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Fluorinated Alkoxides. 16. Structure of a Dinuclear Imino Alkoxy Complex of Copper(II)

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We have recently reported that the condensation of 5,5,5-trifluoro-4-hydroxy-4-(trifluoromethyl)-2-pentanone (hexafluorodiacetone alcohol, HFDA) with various diamines in the presence of a metal ion gives rise to neutral, stable, fluorinated imino alkoxy complexes. Two structural types have been identified: a mononuclear form **1** with short-chain diamines[1] and a dinuclear form **2** with those of longer chain length.[2]
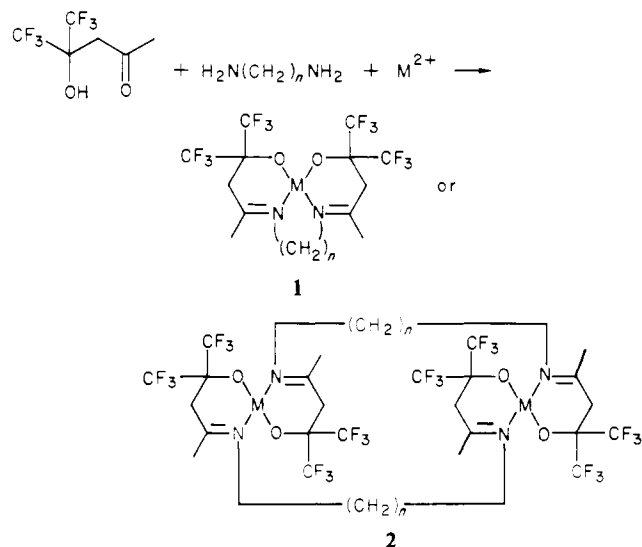
In the case of M = Ni^{2+}, we have demonstrated a dinuclear[3] structure in the solid state for $n = 6$ with a trans-planar arrangement about each Ni atom, the angle between the two coordination planes in the dinuclear unit being 55°. On the basis of solution molecular weights, we concluded that the transition from mononuclear structures **1** to dinuclear structures **2** for Ni^{2+} occurred as n was increased from 3 to 4; in other words, bridging was favored over chelation as the size of the central chelate ring in **1** increased from six to seven members.

In the analogous Cu^{2+} complexes, solution molecular weights in acetonitrile suggested that mononuclear type **1** structures persisted for all chain lengths investigated, up to $n = 12$. In order to discover whether this structural type was present in the solid state and in view of the intrinsic interest of the geometry of large chelate rings, we have now carried out a complete crystallographic structural investigation of the Cu^{2+} complex with $n = 5$.

Experimental Section

The preparation, characterization, and general properties of the complex with $n = 5$ have been described previously.[2]

Collection and Reduction of X-ray Data. Deep blue crystals of the Cu complex were grown from a 3:1 mixture of ethanol and methanol. Preliminary Weissenberg and precession photography suggested the monoclinic system, and cell constants were obtained. Systematic absences of $h0l$ for l odd and $0k0$ for k odd are consistent only with

(1) Martin, J. W. L.; Willis, C. J. *Can. J. Chem.* **1977**, *55*, 2459.
(2) Martin, J. W. L.; Payne, N. C.; Willis, C. J. *Inorg. Chem.* **1978**, *17*, 3478.
(3) Throughout this paper we use the terms mononuclear and dinuclear with reference to the number of metal atoms in one molecule of the complex.

Table I. Crystal Data

$C_{34}H_{40}Cu_2F_{24}N_4O_4$	fw 1151.8
$a = 20.008$ (2) Å	space group $P2_1/c$
$b = 9.009$ (1) Å	$Z = 4$
$c = 29.296$ (3) Å	$V = 4625$ Å^3
$\beta = 118.86$ (1)°	$d(\text{obsd})^a = 1.68$ (1) g cm^{-3}
$\mu(\text{Cu K}\alpha) = 22.27$ cm^{-1}	$d(\text{calcd}) = 1.647$ g cm^{-3}

^{a} By neutral buoyancy in CCl$_4$ and 1,2-dibromoethane.

Table II. Experimental Conditions for Data Collection

radiatn: Cu Kα_1, Ni-foil prefilter (0.018 mm)
takeoff angle: 1.8° (for 90% of max Bragg intens)
aperture: 0.5 × 0.5 mm^2, 32 cm from crystal
data collected: $\pm h$, $k \geqslant -1$, $l \geqslant 0$ for 0° $< 2\theta < 90°$; $\pm h$, $k \geqslant 0$, $l \geqslant 0$ for 90° $< 2\theta < 105°$
scan: θ–2θ, from 0.7° below α_1 peak to 0.9° above α_2 peak, at 2° min^{-1}
bkgd: 10 s, stationary crystal, stationary counter at scan limits
stds: 5 recorded every 200 reflctns; $\overline{2}$00, 002, 200, $\overline{1}$11, 020

space group $P2_1/c$, No. 14.[4] The crystal density, determined by flotation, allows either eight mononuclear or four dinuclear molecules per cell.

A crystal of approximate dimensions 0.33 × 0.20 × 0.33 mm^3 was selected and measured with use of a microscope fitted with a filar eyepiece. An optical goniometry study assigned Miller indices to the 14 crystal faces; in point group 2/m {100}, {001}, {11$\overline{2}$}, {110}, and {10$\overline{2}$} are the forms. The crystal was mounted with the long dimension [$\overline{1}$10] offset by some 18° from the diffractometer ϕ axis. Crystal data are given in Table I.

Intensity data were collected by using a Picker FACS-1 computer-controlled diffractometer, running under the Vanderbilt disk operating system.[5] From a least-squares refinement of 30 intense, carefully centered reflections with 28° $< 2\theta < 48°$, accurate cell constants and an orientation matrix were obtained.[6] Prefiltered Cu Kα_1 radiation ($\lambda = 1.540\,56$ Å) was used. The ω scans of several intense, low-angle reflections, recorded as a check on crystal mosaicity, had an average width at half-height of 0.08°. These scans were repeated 12 days later, after 6286 observations had been recorded and that of 020 had broadened to 0.18° from 0.10°, while the remainder were unchanged. During the collection of data, this standard also decreased in intensity by 30%, while the remainder showed only random fluctuations. No correction was made for this anisotropic crystal decomposition. After removal of the standard reflections, corrections were made for Lorentz and polarization effects, and $\sigma(I)$ values were assigned by using a p value of 0.03.[7,8] The unique data with $I > 0$ were corrected for absorption by using the Gaussian method;[6] transmission coefficients varied from 0.607 to 0.763, with a crystal volume of 0.0073 mm^3. Experimental conditions for data collection are summarized in Table II.

Structure Solution and Refinement

For the solution and refinement of the structure only the 4029 unique data with $F^2 > 3\sigma(F^2)$ were used. The two Cu atoms and 33 of the 66 nonhydrogen atoms were readily located from an E map phased by the program MULTAN.[6] The remaining atoms were found through a series of least-squares refinements and Fourier syntheses. 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

(4) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vols. I and IV.
(5) Lenhert, P. C. *J. Appl. Crystallogr.* **1975**, *8*, 568.
(6) The computer programs used in this analysis include local modifications of the following: cell refinement and orientation matrix, PICKTT, from Hamilton's MODE 1; structure solution, MULTAN, by G. Germain, P. Main, and M. M. Woolfson; 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. Johnson's ORTEP; absorption correction by the analytical method of de Meulanaeur and Tompa in the program AGNOST as modified by: Cahen, D.; Ibers, J. A. *J. Appl. Crystallogr.* **5**, 298 (1972).
(7) Busing, W. R.; Levy, H. A. *J. Chem. Phys.* **1957**, *26*, 563.
(8) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr.* **1975**, *31*, 245.

Table III. Final Atomic Positional ($\times 10^4$) and Thermal Parameters^{a,b} ($\times 10^3$)

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	4162 (1)	2858 (2)	4003 (1)	60 (1)	56 (1)	48 (1)	-2 (1)	34 (1)	2 (1)
Cu(2)	851 (1)	3429 (2)	1378 (1)	62 (1)	67 (1)	62 (1)	-6 (1)	38 (1)	-2 (1)
F(1)	5003 (4)	1262 (8)	5434 (3)	100 (5)	100 (6)	112 (6)	31 (4)	40 (5)	40 (5)
F(2)	4214 (5)	1567 (8)	5718 (2)	177 (7)	105 (6)	57 (4)	25 (5)	66 (5)	21 (4)
F(3)	4065 (5)	-165 (8)	5188 (3)	180 (8)	70 (5)	102 (6)	-4 (5)	84 (5)	10 (4)
F(4)	2877 (4)	2852 (10)	5083 (3)	97 (5)	182 (8)	122 (6)	3 (5)	82 (5)	-8 (6)
F(5)	2675 (4)	976 (9)	4598 (3)	106 (6)	122 (7)	137 (7)	-56 (5)	51 (5)	3 (6)
F(6)	2577 (3)	3142 (9)	4298 (3)	50 (4)	159 (7)	110 (6)	-13 (4)	26 (4)	41 (5)
F(7)	5715 (5)	5670 (11)	3614 (3)	143 (7)	149 (8)	162 (8)	-46 (6)	115 (7)	-7 (7)
F(8)	6019 (4)	3915 (11)	3264 (3)	107 (6)	228 (10)	105 (6)	-36 (6)	85 (5)	-27 (6)
F(9)	6309 (4)	3794 (11)	4056 (3)	85 (5)	211 (9)	79 (5)	-39 (6)	33 (4)	-1 (6)
F(10)	4355 (5)	5261 (10)	2812 (4)	162 (8)	122 (7)	155 (8)	-11 (6)	62 (7)	66 (7)
F(11)	4558 (5)	3254 (12)	2538 (3)	125 (6)	250 (12)	65 (5)	9 (7)	51 (5)	3 (6)
F(12)	3728 (4)	3353 (9)	2780 (3)	77 (5)	155 (7)	92 (5)	5 (5)	37 (4)	43 (5)
F(13)	-683 (7)	1226 (14)	1856 (5)	244 (12)	197 (11)	240 (13)	5 (10)	188 (11)	71 (10)
F(14)	-477 (12)	3430 (15)	2035 (5)	594 (32)	184 (12)	136 (9)	-62 (15)	241 (16)	-13 (9)
F(15)	-1696 (8)	2705 (17)	1340 (8)	221 (13)	291 (17)	532 (29)	70 (13)	303 (18)	162 (20)
F(16)	-1128 (6)	414 (12)	912 (5)	166 (10)	126 (8)	251 (13)	-66 (7)	33 (9)	31 (9)
F(17)	-1815 (6)	2247 (15)	468 (6)	106 (7)	237 (13)	239 (14)	-17 (9)	6 (9)	5 (11)
F(18)	-914 (9)	1839 (12)	415 (5)	287 (17)	146 (10)	141 (10)	-51 (10)	23 (10)	-23 (8)
F(19)	931 (7)	5415 (13)	284 (5)	175 (10)	209 (12)	202 (11)	48 (9)	63 (9)	85 (10)
F(20)	2027 (10)	5138 (15)	305 (5)	408 (21)	255 (15)	184 (11)	72 (14)	229 (15)	69 (10)
F(21)	1956 (8)	6734 (11)	797 (5)	291 (15)	117 (8)	242 (13)	-67 (9)	193 (13)	-28 (8)
F(22)	3124 (7)	4221 (21)	1094 (6)	164 (10)	477 (25)	303 (18)	-97 (14)	185 (13)	-121 (18)
F(23)	2975 (7)	5539 (17)	1614 (5)	222 (13)	268 (15)	235 (14)	-164 (12)	133 (11)	-105 (13)
F(24)	2959 (6)	3055 (19)	1716 (5)	143 (9)	346 (20)	156 (10)	-45 (11)	8 (8)	18 (12)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
O(1)	3874 (4)	1753 (7)	4423 (3)	64 (2)	C(14)	2753 (6)	5177 (12)	3330 (4)	60 (3)
O(2)	4756 (4)	3933 (8)	3786 (3)	71 (2)	C(15)	2319 (5)	6096 (11)	2844 (4)	55 (3)
O(3)	80 (4)	2314 (8)	1392 (3)	77 (2)	C(16)	1628 (6)	5241 (12)	2456 (4)	67 (3)
O(4)	1532 (5)	4612 (9)	1280 (3)	97 (3)	C(17)	3458 (6)	14 (12)	3510 (4)	64 (3)
N(1)	3836 (4)	4790 (8)	4182 (3)	50 (2)	C(18)	-200 (7)	5514 (14)	1430 (5)	81 (4)
N(2)	4057 (4)	1014 (9)	3575 (3)	55 (2)	C(19)	-500 (9)	6853 (18)	1584 (6)	131 (6)
N(3)	501 (5)	5262 (9)	1584 (3)	57 (2)	C(20)	-764 (7)	4410 (15)	1064 (5)	96 (4)
N(4)	1388 (5)	1545 (10)	1375 (4)	75 (3)	C(21)	-633 (7)	2808 (15)	1232 (5)	87 (4)
C(1)	3862 (5)	5028 (11)	4621 (4)	50 (3)	C(22)	-816 (13)	2657 (27)	1696 (9)	149 (7)
C(2)	3602 (6)	6387 (13)	4767 (5)	78 (3)	C(23)	-1183 (15)	1852 (29)	795 (10)	166 (9)
C(3)	4180 (5)	3838 (11)	5025 (4)	53 (3)	C(24)	1717 (8)	1455 (17)	1106 (6)	111 (5)
C(4)	3824 (5)	2280 (11)	4837 (4)	49 (2)	C(25)	2163 (11)	27 (22)	1096 (8)	166 (7)
C(5)	4269 (7)	1223 (14)	5299 (5)	71 (3)	C(26)	1667 (9)	2794 (20)	751 (7)	133 (6)
C(6)	2992 (7)	2279 (16)	4719 (5)	80 (4)	C(27)	1884 (7)	4252 (15)	1001 (5)	82 (4)
C(7)	4500 (6)	761 (12)	3387 (4)	65 (3)	C(28)	1713 (13)	5499 (25)	602 (9)	141 (7)
C(8)	4464 (7)	-609 (15)	3074 (5)	97 (4)	C(29)	2762 (14)	4324 (29)	1367 (10)	166 (8)
C(9)	5143 (6)	1739 (12)	3486 (4)	69 (3)	C(30)	1099 (6)	6220 (12)	1960 (4)	63 (3)
C(10)	5006 (6)	3381 (12)	3454 (4)	69 (3)	C(31)	1302 (7)	308 (14)	1631 (5)	81 (4)
C(11)	4411 (8)	3848 (18)	2894 (6)	94 (4)	C(32)	1576 (7)	588 (14)	2204 (5)	83 (4)
C(12)	5777 (9)	4193 (18)	3602 (6)	98 (4)	C(33)	2434 (6)	448 (13)	2558 (4)	75 (3)
C(13)	3474 (5)	5819 (11)	3746 (4)	57 (3)	C(34)	2664 (6)	538 (12)	3131 (4)	63 (3)

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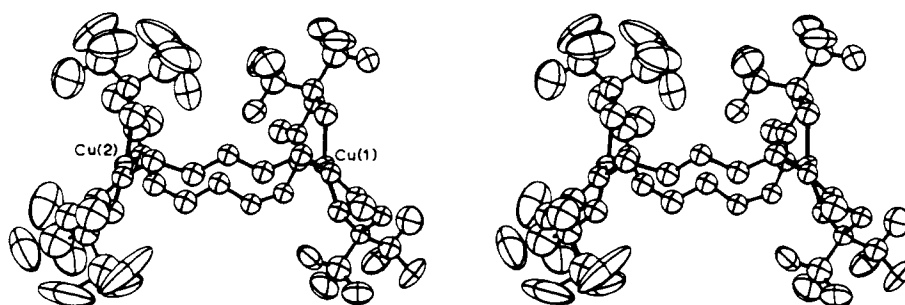

Figure 1. Stereoview of the dinuclear unit. Atoms are plotted as 50% thermal probabilities.

and calculated structure amplitudes, respectively. The neutral atom scattering factors of Cu, F, O, N, and C were taken from Cromer and Waber[9] and those for H from Stewart, Davidson, and Simpson.[10] Anomalous contributions[11] were included for Cu and F atoms. Re-

finement of all 68 nonhydrogen atoms, with isotropic thermal parameters, converged at values of $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.153$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.185$, for a total of 273 variables. When anisotropic thermal parameters were refined for the Cu and F atoms, the total of the variables increased to 403. This model converged at agreement factors $R_1 = 0.106$ and $R_2 = 0.131$.

(9) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.
(10) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(11) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1976**, *53*, 1891.

**Table IV.** Derived Hydrogen Atom Positional ($\times 10^4$) and Thermal Parameters

atom[a]	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H1C(2)	4008	6797	5073	6.78	H1C(15)	2642	6315	2698	4.82
H2C(2)	3436	7087	4489	6.78	H2C(15)	2162	7005	2930	4.82
H3C(2)	3187	6151	4827	6.78	H1C(16)	1181	5374	2487	5.71
H1C(8)	3986	-651	2769	8.40	H2C(16)	1507	5355	2102	5.71
H2C(8)	4863	-560	2983	8.40	H1C(17)	3536	-913	3387	5.46
H3C(8)	4536	-1471	3281	8.40	H2C(17)	3481	-128	3839	5.46
H1C(19)	-132	7156	1926	10.93	H1C(20)	-1255	4681	1013	8.37
H2C(19)	-584	7635	1345	10.93	H2C(20)	-762	4479	741	8.37
H3C(19)	-962	6601	1580	10.93	H1C(26)	1991	2590	606	11.29
H1C(25)	1811	-779	961	13.85	H2C(26)	1154	2862	479	11.29
H2C(25)	2376	204	872	13.85	H1C(30)	874	7013	2056	5.43
H3C(25)	2551	-193	1435	13.85	H2C(30)	1387	6628	1810	5.43
H1C(3)	4715	3770	5145	4.47	H1C(31)	782	36	1467	7.01
H2C(3)	4103	4124	5309	4.47	H2C(31)	1595	-490	1604	7.01
H1C(9)	5544	1525	3825	5.94	H1C(32)	1326	-103	2317	7.06
H2C(9)	5302	1496	3237	5.94	H2C(32)	1424	1567	2238	7.06
H1C(13)	3814	6011	3611	4.90	H1C(33)	2681	1225	2477	6.34
H2C(13)	3371	6728	3866	4.90	H2C(33)	2597	-481	2493	6.34
H1C(14)	2869	4251	3229	5.12	H1C(34)	2623	1551	3209	5.48
H2C(14)	2422	5008	3475	5.12	H2C(34)	2309	-36	3185	5.48

[a] H atoms are numbered according to the atom to which they are bonded; thus H1C(2) is bonded to C(2), etc.

All 40 H atoms were located in a difference Fourier synthesis, at densities ranging from 0.4 to 1.3 e Å^{-3}, and their contributions were included by assuming idealized geometries, C–H = 0.95 Å. Isotropic thermal parameters 10% greater than those of the atom to which they are attached were used, and no attempt was made to refine H atom parameters. Several cycles of refinement, with concomitant idealization of H atom positions, were required before the model converged at $R_1 = 0.087$ and $R_2 = 0.104$ (403 variables, 4029 observations). The largest parameter shift in the final cycle was 0.13 esd, in the y coordinate of C(30). The error in an observation of unit weight is 3.82. A difference Fourier synthesis was essentially featureless; the highest peak, 1.0 (1) e A^{-3} at (0.187, 0.427, 0.151), was of no chemical significance. A statistical analysis of R_2 in terms of $|F_o|$, $\lambda^{-1} \sin \theta$, and diffractometer setting angles χ and ϕ showed no unusual trends. There was no evidence for secondary extinction. Atomic positional and thermal parameters are given in Table III, while derived values for the H atoms are listed in Table IV. A listing of structure amplitudes, as $10|F_o|$ vs. $10|F_c|$, in electrons, is available.[12]

Structure Description

The analysis shows that the Cu(II) complex with $n = 5$ is of structural type **2**, with a dinuclear composition in the solid state. The atom numbering scheme used is given in the line drawing **3** for the Cu, O, N, and C atoms; F atoms are num-

3
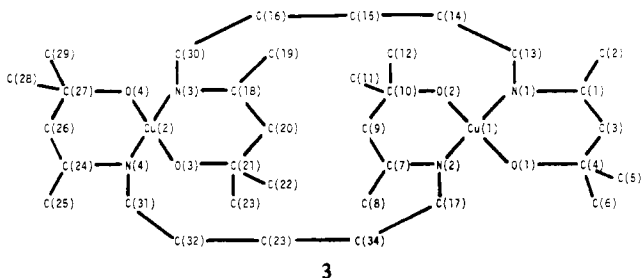
bered from 1 to 24, in the order of their attachment to C(5), C(6), C(11), C(12), C(22), C(23), C(28), and C(29). An ORTEP stereo illustration, with H atoms omitted, is presented as Figure 1. The crystals are built up from discrete, dinuclear units. The closest intermolecular approaches are 2.55 Å, between F(11) and H2C(8), and 2.64 Å, between F(17) and H3C(2). A selection of intramolecular dimensions is given in Table V.

Each Cu atom is coordinated in a distorted square-planar geometry to trans imino nitrogen and alkoxo oxygen donor atoms of separate, quadridentate ligands. The extent of the
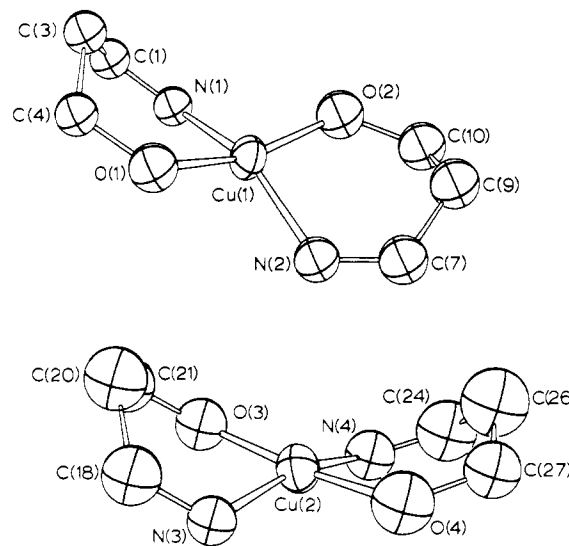
Figure 2. The inner coordination spheres of the Cu atoms.

distortions is apparent from the weighted least-squares plane calculations, Table VI,[12] and from the angles subtended at the Cu atoms. The geometry at Cu(1) is the more distorted, for the angle subtended by the trans O atoms is 161.0 (3)°, compared to a value of 172.9 (4)° at Cu(2); similarly, the trans N atoms subtend an angle of 156.6 (3)° at Cu(1) and 164.8 (4)° at Cu(2). The inner-sphere coordination geometries are illustrated in Figure 2, and the tetrahedral nature of these distortions is apparent. The six-membered chelate rings formed by the ligands adopt distorted boat conformations, as was observed in the Ni species.[2] Torsional angles for these rings, given in Table VII,[12] are far from the values 0, 60, -60, 0, 60, and -60° expected for a regular boat. Much of the "flattening" of the boats occurs at the imino nitrogen atoms as a result of the sp^2 hybridization. The geometries of six-membered rings containing a C=N bond have been discussed in some detail by Hodgson and co-workers, and similar distortions were observed.[13,14]

The coordination planes at the metal atoms are inclined at an angle of 28.2° to each other and are linked by chains of

(12) Supplementary material.

(13) Hodgson, D. J.; Kozlowski, D. L. *J. Chem. Soc., Dalton Trans.* **1975**, 55.

(14) Wilson, R. B.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1976**, *15*, 1712 and references therein.

Table V. Intramolecular Dimensions

Bond Lengths, Å

Cu(1)–O(1)	1.876 (7)	Cu(2)–O(3)	1.857 (7)
Cu(1)–O(2)	1.866 (7)	Cu(2)–O(4)	1.858 (9)
Cu(1)–N(1)	2.015 (8)	Cu(2)–N(3)	1.997 (8)
Cu(1)–N(2)	2.030 (8)	Cu(2)–N(4)	2.012 (9)
N(1)–C(1)	1.28 (1)	N(3)–C(18)	1.27 (1)
C(1)–C(2)	1.47 (1)	C(18)–C(19)	1.51 (2)
C(1)–C(3)	1.49 (1)	C(18)–C(20)	1.50 (2)
C(3)–C(4)	1.55 (1)	C(20)–C(21)	1.51 (2)
C(4)–O(1)	1.35 (1)	C(21)–C(22)	1.58 (2)
C(4)–C(5)	1.54 (1)	C(21)–C(23)	1.49 (2)
C(4)–C(6)	1.53 (2)	C(21)–O(3)	1.34 (1)
N(2)–C(7)	1.27 (1)	N(4)–C(24)	1.25 (2)
C(7)–C(8)	1.52 (2)	C(24)–C(25)	1.58 (2)
C(7)–C(9)	1.47 (1)	C(24)–C(26)	1.57 (2)
C(9)–C(10)	1.50 (1)	C(26)–C(27)	1.46 (2)
C(10)–C(11)	1.55 (2)	C(27)–C(28)	1.54 (2)
C(10)–C(12)	1.57 (2)	C(27)–C(29)	1.56 (2)
C(10)–O(2)	1.38 (1)	C(27)–O(4)	1.35 (1)
N(1)–C(13)	1.46 (1)	N(4)–C(31)	1.40 (1)
C(13)–C(14)	1.49 (1)	C(31)–C(32)	1.52 (2)
C(14)–C(15)	1.51 (1)	C(32)–C(33)	1.52 (1)
C(15)–C(16)	1.51 (1)	C(33)–C(34)	1.51 (1)
C(16)–C(30)	1.59 (1)	C(34)–C(17)	1.51 (1)
C(30)–N(3)	1.45 (1)	C(17)–N(2)	1.44 (1)
mean C–F	1.32 (1)	mean C–F	1.34 (2)

Bond Angles, Deg

O(1)–Cu(1)–O(2)	161.0 (3)	O(3)–Cu(2)–O(4)	172.9 (4)
N(1)–Cu(1)–N(2)	156.6 (3)	N(3)–Cu(2)–N(4)	164.8 (4)
O(1)–Cu(1)–N(1)	92.7 (3)	O(3)–Cu(2)–N(3)	91.4 (3)
N(1)–Cu(1)–O(2)	88.8 (3)	N(3)–Cu(2)–O(4)	87.8 (4)
O(2)–Cu(1)–N(2)	96.2 (3)	O(4)–Cu(2)–N(4)	92.9 (4)
N(2)–Cu(1)–O(1)	89.9 (3)	N(4)–Cu(2)–O(3)	89.7 (4)
Cu(1)–N(1)–C(1)	123.0 (7)	Cu(2)–N(3)–C(18)	121.8 (8)
Cu(1)–N(1)–C(13)	114.1 (6)	Cu(2)–N(3)–C(30)	116.1 (6)
C(13)–N(1)–C(1)	122.4 (8)	C(18)–N(3)–C(30)	121.7 (9)
N(1)–C(1)–C(2)	125.6 (9)	N(3)–C(18)–C(19)	125 (1)
N(1)–C(1)–C(3)	118.1 (9)	N(3)–C(18)–C(20)	117 (1)
C(2)–C(1)–C(3)	116.2 (9)	C(19)–C(18)–C(20)	118 (1)
C(1)–C(3)–C(4)	115.0 (8)	C(18)–C(20)–C(21)	117 (1)
C(3)–C(4)–O(1)	114.7 (8)	C(20)–C(21)–O(3)	115 (1)
C(3)–C(4)–C(5)	106.1 (8)	C(20)–C(21)–C(22)	107 (1)
O(1)–C(4)–C(5)	108.1 (8)	C(20)–C(21)–C(23)	109 (1)
C(3)–C(4)–C(6)	110.1 (9)	C(22)–C(21)–C(23)	108 (2)
C(5)–C(4)–C(6)	107.6 (9)	C(22)–C(21)–O(3)	109 (1)
C(6)–C(4)–O(1)	110.0 (9)	C(23)–C(21)–O(3)	109 (1)
C(4)–O(1)–Cu(1)	125.6 (6)	C(21)–O(3)–Cu(2)	124.4 (8)
Cu(1)–N(2)–C(7)	122.0 (7)	Cu(2)–N(4)–C(24)	120 (1)
Cu(1)–N(2)–C(17)	115.1 (6)	Cu(2)–N(4)–C(31)	117.8 (8)
C(17)–N(2)–C(7)	122.9 (9)	C(24)–N(4)–C(31)	122 (1)
N(2)–C(7)–C(8)	125 (1)	N(4)–C(24)–C(25)	123 (1)
N(2)–C(7)–C(9)	122 (1)	N(4)–C(24)–C(26)	119 (1)
C(8)–C(7)–C(9)	113 (1)	C(25)–C(24)–C(26)	118 (1)
C(7)–C(9)–C(10)	118 (1)	C(24)–C(26)–C(27)	117 (1)
C(9)–C(10)–O(2)	115 (1)	C(26)–C(27)–C(28)	112 (1)
C(9)–C(10)–C(11)	111 (1)	C(26)–C(27)–C(29)	110 (1)
C(9)–C(10)–C(12)	108 (1)	C(26)–C(27)–O(4)	114 (1)
C(11)–C(10)–O(2)	107 (1)	C(28)–C(27)–C(29)	105 (2)
C(11)–C(10)–C(12)	108 (1)	C(28)–C(27)–O(4)	107 (1)
C(12)–C(10)–O(2)	106 (1)	C(29)–C(27)–O(4)	109 (1)
C(10)–O(2)–Cu(1)	123.9 (7)	C(27)–O(4)–Cu(2)	126.2 (8)
N(1)–C(13)–C(14)	110.2 (8)	N(4)–C(31)–C(32)	113 (1)
C(13)–C(14)–C(15)	116.7 (9)	C(31)–C(32)–C(33)	115 (1)
C(14)–C(15)–C(16)	109.4 (8)	C(32)–C(33)–C(34)	112.9 (9)
C(15)–C(16)–C(30)	111.7 (9)	C(33)–C(34)–C(17)	116.6 (9)
C(16)–C(30)–N(3)	107.7 (8)	C(34)–C(17)–N(2)	114.5 (9)
Cu(1) mean F–C–F	107 (1)	Cu(2) mean F–C–F	108 (2)
Cu(1) mean C–C–F	112 (1)	Cu(2) mean C–C–F	110 (2)

five C atoms joining the imino nitrogen atoms of the ligands. The large ring structure so formed is 16-membered. The weighted mean C–C bond within the chains is 1.518 (5) Å, and the weighted mean C–C–C angle is 112.6 (3)°. Both values are indistinguishable from those of 1.512 (6) Å and 113.0 (3)° observed previously.[2] The trifluoromethyl groups attached to the chelate rings are undergoing considerable

thermal motion. Weighted mean dimensions for these groups are given in Table V.

Discussion

In our original report[2] of the preparation of this copper complex and its homologues with n = 2–12, we suggested that they were all mononuclear type **1** structures. This conclusion was based on solution measurements of molecular weight by vapor-pressure osmometry in acetonitrile solution (found, 581; calcd for n = 5, 576), but it is clear from the current result that the solution molecular weight is not a reliable guide to the degree of aggregation in the solid state for n = 5 and, in all probability, analogous copper complexes. In contrast, the nickel complex with n = 6 showed good agreement between the solution molecular weight and the dinuclear structure found in the crystal.[2]

There are two possible explanations for this effect. It could be that, in the original formation of the complex, the dinuclear and mononuclear structures were both formed but were fortuitously separated in the subsequent recrystallization procedure. Alternatively, there could be an equilibrium between a dinuclear structure in the crystal and a mononuclear structure in solution.

The first explanation may be rejected, since we have seen no evidence for the existence of two isomeric forms of any of the copper complexes in this study. Samples used for the molecular weight measurement and the crystallographic study had been treated in the same way, and accidental separation into mononuclear and dinuclear forms can be excluded.

The existence of an equilibrium between mononuclear and dinuclear forms is consistent with an observation made in our previous work: that the solution molecular weight is dependent on the choice of solvent. Good agreement with calculated values was found in a polar solvent (CH_3CN), but use of less polar solvents ($CHCl_3$, C_6H_6) gave higher values, suggesting some degree of aggregation. The tendency to form dinuclear units in the solid state is presumably favored by the trans geometry of N_2O_2 ligand atoms around the metal ion which this permits. It is interesting that the dinuclear unit changes in solution to the mononuclear unit (which would be entropy favored) for the Cu^{2+} complex but not for the less labile Ni^{2+}. Further studies are being undertaken to investigate the generality of this effect.

Supplementary Material Available: A listing of structure amplitudes, as $10|F_o|$ vs. $10|F_c|$ in electrons, weighted least-squares planes, and torsional angles for the six-membered rings (13 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Electrochemistry of Dihalobis(α-benzil oximato)ruthenium(III)

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There is much current interest in the chemistry of ruthenium pertaining to the synthesis of new complexes, structure, reactivity and catalysis, intervalence phenomena, and phenomena related to electron transfer and energy transfer. We have