (112)	d
	16 700 (138)	py

[a] Key: a = acetonitrile, d = dichloromethane, py = pyridine, sh = shoulder, position approximate, br = broad, flat absorption.

majority of cases, unsolvated four-coordinate species remained, even in the presence of a 500-fold excess of pyridine.

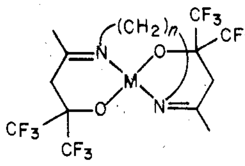
However, a striking difference in the *rate* of solvation was also observed. Whereas production of the spectra characteristic of five-coordinate species occurred immediately on mixing for $n = 2$, 3, or 4, a period of about 2 h was needed for complexes with $n = 5$, 6, 8, or 12 to equilibrate. An appreciable activation energy barrier to solvation may easily be envisaged for trans dinuclear complexes of structure 3, where a rearrangement of the conformation of the bridging hydrocarbon chains or the chelate rings will be needed to allow approach of a solute molecule. Removal of all solvent in vacuo led to recovery of unchanged dinuclear complex, eliminating the possibility that the slow addition was due to rearrangement of a dinuclear to a mononuclear structure.

On the basis of the similar behavior in solution of nickel complexes with $n = 5$, 6, 8, or 12, we suggest that they all have the trans dinuclear structure. However, the $n = 4$ nickel complex is clearly different in that, although dinuclear from its molecular weight, it solvates rapidly. Furthermore, the extinction coefficient for the principal absorption in the visible spectrum of this species (in its unsolvated form) is 138, close to that of the cis mononuclear species with $n = 3$ and considerably greater than that of the other dinuclear species. A cis dinuclear structure, **4**, would explain these anomalies although such a structure must remain speculative in the absence of precise structural data.



4

For the copper complexes, the visible absorption spectra (Table XII) were less informative. In all cases but one, introduction of a strong donor solvent (pyridine) produced a change in the spectra, in the form of a shift to higher energy, consistent with solvation; equilibrium was rapidly reached. The exception was the complex with $n = 5$, for which no solvation was found. Present evidence does not permit a definite explanation of this effect. As an alternative to the cis mononuclear structure **1**, a trans mononuclear structure **5** becomes possible at larger values of n.



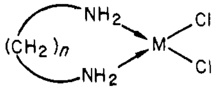
5

The examination of molecular models suggests that this structure is possible without excessive strain at a minimum value of $n = 5$. However, it is not obvious why larger values of n permit a return to ready solvation by pyridine. Whatever the mode of attachment of the ligand in the copper complexes where $n = 5$–12, it is clear that, if mononuclear, they must contain one chelate ring of 9–15 members, and structural studies are continuing on this series.

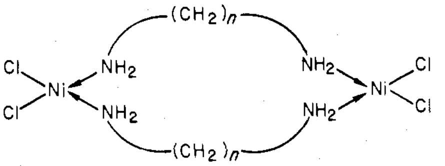
Discussion

Although no definite answer can be given to the question of why mononuclear complexes are formed in some cases and dinuclear complexes in others, we feel that the above results can be rationalized. Since the template condensation reaction must occur on the metal ion and since the diamine, as the stronger donor, will tend to coordinate preferentially in the initial reaction mixture, the nature of the metal–diamine complex (which then reacts with HFDA) will clearly be vital in determining the nature of the products.

With the short-chain diamines ($n = 2$, 3) the intermediates will be cis coordinated: the halide ion being displaced by $CH_3C(O)CH_2C(CF_3)_2O^-$ ions, followed by condensation to produce the observed cis mononuclear structure **1** complexes. In the case of copper(II), this process may continue up to large values of n, although trans mononuclear complexes may be favored at some stage.



For nickel, we suggest that the longer chain diamines ($n = 4$–12) tend to bridge between two Ni^{2+} ions to form dinuclear intermediates:



The reaction of this type of intermediate with HFDA will then lead to formation of a dinuclear complex, in which the geometry at nickel may be either cis (for $n = 4$) or trans (for $n = 5$ and up).

It is not suggested that the above intermediates are the only species produced by interaction of the various diamines with nickel(II) or copper(II) but simply that these undergo ready reaction with HFDA and are therefore instrumental in determining the nature of the product. We feel that kinetic control of this type is much more likely than an equilibration between mononuclear and dinuclear species after condensation of ligands has occurred.

Acknowledgment. This work was funded by the National Research Council of Canada, through grants to C.J.W. and N.C.P.

Registry No. **1**, $n = 2$, M = Ni, 64105-51-7; **1**, $n = 2$, M = Cu, 64105-50-6; **1**, $n = 2$ (from $NH_2CH_2CH(CH_3)NH_2$), M = Ni, 64105-52-8; **1**, $n = 3$, M = Ni, 64105-53-9; **1**, $n = 3$, M = Cu, 67722-50-3; **3**, 67722-51-4; **4**, M = Ni, 67722-52-5; $C_{34}H_{40}F_{24}N_4$-

Ni_2O_4, 67722-53-6; $C_{40}H_{52}F_{24}N_4Ni_2O_4$, 67722-54-7; $C_{48}H_{68}F_{24}N_4Ni_2O_4$, 67722-55-8; $C_{16}H_{18}CuF_{12}N_2O_2$, 67722-56-9; $C_{17}H_{20}CuF_{12}N_2O_2$, 67722-57-0; $C_{18}H_{22}CuF_{12}N_2O_2$, 67722-58-1; $C_{20}H_{26}CuF_{12}N_2O_2$, 67722-59-2; $C_{24}H_{34}CuF_{12}N_2O_2$, 67722-60-5.

Supplementary Material Available: Table VI, a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. W. L. Martin and C. J. Willis, *Can. J. Chem.*, **55**, 2459 (1977).
(2) M. Hariharan and F. L. Urbach, *Inorg. Chem.*, **8**, 556 (1969).
(3) H. Weigold and B. O. West, *J. Chem. Soc. A.*, 1310 (1967).
(4) W. C. Hoyt and G. W. Everett, *Inorg. Chem.*, **8**, 2013 (1969).
(5) H. Krebs, K. Pachali, and H. P. Vogel, *Z. Anorg. Allg. Chem.*, **388**, 113 (1972).
(6) W. S. Cripps and C. J. Willis, *Can. J. Chem.*, **53**, 809 (1975).
(7) J. W. L. Martin and C. J. Willis, unpublished work.
(8) "International Tables for X-Ray Crystallography", Vol. 1 Kynoch Press, Birmingham, England, 1962, pp 89 and 101.
(9) R. G. Ball, N. J. Bowman, and N. C. Payne, *Inorg. Chem.*, **15**, 1704 (1976).
(10) The computer programs used in this analysis include local modifications of the following: cell refinement and orientation matrix, PICKTT, from Hamilton's MODE I; full-matrix least squares, J. A. Ibers' NUCLS; Patterson and Fourier syntheses, A. Zalkin's FORDAP; function and errors, W. R. Busing, K. O. Martin, and H. A. Levy's ORFFE; crystal structure illustrations, C. K. Johnston's ORTEP; absorption correction by the analytical method of de Meulanaer and Tompa in the program AGNOST as modified by D. Cahen and J. A. Ibers, *J. Appl. Crystallogr.*, **5**, 298 (1972).
(11) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(12) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(13) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1976).
(14) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).
(15) N. F. Curtis, J. H. Johnston, and J. W. L. Martin, *J. Chem. Soc., Dalton Trans.*, 68 (1978).
(16) M. R. Fox, E. C. Lingafelter, and L. Sacconi, *Acta Crystallogr.*, **17**, 1159 (1964).
(17) D. J. Hodgson et al., *Inorg. Chem.*, **11**, 1826, 2216 (1972); **12**, 1340, 2157, 2935 (1973); **13**, 143, 147, 1013 (1974); **14**, 1672 (1975); **15**, 1712 (1976).
(18) D. L. Kozlowski and D. J. Hodgson, *J. Chem. Soc., Dalton Trans.*, 55 (1975).
(19) T. B. Vance, L. G. Warner, and K. Seff, *Inorg. Chem.*, **16**, 2106 (1977).
(20) N. F. Curtis et al., *J. Chem. Soc., Dalton Trans.*, 1115 (1972); *J. Chem. Soc. A*, 1051 (1977); *J. Chem. Soc., Chem. Commun.*, 572 (1977).
(21) I. E. Maxwell and M. F. Bailey, *J. Chem. Soc. A*, 935 and 938 (1972).
(22) F. Hanic and M. Serator, *Chem. Zvesti*, **18**, 572 (1964); *Chem. Abstr.*, **61**, 15643 (1961); F. Hanic, F. Pavelcik, and G. Gyepesova, *Kristallografiya*, **17**, 10 (1972).
(23) Throughout this paper, we use the terms mononuclear and dinuclear with reference to the number of metal atoms in one unit of the complex.

Contribution from the Department of Chemistry,
University of Southern California, Los Angeles, California 90007

Crystal and Molecular Structure of the Monoclinic Form of $[Cd(5'\text{-}CMP)(H_2O)]_n$[1]

JANE K. SHIBA and ROBERT BAU*

Received June 9, 1978

Cadmium(II) 5′-cytidine monophosphate monohydrate sesquihydrate, prepared by the reaction of $Na_2(5'\text{-}CMP)$ with $Cd(NO_3)_2$, crystallizes as fine needles in the monoclinic space group *C*2, with $a = 31.480$ (12) Å, $b = 5.349$ (3) Å, $c = 25.200$ (9) Å, $\beta = 128.52$ (2)°, and $Z = 8$. The structure consists of a complex polymeric network in which each CMP group is coordinated to four different cadmium atoms and vice versa. The nucleotide chelates one Cd atom through N(3) and the carbonyl oxygen O(2) of the cytosine base and is further bonded to three other cadmiums through the phosphate group. The Cd atom is seven-coordinate, being connected to four oxygens from phosphate groups, two atoms from a cytosine base, and a water molecule. Average distances: Cd–O(phosphate) = 2.36 Å, Cd–N(3)(cytosine) = 2.33 Å, Cd–O(2)(cytosine) = 2.72 Å, and Cd–O(water) = 2.31 Å. The final *R* factor is 8.0% for 2359 independent reflections collected on a diffractometer.

Introduction

There has been a growing interest in the role of metals in biological processes. A considerable amount of research has been done on interactions between metal ions and nucleotides or polynucleotides, and many excellent reviews are now available on the subject.[2–7]

Cadmium, as well as many metals of the first transition series, has been found to be firmly coordinated to RNA, to the extent that it is not readily removed by the action of strong chelating agents.[8] It has been suggested that some of these metals may have a role in stabilizing the configuration of RNA. An investigation of the cooling curves of DNA in the presence of Cd^{2+} ions has indicated strong binding of the metal ions to DNA. The decrease of the "melting point" of DNA in the presence of cadmium ions is thought to be due to the destabilizing influence of the cadmium ions arising from interactions between Cd^{2+} and the base portions of the DNA molecule.[9]

There has been relatively little spectral work done on the coordination of cadmium ions to cytosine derivatives, except for a Raman study indicating the absence of significant interaction between Cd^{2+} and cytidine.[10] However, a fair amount is known about the binding of related metal ions such as Zn^{2+} and Hg^{2+} on cytosine and cytidine. ^1H NMR studies on these systems by Li and co-workers show that the predominant mode of coordination is through the N(3) atom of the pyrimidine ring.[11] This mode of binding has been confirmed by the results of X-ray crystallographic studies on cytosine and cytidine complexes,[12–17] while for 5′-CMP complexes simultaneous binding to both the N(3) position and the phosphate group seems to be the rule,[18–21] with one exception which shows O(2) binding.[22]

In order to get a clearer idea of the structural basis of the tight Cd^{2+}/DNA binding, several groups of investigators have been studying the structures of cadmium nucleotide complexes by crystallographic methods. With 5′-GMP, cadmium forms discrete molecular complexes having the formula $Cd(5'\text{-}GMP)(H_2O)_5$, consisting of a cadmium ion octahedrally coordinated by the N(7) atom of the guanine base and five water molecules.[23] On the other hand, with 5′-CMP, cadmium forms orthorhombic crystals of empirical formula $[Cd(5'\text{-}CMP)(H_2O)]\cdot H_2O$ consisting of a polymeric network of $[Cd(5'\text{-}CMP)(H_2O)]$ units.[18,19] In this network each CMP molecule was found to be coordinated to Cd through the N(3) position of the pyrimidine ring and also through three oxygen atoms of the phosphate group. This structure will be discussed later.

Around the time the structure of the orthorhombic form of $[Cd(5'\text{-}CMP)(H_2O)]_n$ was published[18,19] we had independently isolated and solved the structure of a different crystalline modification (monoclinic) of this complex.[1] There are many similarities, and also distinct differences, between the two structures. Our results of the monoclinic form of $[Cd(5'\text{-}CMP)(H_2O)]_n$ are described in this paper.

Experimental Section

The cadmium–CMP complex was prepared in a similar manner

0020-1669/78/1317-3484$01.00/0