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Fluorinated Alkoxides. 15. Synthesis and Hydrogenation of Iminoalkoxy Complexes of Copper(2+). Influence of Chelate Ring Size on Structure and Magnetic Properties

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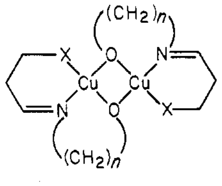
Template condensation of 5,5,5-trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone, $CH_3COCH_2C(CF_3)_2OH$, with a variety of amino alcohols $NH_2(CH_2)_nOH$ ($n = 2$–6) in the presence of Cu^{2+} leads to stable, neutral, iminoalkoxy complexes with a 1:1 metal/ligand ratio for $n = 2$–4 and a 1:2 metal/ligand ratio for $n = 5$ or 6. These are associated into tetranuclear units for $n = 2$, dinuclear units for $n = 3$ or 4, and mononuclear units for $n = 5$ or 6. Magnetic moments are reduced in the dinuclear but not the tetranuclear complexes; this is ascribed to a lack of planarity around the Cu atoms in the latter. Hydrogenation of the above (aminoalkoxy)copper(II) complexes is achieved with $LiAlH_4$; dinuclear structures, all having reduced magnetic moments, are now found with $n = 2$–4, and mononuclear structures are found with $n = 4$–6. Possible structures consistent with observed magnetic and spectroscopic data are discussed.

Introduction

There is considerable interest in the correlation between magnetic properties and structure in dinuclear[1] copper(II) complexes where spin pairing between copper atoms may occur via bridging oxygen atoms. In particular, studies on complexes of tridentate ligands where each copper atom is included in two chelate rings, as in the general structure **1**, show a critical dependence of the degree of interaction upon the size of the ring containing the bridging oxygen atoms.

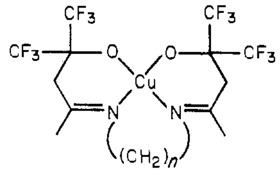


1, X = O or N

Thus, Bertrand and Kelley[2] found that, in the template condensation of acetylacetone with amino alcohols, a planar complex with a substantially reduced magnetic moment was obtained with $n = 3$, whereas the analogous complex with $n = 2$ was nonplanar, was associated into units containing four copper atoms, and was of normal magnetic moment. Curtis and co-workers, in a similar condensation process using acetone, found that the complex with $n = 3$ was planar (with an additional amino alcohol residue incorporated at a fifth, apical, position on copper) and virtually diamagnetic,[3] while the complex with $n = 2$ was nonplanar and paramagnetic.[4] Analogous derivatives incorporating aromatic[5] or pyrrole[6] rings also show very large degrees of coupling between copper atoms when $n = 3$.

From structural studies on numerous examples, it is clear that it is the geometry of the environment around the copper atoms, rather than the electronic properties of the ligands, which determines the degree of coupling, a reduced magnetic moment always being associated with approximate planarity. The geometry may be conveniently expressed either in terms of the departure from planarity toward, in the limit, tetrahedral coordination around copper,[7] or in terms of the Cu–O–Cu bridging angle.[8]

We have recently demonstrated[9,10] that the fluorinated keto alcohol $CH_3COCH_2(CF_3)_2OH$ (hexafluorodiacetone alcohol, HFDA) will readily undergo template condensation with a variety of diamines to give copper(II) complexes of structure **2**.



2, $n = 2$–12

It was reasonable to suppose that the use of amino alcohols in place of diamines in the condensation would result in the formation of dinuclear copper complexes of type **1** in which the value of n could be varied by choice of a suitable amino alcohol. Furthermore, since we have shown that fluorinated imino complexes of copper may readily be hydrogenated to the corresponding amino derivatives,[11] there would be an opportunity to study the effect on the ring geometry and magnetic properties of changing the hybridization at nitrogen from sp^2 to sp^3.

This paper describes the synthesis and properties of iminoalkoxy complexes of copper having $n = 2$–6 and their hydrogenation to the corresponding amino complexes.

Experimental Section

General Methods. Infrared spectra were recorded on a Perkin-Elmer 621 instrument, visible–UV spectra on Cary 14 and 118 spectrometers, and mass spectra on a Varian MAT 311A instrument, and molecular

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Table I. Analytical Data and Mass Spectra

compd	mol formula	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	mp, °C	parent ion *m/e*[a]
3a	$C_{16}H_{18}Cu_2F_{12}N_2O_4$	29.2	29.1	2.74	2.75	4.26	4.12	220-235 dec	656[c]
3b	$C_{18}H_{22}Cu_2F_{12}N_2O_4$	31.5	31.5	3.21	3.18	4.09	4.07	220-230 dec	684[d]
3c	$C_{20}H_{26}Cu_2F_{12}N_2O_4$	33.7	33.5	3.65	3.48	3.93	3.89	214-220 dec	712[e]
4a	$C_{22}H_{32}CuF_{12}N_2O_4$	38.9	39.1	4.71	4.82	4.12	4.24	138-140	679
4b	$C_{24}H_{36}CuF_{12}N_2O_4$	40.7	40.7	5.09	5.10	3.96	3.94	82-85	707
5	$C_{18}H_{24}CuF_{12}N_2O_4$	34.6	34.6	3.85	3.80	4.49	4.51	109-110	623
6a	$C_{18}H_{28}Cu_2F_{12}N_2O_5$[b]	30.6	30.3	3.99	3.84	3.96	3.90	205-210 dec	660
6b	$C_{18}H_{26}Cu_2F_{12}N_2O_4$	31.4	31.4	3.77	3.57	4.06	4.13	215-225 dec	688
6c	$C_{20}H_{30}Cu_2F_{12}N_2O_4$	33.5	33.3	4.22	4.13	3.91	3.82	205-210 dec	716
7a	$C_{20}H_{32}CuF_{12}N_2O_4$	36.6	36.6	4.88	4.71	4.27	4.35	124-125	655
7b	$C_{22}H_{36}CuF_{12}N_2O_4$	38.6	38.7	5.27	5.15	4.10	4.14	108-109	683
7c	$C_{24}H_{40}CuF_{12}N_2O_4$	40.5	40.4	5.62	5.49	3.94	3.90	100-102	711

[a] Mass numbers for the peak containing ^{63}Cu or $^{63}Cu_2$. [b] Crystals contain 1 mol of solvent ethanol/mol of complex. [c] Solution mol wt: found, 1525; calcd for $C_{32}H_{36}Cu_4F_{24}N_4O_8$, 1315. [d] Solution mol wt: found, 753; calcd for $C_{18}H_{22}Cu_2F_{12}N_2O_4$, 684. [e] Solution mol wt: found, 690; calcd for $C_{20}H_{26}Cu_2F_{12}N_2O_4$, 713.

Table II. Infrared[a] and Visible Spectra

compd	ν(O-H), cm^{-1}	ν(N-H), cm^{-1}	ν(C=N), cm^{-1}	vis band max, nm (ϵ)	solvent[b]
3a			1676 s[c]	640 (178)	d
3b			1649 s	356 (4830), 600 (147)	d
3c			1638 s	356 (4170), 590 (163)	d
4a	3420 m		1662 s	572 (124)	m
4b	3410 m		1653 s	550 (145)	d
5			1672 s, 1650 m	588 (86)	d
6a		3140 m, 3180 m		348 (610), 659 (175)	d
6b		3175 m		369 (1715), 602 (150)	d
6c		3200 m		357 (1830), 628 (140)	d
7a	3400 m	3150 m, 3200 m		595 (100)	m
7b	3350 m	3245 m		520 (118)	d
7c	3345 m	3165 m		529 (131)	d

[a] As Nujol mulls. All compounds also showed strong ν(C-F) absorptions in the region 1150-1200 cm^{-1}. [b] d = dichloromethane, m = methanol. [c] s = strong, m = medium.

Table III. Magnetic Susceptibilities

compd	*g*	$\lvert 2J \rvert$, cm^{-1}	$10^6\chi_g$(300 K), cgsu	μ_{eff}(300 K),[a] μ_B
3a			3.59	1.78
3b	2.20	>600	0.03	0.57
3c	2.20	>600	−0.21	0.38
4a			1.02	1.57
4b			0.83	1.51
5			1.23	1.99
6a	2.16	222	2.85	1.62
6b	2.50	352	2.41	1.54
6c	2.06	492	0.78	1.04
7a			1.25	1.67
7b			1.10	1.63
7c			1.03	1.63

[a] Calculated per Cu atom.

weights were determined with a Hewlett-Packard 301A vapor-pressure osmometer. Microanalyses were performed by Malissa-Reuter Laboratories, West Germany; all analytical data are in Table I.

Variable-temperature magnetic susceptibilities were determined by the Faraday method by Dr. A. B. P. Lever, York University; data are summarized in Table III. Diamagnetic corrections were made with the Pascal constants of Figgis and Lewis.[12]

For compounds showing reduced magnetic moments, susceptibilities were fitted to the Bleaney-Bowers equation[13] (eq 1), where χ_A

$$\chi_A = \frac{N\beta^2 g^2}{3kT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} + N\alpha \qquad (1)$$

represents the molar susceptibility per atom of copper, regardless of the degree of aggregation of the complex, and the other symbols have their usual significance. The temperature-independent paramagnetism $N\alpha$, was taken as 60×10^{-6} cgsu per Cu atom. Values of g and J were calculated by minimizing the function

$$V = \sum[(\chi_{obsd} - \chi_{calcd})T]^2$$

over the range of observation, where χ_{calcd} values are calculated from eq 1 and χ_{obsd} are observed values.

5,5,5-Trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone (HFDA) was prepared by the condensation of hexafluoroacetone with acetone as described previously.[9] Amino alcohols were commercial samples (Aldrich, Fluka) and were used without further purification.

Imino Complexes. In a typical preparation, anhydrous copper(II) chloride (1.34 g, 10 mmol) in warm ethanol was added to 2-aminoethanol (0.61 g, 10 mmol) followed by HFDA (2.24 g, 10 mmol) and KOH (1.12 g, 20 mmol), also in ethanol. The solution was heated under reflux for 3 h and cooled to 0 °C, and KCl was removed by filtration. Concentration of the resulting blue solution yielded the imino complex **3a** collected as blue plates from ethanol.

The same method, using the appropriate amino alcohol resulted in the following: **3b**, deep purple plates from ethanol; **3c**, purple plates from ethanol; **4a**, purple crystals from ether/hexane; **4b**, purple crystals from ether/hexane. Use of (2-methoxyethyl)amine gave **5**, collected as blue crystals from acetone.

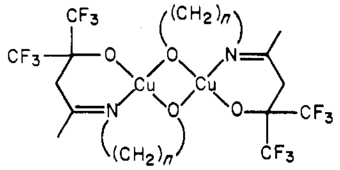
A 1:1 metal/ligand ratio was found suitable in each of the above preparations, although complexes **4a**, **4b**, and **5** have a 1:2 ratio. No evidence of the production of dinuclear type **3** complexes was found with the long-chain amino alcohols or with (2-methoxyethyl)amine.

Reduction of Amino Complexes. In a typical reduction, **3a**, the imino complex of 2-aminoethanol, in anhydrous ether, was added to $LiAlH_4$ (1:3 molar ratio) in ether. Immediate reaction occurred to precipitate a yellow solid. After addition of **3a** was complete, the suspension was stirred for 1 h and the excess hydride destroyed by careful addition of water. The resulting black precipitate was stirred with a continuous flow of air through the water/ether solution for 2 h, when a blue coloration appeared in the ethereal layer. Ether extraction and aeration were continued until no color remained in the aqueous layer. Evaporation of the ethereal layer gave the aminocopper complex **6a**, collected as blue crystals from ethanol.

The same method was successful with other imino complexes: **3b** gave **6b** (green crystals from ethanol), **3c** gave the mononuclear amino complex **7a** (blue crystals from ethanol), **4a** gave **7a** (violet crystals from ether/hexane), and **4b** gave **7c** (purple crystals from ether/hexane). The reduced dinuclear complex of 4-amino-1-butanol, **6c**, was obtained from the mononuclear complex **7a** by the addition of KOH and $CuCl_2$ to **7a** in ethanolic solution (collected as green crystals from ethanol).

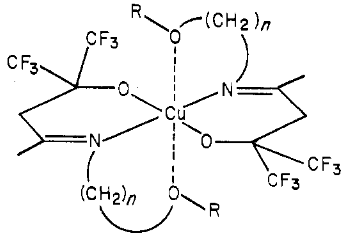
Discussion

The imino complexes of copper prepared in this study fall into two categories. With the shorter chain amino alcohols (n = 2–4) an oxygen-bridged complex of type **3** is formed, the metal/ligand ratio being 1:1.



3a, n = 2
b, n = 3
c, n = 4

With values of n above 4, the complexes have a metal/ligand ratio of 1:2. Infrared spectra (Table II) show a similar imino stretching frequency to the type **3** complexes, but OH is now present. A pseudooctahedral environment for copper, as in structure **4**, may be suggested, but there is no direct evidence for the manner of coordination of the hydroxyl group.



4a, n = 5, R = H
b, n = 6, R = H
5, n = 2, R = CH_3

The change in structural type on increasing n above 4 is not surprising, since we have previously noted the tendency to avoid the formation of chelate rings in excess of seven members for both nickel[10] and copper[14] in type **2** complexes of this type.

A neutral complex with a 1:2 metal/ligand ratio **5**, was also obtained by the condensation of HFDA with (2-methoxyethyl)amine in the presence of Cu^{2+}. We assume this to have a similar structure, with the methoxy group coordinated singly or not at all. Since an ethereal oxygen atom is a weaker donor than an ionized alkoxy oxygen atom, a bridging linkage involving coordination of two copper atoms would not be expected here.

The molecular complexity of each complex was established by mass spectral measurements (Table I). For the dinuclear complexes **3**, the highest mass peak corresponded in each case to the dinuclear structure, with a more intense peak present corresponding to a mononuclear fragment at half this value. Solution molecular weights (osmometric in benzene) showed values close to those required for dinuclear units for **3b** and **3c** but suggested association into a tetranuclear unit for **3a**. Although solution measurements of molecular weight are always subject to the reservation that a change in aggregation may occur between the solid and the solution, we feel that this result is significant, since it has been shown that the copper complex formed by the condensation of acetylacetone with ethanolamine, tetranuclear in the solid state,[2] is also tetranuclear in benzene solution.[15]

As would be expected, such structural differences between imino complexes of different ring size led to radically different magnetic properties, depending on the degree of copper–copper coupling. Magnetic susceptibility was measured over the range from 77 K to the point where significant decomposition became apparent, usually 350–400 K, and results are shown in Figure 1.

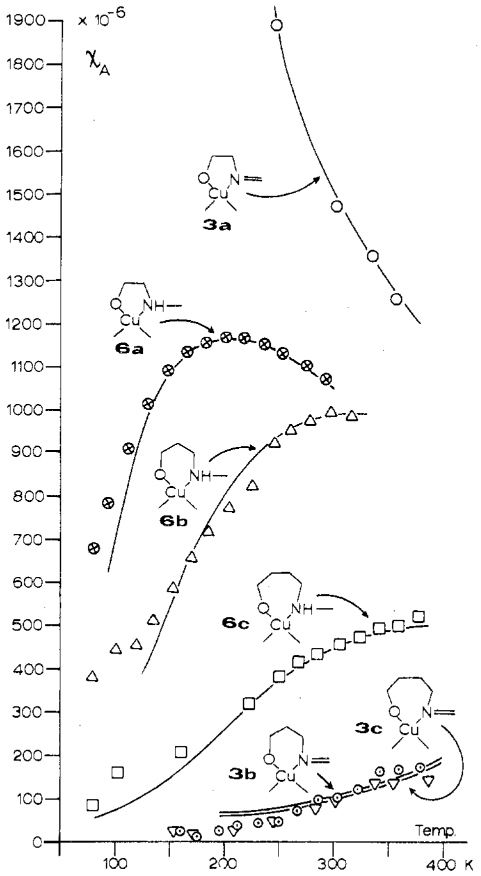
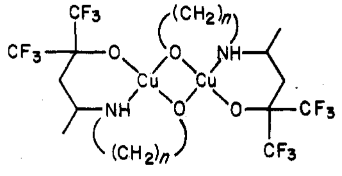


Figure 1. Susceptibilities of imino- and aminoalkoxy complexes over the temperature range 77–400 K. Solid lines are calculated by eq 1 and values of J and g in Table III.

The aminoethanol adduct **3a** showed entirely normal magnetic properties. The room-temperature magnetic moment, 1.78 μ_B, was normal for Cu^{2+} and a plot of $1/\chi_A$ against T was linear down to 77 K, giving by extrapolation a Weiss constant Θ = 24 K (experimental values of χ_A for this compound below 240 K are not shown in Figure 1). In sharp contrast, the complexes **3b** and **3c**, where n = 3 or 4, were virtually diamagnetic. Uncertainties in the very small experimental susceptibility values were too large to permit accurate fitting to eq 1, but it could be estimated that the singlet–triplet splitting, $|2J|$, was in excess of 600 cm^{-1}.

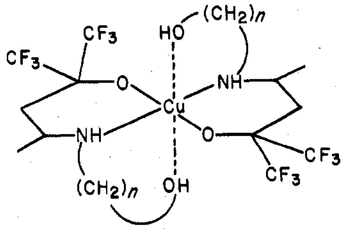
The molecular weights and magnetic data on these iminoalkoxy complexes are entirely consistent with earlier results and may be rationalized in terms of a nonplanar structure, aggregated into a tetranuclear complex with a Cu_4O_4 "cubane" core, for the aminoethanol adduct. The dramatic reduction in magnetic moment on increasing the size of the ring containing the bridging oxygen from five to six members is associated with the now permitted planarity of the coordination plane containing the copper atoms. To the best of our knowledge, however, this is the first occasion on which it has been observed that this effect persists when the ring size is increased to seven members. Clearly, the planar geometry is a favorable arrangement which will dominate in determining the conformation of both six- and seven-membered rings.

Hydrogenation of the three dinuclear complexes proceeded smoothly with lithium aluminum hydride. As we have previously noted,[11] the intermediate in this process is a copper(I) complex, not isolated, which is converted to the amino complex of copper(II) by air oxidation. However, there is no evidence that the dinuclear structure of the complex remains intact throughout this process. Although the imino complexes of the five- and six-membered rings, **3a** and **3b**, yielded the corresponding dinuclear amino complexes **6a** and **6b**, the seven-membered ring complex, **3c**, did not directly give **6c**.



6a, $n = 2$
b, $n = 3$
c, $n = 4$

Instead, 1:2 metal/ligand mononuclear **7a** was produced, analogous to those given by hydrogenation of the mononuclear complexes **4a** and **4b**. As with imino complexes, the mode of attachment of the ligand and coordination number of the copper ion in type **7** complexes cannot be assigned with certainty.



7a, $n = 4$
b, $n = 5$
c, $n = 6$

Treatment of **7a** with $CuCl_2$ in the presence of KOH in ethanolic solution led to rearrangement to the dinuclear complex **6c**; this is the only example among the ligands studied in this series for which we have been able to isolate stable complexes in both the mononuclear and the dinuclear stoichiometry.

As with the imino complexes, the dinuclear structures of the amino complexes **6** were evident in the mass spectra, but in this case measurements of solution molecular weights were inconclusive because of solubility limitations.

Their magnetic properties (Figure 1) showed a considerable difference from those of the imino complexes. In all three cases, considerable antiferromagnetic interactions were apparent. Values of $|2J|$ were 222, 352, and 492 cm^{-1} for **6a**, **6b**, and **6c**, respectively, indicating that the degree of copper–copper coupling via bridging oxygen was increasing as the ring size increased. These numerical values were obtained by fitting the experimental points to eq 1; calculated curves are shown in Figure 1. Agreement was optimized by varying both g and J and was poorest for **6b**, for which the curve shown has g set at the rather high value of 2.50 (Table III). Other workers have commented on the occasional difficulty of fitting experimental data to this equation and have suggested that this may be due to interactions between dinuclear units[16] or possibly to paramagnetic impurities.[17]

Differences between the degree of coupling in imino and amino complexes may be rationalized in terms of their probable structures. Hydrogenation of the imine formed from aminoethanol, by removing the requirement that there must be planar geometry around nitrogen, permits approximate coplanarity of the coordination around each copper ion and, hence, coupling, even when each bridging oxygen is part of a five-membered ring. However, for the larger ring sizes, hydrogenation brings about a decrease in coupling from the virtually diamagnetic imino complexes. This may be ascribed to the presence of imino bonds coplanar with the coordination plane of the copper ions which, by conjugation, may increase the degree of copper–oxygen–copper coupling via the π system, whereas conjugation is absent in the amino complexes. In other words, we suggest that, provided the ring size permits coplanarity across the oxygen bridges, a complex with unsaturation in the chelate ring will give greater coupling than one without.

The progressive increase in coupling associated with the increase in ring size in the amino complexes presumably reflects small changes in the bond angles in structures of basically similar geometry; many previous studies have shown the sensitivity of magnetic moments to such small variations. It is hoped that confirmation of these suggestions will result from structural studies now in progress.

Visible spectra of the complexes are given in Table II. For each dinuclear complex, there is an absorption associated with a d–d transition at 590–650 nm, having an extinction coefficient in the region 140–180. However, each of the five complexes where significant antiferromagnetic coupling is present also shows a charge-transfer band at 348–370 nm, an effect which has been noted by previous workers.[18] Extinction coefficients of these bands are significantly greater, increasing to a maximum of over 4000 in the two complexes **3b** and **3c**, where the greatest reduction of magnetic moment is observed. It would appear that the strict planarity of the central core of the dinuclear complexes, essential for reduction of the magnetic moment in the solid state, is preserved in solution, suggesting that it is an essential feature of the bonding at the metal atoms, rather than in artifact of packing forces in the solid state.

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Registry No. **3a**, 71328-88-6; **3b**, 71328-82-0; **3c**, 71328-83-1; **4a**, 71328-84-2; **4b**, 71328-85-3; **5**, 71328-86-4; **6a**, 71328-77-3; **6b**, 71328-78-4; **6c**, 71328-79-5; **7a**, 71328-80-8; **7b**, 71328-81-9; **7c**, 71328-75-1; 2-aminoethanol, 141-43-5; 3-aminopropanol, 156-87-6; 4-aminobutanol, 13325-10-5; 5-aminopentanol, 2508-29-4; 6-aminohexanol, 4048-33-3; (2-methoxyethyl)amine, 109-85-3; HFDA, 10487-10-2.

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