DALTON
FULL PAPER

Ligand oxidation in N_4 tetradentate Schiff base complexes catalyzed by copper(II) hexafluoroacetylacetonate dihydrate: reaction details and structures

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The ethylene unit connecting the two anilino nitrogen atoms of the copper or nickel complexes of 7,8,15,16,17,18-hexahydro-dibenzo[*e,m*][1,4,8,11]tetraazacyclotetradecine [H_2(2,2 mac)] and 8,9,16,17,18,19-hexahydro-7*H*-dibenzo[*e,n*][1,4,8,12]tetraazacyclopentaadecine [H_2(3,2 mac)], *i.e.* M(2,2 mac) and M(3,2 mac), are oxidized in chloroform at room temperature under atmospheric conditions in the presence of $Cu(hfa)_2{\cdot}(H_2O)_2$ to the oxamide ($N–CH_2–CH_2–N–$ to $N–CO–CO–N–$). If $Cu(hfa)_2{\cdot}(H_2O)_2$ is present in stoichiometric amounts the isolated product of the reaction is the dinuclear complex, M(3,2 oxomac)$Cu(hfa)_2$. The dinuclear complex can also be prepared by direct reaction of M(3,2 oxomac) (prepared by another method) with $Cu(hfa)_2{\cdot}(H_2O)_2$. The dinucleation reaction of M(3,2 oxomac) with $M(hfa)_2$ is quite general but the ligand oxidation of M(3,2 mac) is specific for $Cu(hfa)_2{\cdot}(H_2O)_2$. Reaction of Cu(3,2 mac) with Hhfa or H_2(3,2 mac) with $Cu(hfa)_2{\cdot}(H_2O)_2$ results not in oxidation of the macrocycle but in protonation to give $Cu\{H_2(3,2\ mac)\}(hfa)_2$. The oxidation of Cu(3,2 mac) in an $^{18}O_2$ atmosphere does not result in a significant incorporation of ^{18}O. However, nearly quantitative incorporation of ^{18}O is achieved when the reaction is carried out under air in the presence of $H_2{}^{18}O$. The structures of Cu(3,2 mac), Cu(3,2 oxomac), Cu(3,2 oxomac) $Cu(hfa)_2$ and $Cu\{H_2(3,2\ mac)\}(hfa)_2$ are reported.

Introduction

Recent work in this laboratory has focused on copper(II), nickel(II), and iron(III) complexes with the Schiff bases derived from *o*-aminobenzaldehyde (Chart 1).[1] These ligands are tetradentate, diprotic, and favor square planar geometry as do salen and the porphyrins but exhibit unique structures, electronic properties, and reactivity in their complexes. An example of the latter is the oxidation of the ethylene unit bridging the anilino nitrogen atoms. Studies of ligand oxidation may lead to a greater understanding of the role that metal complexes in general and oxidative enzymes in particular play in the oxidation of substrates.

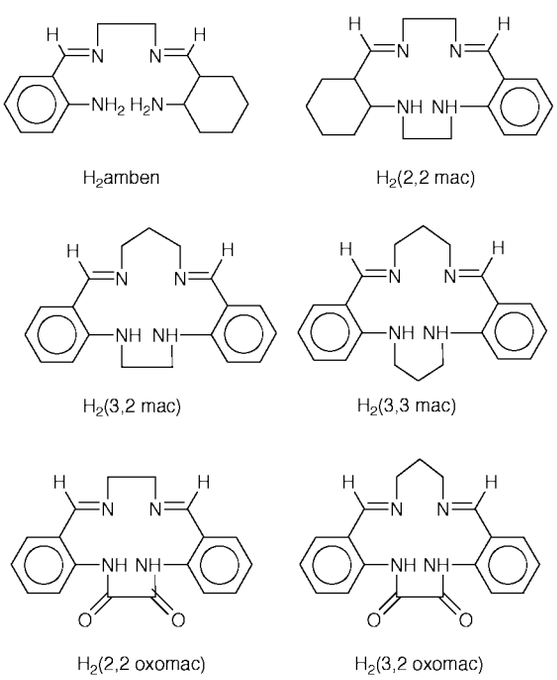
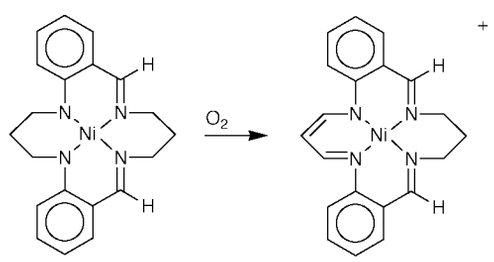


Chart 1

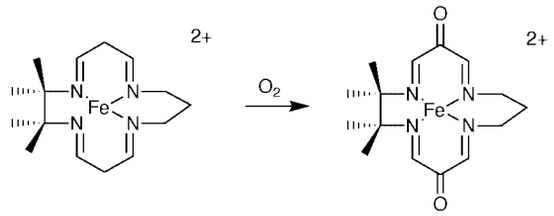
The most extensively studied type of ligand oxidation is ligand dehydrogenation in divalent metal complexes.[2] The reactions of cobalt(II), nickel(II), and copper(II) complexes of H_2(3,3 mac) and H_2(2,3 mac) with dioxygen and halogens have been investigated [Scheme 1, example shown is for nickel(3,3 mac)].



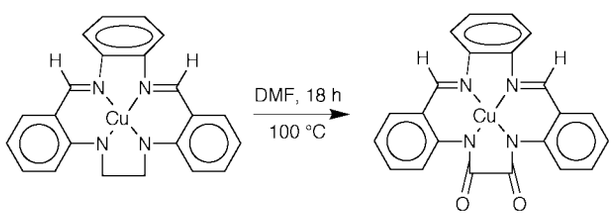
Scheme 1

The literature reaction mechanisms begin with a one-electron oxidation of the metal resulting in the formation of an M^{3+} complex, with subsequent ligand-to-metal electron transfer, deprotonations, and abstraction of the second electron to give the observed product.

Less information is available about the process of ligand oxygenation, *i.e.* the oxidation of carbon to a carbonyl group (Scheme 2). In most cases reactivity was observed for macrocycles containing the β-diimine moiety.[3] The suggested mechanism involves the formation of an α-carbon radical and its subsequent reaction with O_2 or the product of its partial reduction—the HO_2 radical. Ligand oxygenation was also observed[4] for the iron(III) and copper(II) complexes of a ligand



Scheme 2



Scheme 3

similar to the present example (Scheme 3). However, this reaction required prolonged refluxing of the starting complex in DMF and was not catalyzed. The unsupported mechanism suggested the formation of a radical and its subsequent reaction with dioxygen. Ligand oxidation is also one of the factors responsible for autoxidation of transition metal dioxygen carriers.[5]

In the present paper the oxidation of M(3,2 mac) (M = Cu or Ni) to M(3,2 oxomac) under ambient conditions which is catalyzed by copper(II) hexafluoroacetylacetonate dihydrate, ($Cu(hfa)_2 \cdot 2H_2O$), is described. ^{18}O labelling experiments indicate that the oxidizing agent (dioxygen) in this reaction is different than the oxygen transfer agent (water). The structures of Cu(3,2 mac), Cu(3,2 oxomac), Cu(3,2 oxomac)$Cu(hfa)_2$ and $Cu\{H_2(3,2\ mac)\}(hfa)_2$ are presented. The overall changes in the conformation of the starting complex are greater on protonation than on oxidation.

Experimental

General

UV and IR spectra were obtained on Perkin-Elmer Lambda 4 and 1750-FTIR spectrophotometers respectively. Faraday measurements were performed as described previously.[6] Mass spectra (electrospray technique) were performed by Mass Consortium (San Diego, CA). Elemental analyses were performed by MHW Laboratories (Phoenix, AZ). Chloroform was stored in the dark since it was found that Cu(3,2 mac) oxidizes faster in chloroform that has been subjected to light for a substantial period of time before the preparation of the solution.

M(3,2 mac) (M = Cu or Ni). Ni(3,2 mac) was synthesized by the literature procedure.[7] Cu(3,2 mac) was synthesized from the reaction of copper methoxide and free ligand by the method described earlier [1a] with 91% yield. The crystals of Cu(3,2 mac) for X-ray crystallography were obtained from acetone.

M(3,2 oxomac) (M = Cu or Ni). Authentic samples of these complexes were synthesized by the literature procedure.[8] Single crystals of Cu(3,2 oxomac) for X-ray crystallography were obtained from DMF–methanol.

Cu(3,2 oxomac)–$Cu(hfa)_2$. *Method A. Synthesis from Cu(3,2 mac).* Chloroform solutions of Cu(3,2 mac) (34.1 mg, 0.093 mmol, 5.4 ml) and $Cu(hfa)_2 \cdot 2H_2O$ (48.0 mg, 0.093 mmol, 3.6 ml) were mixed and left to stand for one day. The green precipitate, which began forming in 30 minutes, was filtered the next day to yield 41.5 mg (51%) of the product. The crystals of Cu(3,2 oxomac)$Cu(hfa)_2$ for X-ray structure determination were obtained by recrystallization of the above material from ethanol. Anal. Calc. for $C_{29}H_{18}N_4O_6Cu_2F_{12}$: C, 39.86; H, 2.06; N, 6.41. Found: C, 40.04; H, 1.78; N, 6.42%. ν_{max} (cm^{-1}): 1647s, 1606s, 1588m, 1556s, 1528m, 1487m, 1465m, 1419w, 1352m, 1256s, 1199s, 1148s, 1087m, 924w, 795m, 762m, 743w, 670m, 589m.

Method B. In the presence of $^{18}O_2$. A side armed Erlenmeyer flask containing Cu(3,2 mac) (75.3 mg, 0.20 mmol) and $Cu(hfa)_2 \cdot 2H_2O$ (105.6 mg, 0.21 mmol) was equipped with a rubber septum and a balloon on the side arm. The flask was deaerated on a Schlenk line and deaerated chloroform (20 ml) was transferred into the flask. The flask containing the reaction mixture was pressurized (indicated by balloon), evacuated, and repressurized with $^{18}O_2$ (Isotec). The precipitate of Cu(3,2 oxomac)-$Cu(hfa)_2$ was removed by filtration after six hours. The solid was chromatographed as described below to obtain Cu(3,2 oxo mac) for MS analysis.

Method C. In the presence of $H_2{}^{18}O$. $H_2{}^{18}O$ (0.250 g, Aldrich) was added to a mechanically stirred chloroform solution (15 ml) of Cu(3,2 mac) (75.3 mg, 0.20 mmol) (water saturated the chloroform forming a drop). A chloroform (5 ml) solution of $Cu(hfa)_2 \cdot 2H_2O$ (101.9 mg, 0.20 mmol) was added to this mixture. The green precipitate (42.6 mg) of Cu(3,2 oxomac)-$Cu(hfa)_2$ was removed by filtration after nine hours. The solid was chromatographed as described below to obtain Cu(3,2 oxomac) for MS analysis.

Method D. Synthesis from Cu(3,2 oxomac). Cu(3,2 oxomac) (47.5 mg, 0.12 mmol) was stirred in chloroform (50 ml) overnight to allow the complex to completely dissolve. A solution of $Cu(hfa)_2 \cdot 2H_2O$ (61.9 mg, 0.12 mmol) in chloroform (10 ml) was added. A green precipitate formed immediately and was filtered off to yield 84.9 mg (81%) of the product. ν_{max} (cm^{-1}): 1646s, 1606s, 1585m, 1554s, 1527s, 1484m, 1464m, 1416w, 1353m, 1261s, 1204s, 1148s, 1088m, 1052w, 980w, 945w, 923m, 795m, 762m, 743w, 670m, 589m.

Ni(3,2 oxomac)$Cu(hfa)_2$. Chloroform solutions of Ni(3,2 mac) (39.4 mg, 0.11 mmol) and $Cu(hfa)_2 \cdot 2H_2O$ (56.6 mg, 0.11 mmol, 4.5 ml) were mixed in chloroform. The precipitate was filtered the next day to yield 27.7 mg (29%) of product. Anal. Calc. for $C_{29}H_{18}N_4O_6CuNiF_{12}$: C, 40.08; H, 2.07; N, 6.45. Found: C, 40.19; H, 1.85; N, 6.55%. ν_{max} (cm^{-1}): 1646s, 1613s, 1591m, 1554m, 1525m, 1486s, 1351m, 1325m, 1259s, 1204s, 1147s, 1097m, 950w, 931w, 795m, 761m, 673m, 588m, 528w, 460w.

Ni(3,2 oxomac)$Ni(hfa)_2$. A chloroform solution (40 ml) of Ni(3,2 oxomac) (49.0 mg, 0.13 mmol) was mixed with an ethanol solution (4 ml) of $Ni(hfa)_2 \cdot 2H_2O$ (64.3 mg, 0.13 mmol). A light brown precipitate immediately formed and was removed by filtration to yield 96.9 mg (86%) of the product. ν_{max} (cm^{-1}): 1646s, 1615s, 1591m, 1569w, 1555m, 1525m, 1488m, 1454w, 1417w, 1351m, 1326m, 1257s, 1201s, 1148s, 1098m, 1054w, 950w, 931w, 812w, 796m, 760m, 674m, 588m, 529w, 459w.

Chromatography of M(3,2 oxomac)M′$(hfa)_2$ (M = Cu or Ni, M′ = Cu or Ni). M(3,2 oxomac)M′$(hfa)_2$ was dissolved in methanol and the solution was passed through a short neutral alumina chromatographic column. A colored component eluted in methanol leaving a faintly colored component near the top of the column. The UV-visible spectrum of the eluate showed no presence of hfa^-. The solvent was removed from the eluate by rotary evaporation to yield M(3,2 oxomac).

Cu$\{H_2(3,2$ mac)$\}(hfa)_2$. *Method I.* A chloroform solution (12 ml) of H_2(3,2 mac) (102.3 mg 0.334 mmol) was mixed with a chloroform solution (17 ml) of $Cu(hfa)_2 \cdot 2H_2O$ (68.1 mg 0.335 mmol). After five minutes a black precipitate started forming which was removed by filtration the next day to yield 142.0 mg

Table 1 Crystal data for Cu(3,2 mac), Cu(3,2 oxomac), Cu(3,2 oxomac)$Cu(hfa)_2$, and $Cu\{H_2(3,2\ mac)\}(hfa)_2$

	Cu(3,2 mac)	Cu(3,2 oxomac)·CH_3OH	Cu(3,2 oxomac)$Cu(hfa)_2$	$Cu\{H_2(3,2\ mac)\}(hfa)_2$
Chemical formula	$C_{19}H_{20}CuN_4$	$C_{20}H_{20}CuN_4O_3$	$C_{29}H_{18}Cu_2F_{12}N_4O_6$	$C_{29}H_{24}CuF_{12}N_4O_4$
Formula weight	367.93	427.94	873.55	784.06
T/K	193(2)	173(2)	173(2)	130(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	*Pbca*	*P*2(1)/*n*	*P*-1	*P*1
a/Å	14.976(2)	9.2260(10)	9.828(3)	9.6902(7)
b/Å	8.6080(10)	15.970(2)	11.223(2)	11.2495(6)
c/Å	25.208(2)	12.050(2)	15.959(2)	15.391(2)
α/°			96.250(10)	93.936(3)
β/°		91.990(10)	99.02(2)	106.152(6)
γ/°			108.12(3)	100.996(5)
V/Å^3	3249.6(6)	1774.4(4)	1628.8(6)	1568.8(2)
Z	8	4	2	2
μ/mm^{-1}	1.351	1.262	1.424	0.810
Reflections collected	4697	3617	8733	14698
Independent reflections	3725 [*R*(int) = 0.0479]	2764 [*R*(int) = 0.0264]	7402 [*R*(int) = 0.0414]	7744 [*R*(int) = 0.0403]
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0518, *wR*2 = 0.1334	*R*1 = 0.0367, *wR*2 = 0.1176	*R*1 = 0.0517, *wR*2 = 0.1374	*R*1 = 0.0454, *wR*2 = 0.1064
R indices (all data)	*R*1 = 0.0763, *wR*2 = 0.1958	*R*1 = 0.0458, *wR*2 = 0.1273	*R*1 = 0.0797, *wR*2 = 0.1577	*R*1 = 0.0583, *wR*2 = 0.1144

(54%) of the product. Anal. Calc. for $C_{29}H_{24}N_4O_4CuF_{12}$: C, 44.42; H, 3.06; N, 7.15. Found: C, 44.00; H, 3.49; N, 7.02%. ν_{max} (cm^{-1}): 1663s, 1605m, 1582m, 1526s, 1452m, 1405w, 1311w, 1253s, 1204s, 1151s, 1096w, 941w, 894w, 790m, 756m, 736w, 658m, 575m, 520w. The crystals of $Cu\{H_2(3,2\ mac)\}(hfa)_2$ for the X-ray structure determination were obtained by reacting H_2(3,2 mac) with $Cu(hfa)_2·2H_2O$ in 1:2 mol ratio in chloroform. The crystals were collected three days after the reagents were mixed. The better quality of the crystals compared to the 1:1 reaction may have resulted not from different stoichiometry but simply from the larger volume of chloroform used to dissolve the $Cu(hfa)_2·2H_2O$.

Method II. A chloroform solution (4 ml) of Cu(3,2 mac) (41.9 mg, 0.114 mmol) was mixed with a chloroform solution (6 ml) of hexafluoroacetylacetone (Hhfa) (48.0 mg, 0.231 mmol). A precipitate started forming within ten minutes and was removed by filtration after three days to give 19.4 mg (22%) of the product. The UV-visible spectrum of the product was identical to the UV-visible spectrum of $Cu\{H_2(3,2\ mac)\}(hfa)_2$ obtained by Method I.

Crystal structures

Data for the structures of Cu(3,2 mac), Cu(3,2 oxomac), and Cu(3,2 oxomac)$Cu(hfa)_2$ were collected on a Siemens P4/RA diffractometer at −100 °C. Data for $Cu\{H_2(3,2\ mac)\}(hfa)_2$ was collected on an Enraf-Nonius FAST area detector diffractometer at 130 K by published procedures.[9] The structures were solved by Patterson methods, using SHELXS-86 program package and refined on F_o^2 using the SHELXL-93 program.[10] Crystallographic data and other parameters for all compounds are given in Table 1.

CCDC reference number 186/1703.

Results and discussion

Structures

Table 2 gives selected bond distances and angles for Cu(3,2 mac), Cu(3,2 oxomac), Cu(3,2 oxomac)$Cu(hfa)_2$, and $Cu\{H_2(3,2\ mac)\}(hfa)_2$. The numbering scheme for the macrocycle is shown below (Chart 2) and the ORTEP[17] diagrams are shown in Figs. 1–4. There are many points of commonality among these structures. These are: (1) tetrahedral distortion of the four nitrogen atoms around the copper(II) ion; (2) the twist boat conformation of the six-membered ring containing the copper atom, azomethine nitogen atoms (N2 and N3) and three methylene carbon atoms (C8, C9, and C10); (3) the noncoplanar arrangement of the planes of the phenyl rings (C1–C6 and C12–C17); (4) unequal displacement of the copper ion

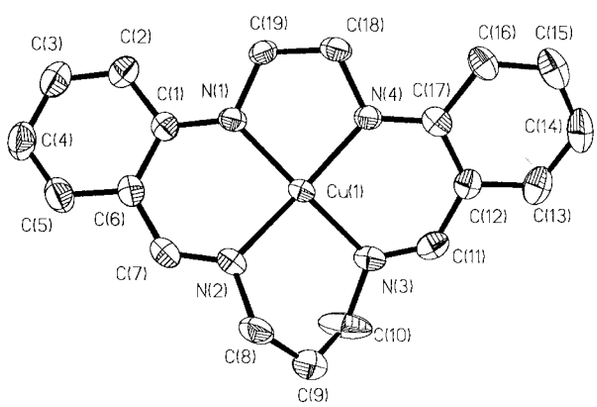


Fig. 1 ORTEP of Cu(3,2 mac).

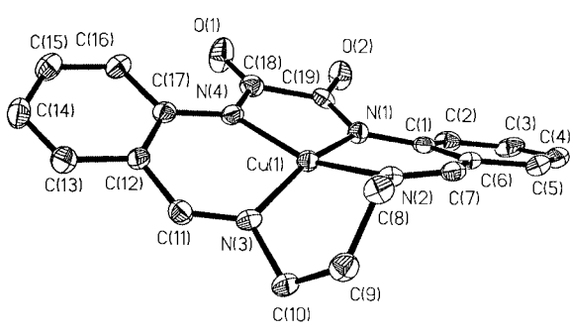


Fig. 2 ORTEP of Cu(3,2 oxomac).

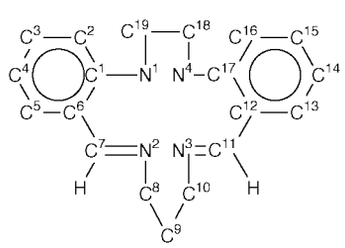


Chart 2

from the planes of the phenyl rings; and (5) similar distances and angles for all but a few positions that are discussed below.

Collectively these structures allow for the direct examination of the effects of both oxidation and protonation of the Cu(3,2 mac). The observed structural differences between the molecules are consistent with the chemical changes that have taken place. The oxidized macrocycle, Cu(3,2 oxomac), is present in both its structure and in the dinuclear complex, Cu(3,2 oxo-

Table 2 Selected intramolecular distances (Å) and bond angles (°) for (a) Cu(3,2 mac), (b) Cu(3,2 oxomac), (c) Cu(3,2 oxomac)$Cu(hfa)_2$ and (d) $Cu\{H_2(3,2\ mac)\}(hfa)_2$. Estimated standard deviations in the least significant figure are given in parentheses

	(a)	(b)	(c)	(d)
Cu–O2B			2.026(3)	
Cu–O2			2.047(3)	
Cu–O1A			2.146(3)	
Cu–O1			2.183(3)	
Cu–O2A (O1)*			1.982(3)	2.404(2)
Cu–O1B (O3)*			1.989(3)	2.408(2)
Cu–N1	1.927(3)	1.935(3)	1.945(3)	2.016(2)
Cu–N4	1.930(3)	1.933(3)	1.939(3)	2.007(2)
Cu–N3	1.953(3)	1.939(3)	1.943(3)	1.970(2)
Cu–N2	1.977(3)	1.954(3)	1.948(3)	1.954(2)
N1–C19	1.453(5)	1.324(4)	1.318(5)	1.476(3)
N1–C1	1.344(5)	1.416(4)	1.412(5)	1.440(3)
N4–C17	1.343(5)	1.406(4)	1.421(5)	1.463(3)
N4–C18	1.460(5)	1.355(4)	1.331(5)	1.481(3)
O1–C18		1.222(4)	1.245(4)	
O2–C19		1.236(4)	1.261(4)	
N1–Cu–O1				84.56(7)
N2–Cu–O1				100.77(8)
N3–Cu–O1				86.90(7)
N4–Cu–O1				86.18(7)
N1–Cu–O3				85.23(7)
N2–Cu–O3				87.48(7)
N3–Cu–O3				103.07(7)
N4–Cu–O3				85.27(7)
N1–Cu–N4	86.16(13)	87.01(11)	86.53(13)	86.73(8)
N1–Cu–N3	166.69(14)	160.57(12)	161.56(13)	171.40(8)
N4–Cu–N3	92.97(13)	94.94(11)	94.10(14)	91.67(8)
N1–Cu–N2	91.61(13)	93.85(11)	93.53(13)	91.57(8)
N4–Cu–N2	162.98(13)	158.67(11)	160.17(13)	172.67(8)
N3–Cu–N2	93.00(13)	91.28(11)	92.04(14)	91.05(8)
O2A(O1)–Cu–O1B(O3)*			170.18(11)	167.03(7)
O2A–Cu2–O2B			88.23(13)	
O1B–Cu2–O2B			89.63(12)	
O2A–Cu2–O2			91.51(13)	
O1B–Cu–O2			92.92(11)	
O2B–Cu–O2			165.74(12)	
O2A–Cu2–O1A			88.06(12)	
O1B–Cu2–O1A			83.03(11)	
O2B–Cu2–O1A			102.26(13)	
O2–Cu2–O1A			91.98(12)	
O2A–Cu2–O1			98.22(11)	
O1B–Cu–O1			91.31(11)	
O2B–Cu–O1			88.60(12)	
O2–Cu2–O1			77.32(11)	
O1A–Cu2–O1			167.66(12)	

* O1 and O3 refer to d as shown in Fig. 4.

mac)$Cu(hfa)_2$. There is very close similarity between these two structures and in fact they are nearly superimposable as evidenced by a weighted rms deviation of 0.0862 Å in the OFIT calculation. Thus, the following structural comparisons of the reduced and oxidized forms are based on both structures of the oxidized macrocycle.

The overall shape of Cu(3,2 mac) does not change significantly upon oxidation. The tetrahedral distortion, defined as the CuN1N2 CuN3N4 dihedral angle increases from 20.7 to 27.8°. In addition the following localized changes are observed. Upon oxidation of Cu(3,2 mac) to Cu(3,2 oxomac) or Cu(3,2 oxomac)$Cu(hfa)_2$ the N1–C1 and N4–C17 bond distances slightly increase from 1.344(5) to 1.414(5) Å while the N1–C19 and N4–C18 bond distances decrease from 1.457(5) to 1.332(5) Å. The N1–C19–C18 and N4–C18–C19 angles increase from 109.1(3) to 114.6(3)°. The newly created bonds C19–O2 and C18–O1 are short, averaging 1.241(4) Å. These changes are consistent with partial double bond character between N1 and C19 and N4 and C18 due to resonance delocalization of the amide functionality in the oxidized product and the change in hybridization of C18 and C19 from sp^3 to sp^2.

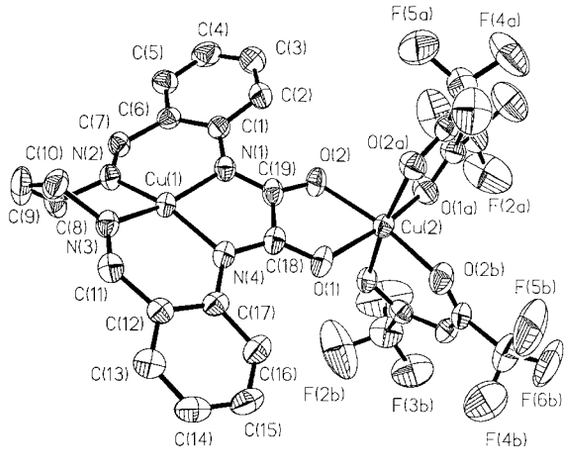


Fig. 3 ORTEP of Cu(3,2 oxomac)$Cu(hfa)_2$.

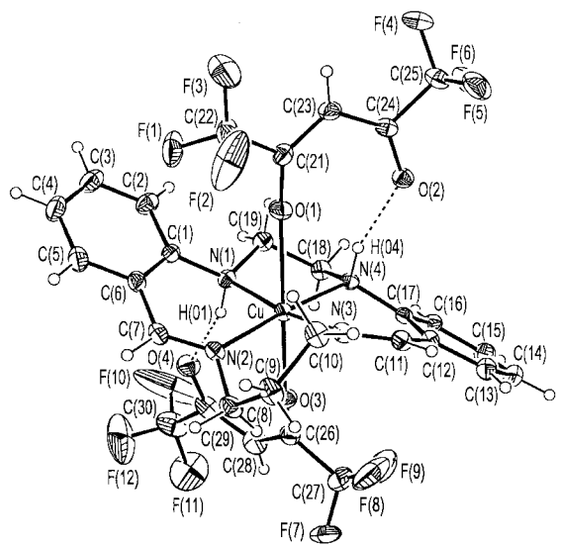


Fig. 4 ORTEP of $Cu\{H_2(3,2\ mac)\}(hfa)_2$.

The *meso* conformation of the five-membered ring Cu–N1–C19–C18–N4 in Cu(3,2 mac) is replaced with a planar arrangement of these same atoms. The displacements of O1 and O2 from this plane are 0.03 and 0.02 Å respectively. These structural changes suggest significant delocalization in the planar five membered ring. The oxidation causes no significant change in the bond distances or angles of the copper nitrogen positions or the remaining portions of the ligand.

Protonation of the N1 and N4 positions of Cu(3,2 mac) to give $Cu\{H_2(3,2\ mac)\}(hfa)_2$ results in the copper of the macrocycle becoming six coordinate as it is also ligated in a monodentate mode by two hfa anions which are hydrogen bonded to N1 and N4. In contrast to the structural changes observed upon oxidation, protonation of Cu(3,2 mac) and its subsequent anation (with accompanying change in coordination number) results in greater conformational change from overall tetrahedrally distorted square planar to a stepped conformation. The hydrogens which have been added to N1 and N4 point to opposite sides of the macrocycle and are hydrogen bonded to the non-ligating oxygens of the hfa anions. This overall conformation change does not affect the conformation of the Cu–N2–C8–C9–C10–N3 or Cu–N1–C19–C18–N4 rings which remain twist boat and *meso* as in Cu(3,2 mac). In $Cu\{H_2(3,2\ mac)\}(hfa)_2$ the Cu–N1 and Cu–N4 bond distances (2.012(2) Å) are longer (0.083 Å) than those of Cu(3,2 mac) (1.929(3) Å) without affecting the Cu–N2 and Cu–N3 bond distances or the bond angles of the inner coordination sphere. In addition the N1–C1 and N4–C17 bond distances increase from 1.344(5) to 1.452(3) Å without

any decrease (as was observed in oxidation) in the N1–C19 and N4–C18 distances. These changes reflect a lowering of the ligand field of the neutral macrocycle from that of the dianion.

The mode of coordination of hfa^- is quite different in Cu(3,2 oxomac)Cu$(hfa)_2$ than in Cu{H_2(3,2 mac)}$(hfa)_2$. In the former each hfa^- binds to the copper(II) ion as a bidentate ligand through both of its oxygen donors while in the latter each hfa^- binds to the copper(II) ion as a monodentate ligand while the unbound oxygen atom interacts with the aniline nitrogen atoms through hydrogen bonding. The latter mode of coordination has been observed in a copper complex of dimethylethylenediamine[11] but this appears to be the first report involving a macrocycle.

Jahn–Teller distortion

Two of the compounds, Cu(3,2 oxomac)Cu$(hfa)_2$ and Cu{H_2-(3,2 mac)}$(hfa)_2$, have an octahedral copper ion subject to distortion. In Cu(3,2 oxomac)Cu$(hfa)_2$ it is the Cu$(hfa)_2$ adducted to O1 and O2 while in the latter there is only one copper atom. The Jahn–Teller distortion is obvious and different in the two molecules. In Cu(3,2 oxomac)Cu$(hfa)_2$ the octahedral copper atom is surrounded by six oxygen atoms with three distinct values of *trans* axis, ≈2.16, ≈2.03 and 1.98 Å. The distortion axis contains one oxygen atom from Cu(3,2 oxomac), O1, and one from an hfa, O1A. The inclusion of O1 in the distortion axis may indicate a slightly unfavorable bite angle of Cu(3,2 oxomac) for Cu$(hfa)_2$ as the Cu, C19, C18, O1, O2 portion of Cu(3,2 oxomac) is planar and symmetric. There are also three distinct values of *trans* axis in Cu{H_2(3,2 mac)}$(hfa)_2$, 2.40, ≈2.00 and ≈1.96 Å. These are quite similar to what is observed in Cu(3,2 oxomac)Cu$(hfa)_2$ with the exception of the magnitude of the distortion axis, 2.40 as opposed to 2.16 Å. The distortion axis contains oxygen atoms from two different hfa anions which probably explains the size of the distortion exhibited in this complex.

Dinuclear structures

In the one dinuclear structure the copper ions are 5.385 Å apart and bridged by the N1–C19–O2 and N4–C18–O1 pathways. The distances of O1, O2, and Cu2 from the Cu–N1–N4–C18–C19 plane are −0.07, 0.11, and 0.10 Å. Thus, there is near coplanarity of all of the bridging atoms. Distances between analogous pairs of atoms along the bridge are very similar except the slight asymmetry in the Cu2–O1 and Cu2–O2 distances due to the choice of Jahn–Teller distortion axis discussed previously. This bridge is similar to oxalato with replacement of two oxygen atoms with nitrogen atoms.

Axial Bonding

A general trend observed with the copper(II) and nickel(II) N_4 Schiff base complexes derived from *o*-aminobenzaldehyde is that the metal does not react with additional donors. This trend is observed in the present complexes of the anionic ligands but not in the complex of the neutral ligand. In Cu{H_2(3,2 mac)}-$(hfa)_2$ the copper atom reacts with a single oxygen atom from two different hfa anions. The other oxygen atoms of the hfa anions are hydrogen bonded to the aniline nitrogens, N1 and N4 with N–H–O angles of 162°. This creates some distortion in the hfa backbone which is indicated by the C–O–Cu angles of 174.8 and 170.0°. The only other instance of hydrogen bonding observed in these structures is with that of Cu(3,2 oxomac) which crystallizes as a methanol solvate. The methanol proton (O–H 1.017 Å) is hydrogen bonded to O2 at a distance of 1.772 Å and with a O–H–O angle of 162.8°. There is no interaction of the oxygen atom of the methanol with the copper atom as is expected.

Magnetism

Variable temperature (80–295 K) magnetic susceptibility studies were carried out for the new complexes, Cu{H_2(3,2 mac)}$(hfa)_2$ and Cu(3,2 oxomac)Cu$(hfa)_2$, by the Faraday method. Cu{H_2(3,2 mac)}$(hfa)_2$ behaved as a simple mononuclear copper(II) with magnetic moment of 1.90 μ_B at 295 K. The dinuclear complex, Cu(3,2 mac)Cu$(hfa)_2$, exhibited a temperature dependent magnetic moment. Fig. 5 shows the experimental susceptibility data and the theoretical curve resulting from fitting the data to the Bleany–Bowers equation for a pair of interacting $S = 1/2$ ions. The interaction is antiferromagnetic as expected for this geometry.[12] The magnitude of the coupling is consistent with the fairly planar arrangement of the bridging atoms. The choice of Jahn–Teller distortion axis involving O1 and O1A may result in some weakening of the magnetic coupling as the Cu–O1 distance is longer than the Cu–O2 distance.

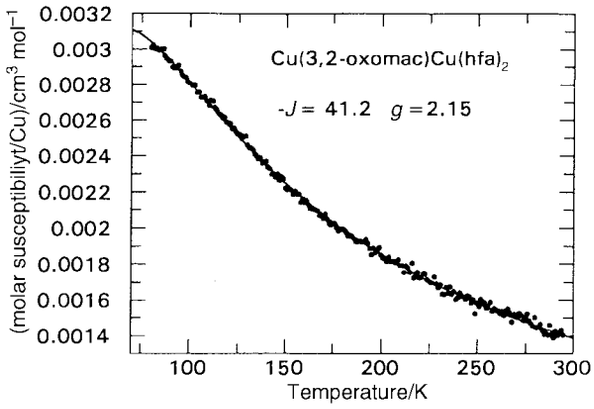


Fig. 5 Plot of molar susceptibility *vs.* temperature for Cu(3,2 oxomac)-Cu$(hfa)_2$.

Reactions

The conversion of M(3,2 mac) to M(3,2 oxomac) is an overall $8e^-$ oxidation which occurs under ambient conditions. Several questions arise concerning this reaction. They are the (a) ligand and metal reactivity relationships (b) identity of oxidizing agent (c) identity of oxygen transfer agent, and (d) the role of $Cu(hfa)_2 \cdot (H_2O)_2$.

The reaction shows sensitivity to the number of methylene units connecting the anilino nitrogen atoms of the macrocycle but not the metal in the macrocycle. Thus, the oxidation occurs for the nickel and copper complexes of H_2(3,2 mac) as reported here and also for Cu(2,2 mac)[13] but not for Cu(3,3 mac). Altering the number of methylenes between the Schiff base nitrogen atoms does not disrupt the reaction unlike what is observed when the ethylene unit connecting the anilino nitrogen atoms is altered. It may be that this ethylene unit is activated toward oxidation due to some favorable interaction with $Cu(hfa)_2 \cdot (H_2O)_2$. Clearly the resultant product has a favorable chelate angle with $Cu(hfa)_2 \cdot (H_2O)_2$ and if this was present in some initial adduct or one of the reaction intermediates it may have an impact on reactivity. The failure of Cu(3,3 mac) to react under these conditions to give an analogous product does not rule out reactivity under different conditions or to give some other product.

A 1:1 reaction of Cu(3,2 mac) with $Cu(hfa)_2 \cdot (H_2O)_2$ in chloroform was performed in a dry box to determine the importance of dioxygen to the reaction. A dark green-brown precipitate formed in a day which contained C, H, N in approximately the same proportions as in Cu(3,2 mac), but with substantially lower percentages. The nature of the product could not be established. Thus, dioxygen is needed for the observed reaction but there is reactivity of some sort between the reagents even in the absence of dioxygen. The role of dioxygen as both oxidizing agent and oxygen transfer agent or just the former was investigated with isotopic labels.

The dinuclear product, Cu(3,2 oxomac)Cu(hfa)$_2$, was prepared in the presence of $^{18}O_2$ or $H_2{}^{18}O$ as described in the Experimental section. The products were chromatographed to separate Cu(3,2 oxomac) from Cu(hfa)$_2$ and the former was analyzed by MS. The reason that the dinuclear product was not analyzed directly is because it fails to give a molecular ion. It was demonstrated that both M(3,2 mac) and M(3,2 oxomac) were unchanged by the chromatographic process. Natural abundance Cu(3,2 oxomac) exhibits molecular ions, MNa^+, at *m*/*z* 418/20 due to the isotopic distribution of copper. Complete incorporation of the labels would result in ions at *m*/*z* 422/24. The reaction that was conducted under $^{18}O_2$ showed a base peak at *m*/*z* 420 ($^{63}Cu^{16}O^{18}O$ and $^{65}Cu^{16}O^{16}O$), significant peaks (≈80%) at 418 ($^{63}Cu^{16}O^{16}O$) and 422 ($^{63}Cu^{18}O^{18}O$ and $^{65}Cu^{16}O^{18}O$) and a smaller peak at 424 ($^{65}Cu^{18}O^{18}O$). These observations exclude dioxygen as the only source of oxygen incorporation but do support that some oxygen may be incorporated from dioxygen or its reaction products. The reaction done in the presence of $H_2{}^{18}O$ exhibited a base peak at *m*/*z* 422 ($^{63}Cu^{18}O^{18}O$ and $^{65}Cu^{16}O^{18}O$) and significant peaks (≈45%) at 420 ($^{63}Cu^{16}O^{18}O$ and $^{65}Cu^{16}O^{18}O$) and 424 ($^{65}Cu^{18}O^{18}O$) and a minor peak (<10%) at 418 ($^{63}Cu^{16}O^{16}O$). These experiments, in conjunction with the former, clearly indicate that dioxgen is the oxidizing agent but not the direct source of the oxygen atoms in the product which in fact come from water. The incorporation of the label in the $^{18}O_2$ experiment can be explained by its probable reduction to $H_2{}^{18}O$ and subsequent competition with water from solvent or Cu(hfa)$_2$·(H$_2$O)$_2$ for incorporation into product. Similarly less than quantitative incorporation of the label in the $H_2{}^{18}O$ experiment is due to the presence and production (from dioxygen) of natural abundance water.

Perhaps the most unusual aspect of this reaction is the role of Cu(hfa)$_2$·(H$_2$O)$_2$. Substitution of Cu(tfa)$_2$ or Cu(acac)$_2$ for Cu(hfa)$_2$·(H$_2$O)$_2$ in the oxidation of Cu(3,2 mac) did not produce the product under the same reaction conditions. In addition the reaction of Ni(3,2 mac) with Ni(hfa)$_2$·2H$_2$O (1 : 1) also yielded no product. This reaction was done rather than Cu(3,2 mac) with Ni(hfa)$_2$·(H$_2$O)$_2$ to avoid the possibility that a ligand exchange reaction could occur which would produce a small amount of Cu(hfa)$_2$·(H$_2$O)$_2$. A blank reaction of Ni(3,2 oxomac) with Ni(hfa)$_2$·2H$_2$O yielded an immediate precipitate. Thus, it can be concluded that Ni(3,2 oxomac) was not produced in significant amounts. To determine if the role of Cu(hfa)$_2$·(H$_2$O)$_2$ is stoichiometric or catalytic a reaction was done in which the [Cu(3,2 mac)]/[Cu(hfa)$_2$·(H$_2$O)$_2$] was 26 : 1. The reaction was monitored by UV-visible spectroscopy and it was shown that oxidation to Cu(3,2 oxomac) was approximately 50% complete in seven days and essentially complete in twelve days. A blank experiment which contained no Cu(hfa)$_2$·(H$_2$O)$_2$ showed only slight changes in seven days and at twelve days was still less than 50% complete. Further, it was shown that a small amount of Cu(3,2 oxomac)Cu(hfa)$_2$, when added as a solid to a solution of Cu(3,2 mac), would catalyze the oxidation of the latter. This can be explained simply by dissociation of the dinuclear product to give mononuclear Cu(hfa)$_2$ which can then act as a catalyst as described above.

Further evidence that the facile oxidation of M(3,2 mac) to M(3,2 oxomac) is dependent on the copper(II) ion in Cu(hfa)$_2$·(H$_2$O)$_2$ comes from the reaction of Cu(3,2 mac) with pure Hhfa. In this reaction Hhfa simply protonates the macrocycle at N1 and N4 to yield Cu{H$_2$(3,2 mac)}(hfa)$_2$. This same product is also produced by the reaction of H$_2$(3,2 mac) with Cu(hfa)$_2$·(H$_2$O)$_2$. These reactions demonstrate that Hhfa is not directly involved in any oxidation reaction and the ability of N1 and N4 to act as Brønsted Lowry bases to other centers while still bonding to the copper(II) ion of the macrocycle. The protonation reaction has some generality as an analogous product results from the reactions of the acyclic Cu(amben) with Hhfa or H$_2$amben with Cu(hfa)$_2$·(H$_2$O)$_2$. The protonated macrocycle, Cu{H$_2$(3,2 mac)}$^{2+}$, is protected from oxidation even in the presence of stoichiometric amounts of Cu(hfa)$_2$·(H$_2$O)$_2$ as evidenced by the 1 : 2 reaction of H$_2$(3,2 mac) with Cu(hfa)$_2$·(H$_2$O)$_2$.

Conclusion

Structural data is given for the copper(II) complex of a 15 member N_4 macrocycle and its oxidation, oxidation and dinucleation, and protonation products. The changes associated with protonation are more significant than those of oxidation. The eight electron oxidation of the ethylene unit of M(3,2 mac) to M(3,2 oxomac) proceeds readily under ambient conditions in the presence of Cu(hfa)$_2$·(H$_2$O)$_2$. Isotopic studies allow for distinction between an authentic oxygenation reaction and hydrolysis of a dehydrogenated intermediate. In this reaction dioxygen serves as the oxidizing agent and water as the oxygen transfer agent. Thus mechanisms which involve direct reaction between dioxygen and a ligand based radical as was proposed for a related complex are not indicated. Instead the evidence suggests a dehydrogenation to give an imine species which in turn reacts with water, followed by proton loss, and subsequent tautomerization to give the product. Certainly there are alternatives to the proposed mechanism but this one is consistent with the lack of evidence for a direct oxygenation and other observations of copper mediated amine to amide oxidations.[14] The role of Cu(hfa)$_2$·(H$_2$O)$_2$ is catalytic and not stoichiometric. Protonation of the macrocycle protects it from oxidation which is consistent with a mechanism which requires oxidation of Cu(II) to Cu(III) as it has been shown that the oxidation potentials of deprotonated metal tetraazamacrocycles are substantially below those of the neutral ligands.[15] Specifically Cu(hfa)$_2$·(H$_2$O)$_2$ may facilitate the slow electron transfer between dioxygen and Cu(II) to give superoxide and Cu(III) (or Cu(II), ligand radical cation) or it may react directly with Cu(3,2 mac) to give Cu(hfa)$_2^-$ and Cu(III) (or Cu(II), ligand radical cation). Subsequently the Cu(hfa)$_2^-$ is oxidized by dioxygen to regenerate Cu(hfa)$_2$. Consistent with the latter is the ease of reduction of Cu(hfa)$_2$ ($E_{1/2}$ = +0.038 V) which is a feature that differentiates it from Ni(hfa)$_2$ ($E_{1/2}$ = −1.00 V), Cu(tfa)$_2$ ($E_{1/2}$ = −0.169 V), and Cu(acac)$_2$ ($E_{1/2}$ = −0.502 V) all of which fail to exhibit activity.[16] Also consistent with a direct electron transfer between Cu(3,2 mac) and Cu(hfa)$_2$·(H$_2$O)$_2$ is the fact that a product (as yet unidentified) is produced from direct reaction of these two in the absence of dioxygen.

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