trophilic attack by both protons[25] and metal electrophiles.[24] These reactions are the subject of a forthcoming publication.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support.

Registry No. $Fe_2(CO)_6[C\{NHCH_3\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 73970-08-8; $Fe_2(CO)_6[CHC\{NHCH_3\}\{C_6H_5\}][P(C_6H_5)_2]$, 70657-55-5; $Fe_2(CO)_6[C\{NHC_2H_5\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 73979-53-0; $Fe_2(CO)_6[CHC\{NHC_2H_5\}\{C_6H_5\}][P(C_6H_5)_2]$, 70657-57-7; $Fe_2(CO)_6[CHC\{NHC_2H_5\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$, 86196-56-7; $Fe_2(CO)_6[C\{NHC_4H_9\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 82647-72-1; $Fe_2(CO)_6[CHC\{NHC_4H_9\}\{C_6H_5\}][P(C_6H_5)_2]$, 82647-70-9; $Fe_2(CO)_6[C\{NHC_4H_9\}CH\{C_6H_4Br\text{-}o\}][P(C_6H_5)_2]$, 82647-76-5; $Fe_2(CO)_6[CHC\{NHC_4H_9\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 82647-74-3; $Fe_2(CO)_6[C\{NHC_4H_9\}CH\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 82647-68-5; $Fe_2(CO)_6[CHC\{NHC_4H_9\}\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 82647-66-3; $Fe_2(CO)_6[CHC\{NHC_6H_5\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-57-8; $Fe_2(CO)_6[CHC\{NHC_6H_5\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$, 86196-58-9; $Fe_2(CO)_6[C\{NHCH_2CH_2NH_2\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 86196-59-0; $Fe_2(CO)_6[CHC\{NHCH_2CH_2NH_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 86217-11-0; $Fe_2(CO)_6[C\{NHCH_2CH_2N(CH_3)_2\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 86196-60-3; $Fe_2(CO)_6[CHC\{NHCH_2CH_2N(CH_3)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-61-4; $Fe_2(CO)_6[C\{NHC_6H_{11}\text{-}c\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 67168-86-9; $Fe_2(CO)_6[CHC\{NHC_6H_{11}\text{-}c\}\{C_6H_5\}][P(C_6H_5)_2]$, 67168-85-8; $Fe_2(CO)_6[C\{NHC_6H_{11}\text{-}c\}CH\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 86196-62-5; $Fe_2(CO)_6[CHC\{NHC_6H_{11}\text{-}c\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 86196-63-6; $Fe_2(CO)_6[CHC\{NHC_6H_{11}\text{-}c\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$, 86196-64-7; $Fe_2(CO)_6[C\{NHCH(CH_3)_2\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 82647-71-0; $Fe_2(CO)_6[CHC\{NHCH(CH_3)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 82647-69-6; $Fe_2(CO)_6[C\{NHCH(CH_3)_2\}CH\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 82647-67-4; $Fe_2(CO)_6[CHC\{NHCH(CH_3)_2\}\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 82647-65-2; $Fe_2(CO)_6[C\{NHCH(CH_3)_2\}CH\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 82647-75-4; $Fe_2(CO)_6[CHC\{NHCH(CH_3)_2\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 82647-73-2; $Fe_2(CO)_6[CHC\{NHCH(CH_3)_2\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$, 86196-65-8; $Fe_2(CO)_6[C\{NHCH(CH_3)(C_2H_5)\}CH\{C_6H_5\}][P(C_6H_5)_2]$, 86196-66-9; $Fe_2(CO)_6[CHC\{NHCH(CH_3)(C_2H_5)\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-67-0; $Fe_2(CO)_6[CHC\{NHC(CH_3)_3\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-68-1; $Fe_2(CO)_6[CHC\{NHC(CH_3)_3\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 86196-69-2; $Fe_2(CO)_6[CC\{NH(CH_3)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-70-5; $Fe_2(CO)_6[CC\{NH(C_2H_5)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-71-6; $Fe_2(CO)_6[CC\{NH(C_2H_5)_2\}\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 86196-72-7; $Fe_2(CO)_6[CHC\{N(CH_3)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-73-8; $Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 59584-64-4; $Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 86196-74-9; $Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 86196-75-0; $Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{c\text{-}C_6H_{11}\}][P(C_6H_5)_2]$, 59584-65-5; $Fe_2(CO)_6[CHC\{N(C_3H_7)_2\}\{C_6H_5\}][P(C_6H_5)_2]$, 70657-56-6; $Fe_2(CO)_6[CHC\{\overline{NCH_2(CH_2)_3CH_2}\}\{C_6H_5\}][P(C_6H_5)_2]$, 70657-58-8; $Fe_2(CO)_6[CHC\{\overline{NCH_2CH_2OCH_2CH_2}\}\{C_6H_5\}][P(C_6H_5)_2]$, 86196-76-1; $Fe_2(CO)_6[CC\{NH(C_2H_5)_2\}\{C_6H_{11}\text{-}c\}][P(C_6H_5)_2]$, 86196-77-2; $Fe_2(CO)_6[CC\{C(CH_3)_3\}][P(C_6H_5)_2]$, 59584-68-8; $Fe_2(CO)_6[CC\{C_6H_{11}\text{-}c\}][P(C_6H_5)_2]$, 59584-69-9; $Fe_2(CO)_6[CC\{C_6H_4OCH_3\text{-}p\}][P(C_6H_5)_2]$, 86196-78-3; $Fe_2(CO)_6[CC\{C_6H_5\}][P(C_6H_5)_2]$, 52970-25-9; $Fe_2(CO)_6[CC\{C_6H_4Br\text{-}p\}][P(C_6H_5)_2]$, 86196-79-4; $p\text{-}BrC_6H_4C_2[P(C_6H_5)_2]$, 86196-80-7; $p\text{-}MeOC_6H_4C_2[P(C_6H_5)_2]$, 86196-81-8; $Fe_2(CO)_5[P\{\overline{NCH_2(CH_2)_3CH_2}\}\{C_6H_5\}_2](C_2C(CH_3)_3)[P(C_6H_5)_2]$, 86196-82-9; Fe, 7439-89-6; chlorodiphenylphosphine, 1079-66-9; *p*-bromophenylacetylene, 766-96-1; *p*-methoxyphenylacetylene, 768-60-5.

Supplementary Material Available: Tables S1-S3, showing IR stretching frequencies for the complexes $Fe_2(CO)_6[C\{NHR^1\}CHR][P(C_6H_5)_2]$, $Fe_2(CO)_6[CHC\{NHR^1\}R][P(C_6H_5)_2]$, $Fe_2(CO)_6[CC\{NH(R^1)_2\}R][P(C_6H_5)_2]$, $Fe_2(CO)_6[CHC\{N(R^1)_2\}R][P(C_6H_5)_2]$, and $Fe_2(CO)_6[CHC\{\overline{NR^1}\}R][P(C_6H_5)_2]$, and Tables S4-S6, showing ^1H and ^{31}P NMR data and Mössbauer parameters for the complexes $Fe_2(CO)_6[C(NHR^1)CHR][P(C_6H_5)_2]$, $Fe_2(CO)_6[CHC\{NHR^1\}R][P(C_6H_5)_2]$, $Fe_2(CO)_6[CC\{NH(R^1)_2\}R][P(C_6H_5)_2]$, $Fe_2(CO)_6[CHC\{N(R^1)_2\}R][P(C_6H_5)_2]$ and $Fe_2(CO)_6[CHC\{\overline{NR^1}\}R][P(C_6H_5)_2]$ (10 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, Absolute Configuration, and Magnetic Studies of Some Copper(II) Complexes of Chiral Bidentate and Tridentate Fluorinated Aminoalkoxy Ligands[1]

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Template condensation of 5,5,5-trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone, $CH_3COCH_2C(CF_3)_2OH$, with primary amines RNH_2 in the presence of Cu^{2+} leads to Cu^{2+} complexes of bidentate iminoalkoxy ligands. Hydrogenation of these gives the amino alcohols, $RNHCH(CH_3)CH_2C(CF_3)_2OH$, in which a new chiral center is present; these also act as bidentate ligands toward Cu^{2+}, giving stable, neutral complexes. A complete structural determination for the latter with R = menthyl has been carried out. The complex, of molecular formula $C_{32}H_{52}CuF_{12}N_2O_2$, crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units per unit cell. The unit cell dimensions are a = 16.225 (5) Å, b = 18.021 (5) Å, and c = 13.248 (5) Å. Knowledge of the absolute configuration of the chiral substituent enables that of the new center in the ring to be assigned. Through the use of CD spectra, assignments of configuration are then made to complexes where other R groups are present. Tridentate iminoalkoxy ligands are formed by similar template condensation reactions using chiral-substituted amino alcohols, $NH_2CH(R')CH_2OH$. Hydrogenation of their Cu^{2+} complexes leads to amino diols, $HOCH_2CH(R')NHCH(CH_3)C(CF_3)_2OH$, where two chiral centers are now present. By formation of Cu^{2+} complexes and comparison of CD spectra with those of bidentate ligands, assignments of absolute configuration are made. The amino diol Cu^{2+} complexes are dinuclear, and magnetic studies show antiferromagnetic interactions between Cu^{2+} ions; the degree of interaction is related to the bulk of the substituent R′ group.

Introduction

The correlation between magnetic properties and structural parameters in multinuclear copper(II) complexes has received considerable attention recently. Apart from the intrinsic interest of the magnetic exchange interaction, such complexes may serve as models for the copper(II) sites ("type III blue copper") in biological systems.

Previous work here[3-5] has shown that template condensation of 5,5,5-trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone

(1) Taken in part from a thesis submitted by S. J. L. to the Faculty of Graduate Studies, University of Western Ontario, for the Ph.D. degree.
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(3) Loeb, S. J.; Martin, J. W. L.; Willis, C. J. *Inorg. Chem.* **1979**, *18*, 3160.
(4) Timmons, J. H.; Martin, J. W. L.; Martell, A. E.; Rudolf, P.; Clearfield, A.; Loeb, S. J.; Willis, C. J. *Inorg. Chem.* **1981**, *20*, 181.
(5) Loeb, S. J.; Willis, C. J. *Inorg. Chem.* **1981**, *20*, 2791.

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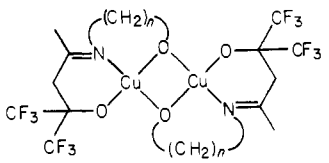
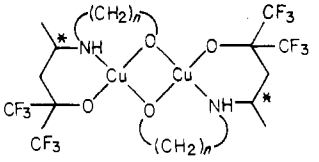
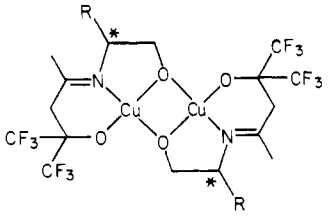
(hexafluorodiacetone alcohol, HFDA) with amino alcohols in the presence of Cu^{2+} yields a variety of dinuclear[6] iminoalkoxy complexes; these may then be hydrogenated to the corresponding aminoalkoxy compounds.



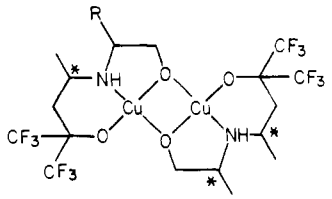
1a, $n = 2$
b, $n = 3$
c, $n = 4$



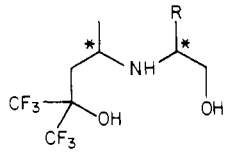
2a, $n = 2$
b, $n = 3$
c, $n = 4$



3a, R = CH_3
b, R = C_2H_5
c, R = C_6H_5
d, R = $(CH_3)_2CH$



5a, R = CH_3
b, R = C_2H_5
c, R = C_6H_5
d, R = $(CH_3)_2CH$



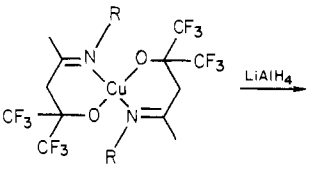
4a, R = CH_3
b, R = C_2H_5
c, R = C_6H_5
d, R = $(CH_3)_2CH$

* = chiral centers

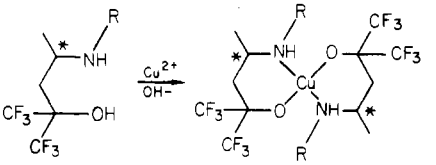
For the iminoalkoxy complexes of type **1**, the magnetic susceptibility shows a striking variation with ring size. When the bridging oxygen atoms are part of an unsubstituted, five-membered ring (**1a**), the compound has a normal magnetic moment in the range expected for d^9 Cu^{2+}, but an increase to six- or seven-membered rings (**1b**, **1c**) is accompanied by spin-pairing and the complexes are virtually diamagnetic at 25 °C.[3] A structural investigation[4] has shown that this is associated with almost exact coplanarity of the coordination planes around the two Cu^{2+} ions. The smaller ring in complex **1a** prevents this coplanarity (and the resulting spin-pairing) and appears to favor association of the molecules into tetranuclear units through additional Cu–O interactions.[5]

After hydrogenation of the C=N bond, the resulting aminoalkoxy complexes are of intermediate magnetic moment, showing considerable antiferromagnetic interactions on cooling, and the amount of spin-pairing between the two Cu^{2+} ions increases as the size of the chelate ring increases.

In extending this study in the present paper, we have prepared the analogous aminoalkoxy complexes **5a–5d** and measured their magnetic properties. However, the presence in the ligand of two chiral centers, leading to differing ring conformations, complicates the correlation of magnetic interactions with structural parameters. It would therefore be desirable to know the configuration at the second chiral center (that at the original center, where the substituent R is attached, being already known from the structure of the amino alcohol). It proved difficult to obtain data crystals of type **5** complexes for a complete structural determination, and we have therefore approached this problem through the use of model compounds of somewhat simpler structure. Whereas all our previous work on the formation of copper(II) complexes by template condensation reactions has involved the production of multidentate ligands through the use of diamines[7] or amino alcohols, we now find that complexes of bidentate iminoalkoxy ligands may be produced by the template condensation of primary alkylamines with HFDA; as with the multidentate ligands, they may then be hydrogenated to complexes of the corresponding aminoalkoxy ligands.

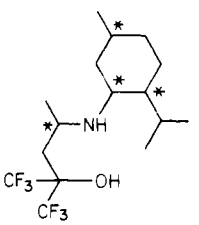


6



7 **8**

This reaction sequence appears to be of fairly general application, and ready condensation occurs with R = *n*-butyl, cyclohexyl, or benzyl. However, its particular advantage for our current work is that a chiral R group of known absolute configuration may readily be incorporated into the complex, and we have used optically pure primary amines with R = *sec*-butyl, phenethyl, or menthyl. The amino complex derived from menthylamine proved suitable for a complete structural determination, from which we were able to find the absolute configuration of the new chiral center in the aminoalkoxy ring by its relationship to the known configuration of the menthyl group.



7 (R = menthyl)

From a comparison of CD spectra, we could assign absolute configurations in the remaining chiral complexes of both the bidentate ligands (**8**) and the tridentate ligands (**5**) and the resulting knowledge of their stereochemistry was then applied in the rationalization of their magnetic properties.

Experimental Section

General Methods. Infrared spectra were recorded on Perkin-Elmer 621 and Beckman 4250 instruments, visible–UV spectra on Cary 14 and 118 spectrometers, ORD spectra on a Jasco 5 instrument, and mass spectra on a Varian MAT 311A instrument. Microanalysis was performed by Malessa-Reuter Laboratories and Guelph Chemical Laboratories; all analytical data are in Table S-I of the supplementary material.

Variable-temperature magnetic susceptibilities were determined by Dr. A. B. P. Lever, York University, using the Faraday method. Diamagnetic corrections were made with use of the Pascal constants of Figgis and Lewis,[8] and the temperature-independent paramagnetism,

(6) We use the term dinuclear or tetranuclear with reference to the number of copper atoms contained in one unit of the complex.

(7) Martin, J. W. L.; Willis, C. J. *Can. J. Chem.* **1977**, *55*, 2459; 1978, *56*, 2966.

N_α, was taken as 60×10^{-6} cgsu/Cu atom. Experimental susceptibility data were fitted to the Bleaney–Bowers equation with use of a nonlinear regression by the Gauss–Newton method, employing a least-squares objective function $\sum(\chi_{calcd} - \chi_{obsd})^2$ as the fitting criterion. Magnetic data are in Table S-II of the supplementary material.

Synthesis. (i) Tridentate Ligands. The (iminoalkoxy)copper complexes were prepared by the template condensation of β-substituted amino alcohols (NH_2CHRCH_2OH) with hexafluorodiacetone alcohol, HFDA ($CH_3COCH_2C(CF_3)_2OH$), in the presence of Cu^{2+} ions as previously described.[5]

Each amino diol ligand was prepared by hydride reduction of the appropriate (iminoalkoxy)copper(II) complex. In a typical preparation [Cu((−)(*R*)-2-amino-1-butanol)(HFDA))]$_4$ (7.14 g, 5 mmol) in 250 mL of anhydrous Et_2O was added dropwise to a slurry of $LiAlH_4$ (2.28 g, 30 mmol) in 15 mL of anhydrous Et_2O, over 2 h. After addition of the complex, the resultant yellow suspension was stirred for 1 h and the excess hydride reagent destroyed by careful addition of $EtOH/H_2O$. The black precipitate that formed was then stirred overnight with a continuous flow of air through the solution, yielding a blue solution with a white precipitate. The solution was filtered over celite and evaporated to a blue oil, which was dissolved in dilute HCl and adjusted to pH 3. To this green solution was added dropwise aqueous K_2S until no more brown CuS precipitate was observed. This clear solution was filtered over Celite and the pH adjusted to 8 by addition of aqueous KOH. The organic product was extracted with Et_2O and dried ($MgSO_4$) and then precipitated as the hydrochloride by passing gaseous HCl. Recrystallization of the resulting oil from $(CH_3)_2CO/CH_2Cl_2$ gave the monohydrochloride of **4b** (R = C_2H_5) (4.3 g (64%); mp 153–155 °C; $[\alpha]^{24}_D = +11.4°$).

A similar procedure gave **4a** (R = CH_3) (73%; mp 113–116° C; from $(CH_3)_2CO/CH_2Cl_2$; $[\alpha]_D^{24} = -21.6°$) **4c** (R = C_6H_5) (88%; mp 183–184 °C; from $(CH_3)_2CO/Et_2O$; $[\alpha]_D^{24} = -5.5°$), and **4d** (R = $CH(CH_3)_2$) (68%; mp 177–178° C; from $(CH_3)_2CO/Et_2O$; $[\alpha]_D^{24} = -20.5°$). Since each hydrogenation led to a compound with two chiral centers, which could exist in two diastereomeric forms, a check for optical purity of the products was carried out by running ORD spectra after further recrystallization; in no case was any further change observed.

Copper(II) complexes were then regenerated from the pure ligands by interaction with Cu^{2+}. In a typical preparation of an aminoalkoxy copper complex, the optically pure amino diol ligand hydrochloride **4b** (R = C_2H_5) (1.67 g, 5 mmol) and anhydrous copper(II) chloride (0.67 g, 5 mmol) were dissolved in warm EtOH, and KOH (0.9 g, 17 mmol) in EtOH was added dropwise. The solution was cooled to 0 °C and precipitated KCl removed by filtration. Concentration of the resulting blue solution followed by recrystallization yielded the aminoalkoxy complex **5b** as blue crystals from $(CH_3)_2CO/EtOH$. Similarly were prepared optically pure **5a**, **5c**, **5d**, and the racemic form of the unsubstituted complex **2a**.

(ii) Bidentate Ligands. In a typical preparation of an iminoalkoxy complex, anhydrous $CuCl_2$ (1.34 g, 10 mmol) in warm EtOH was added to 1-amino-*n*-butane (1.46 g, 20 mmol) in EtOH, followed by HFDA (4.48 g, 20 mmol) and ethanolic KOH (1.29 g, 23 mmol). The solution was heated to reflux for 2 h, followed by stirring at 25°C for 6 h, and then filtered at 0 °C to remove precipitated KCl. Removal of solvent by vacuum rotoevaporation followed by recrystallization from $CH_2Cl_2/EtOH$ gave the product **6** (R = *n*-C_4H_9) (4.46 g, 72%; mp 70–71 °C). In a similar manner, starting with the appropriate amine, were prepared the cyclohexyl derivative **6** (R = C_6H_{11}) (mp 175–176 °C) from EtOH and the benzyl derivative **6** (R = $C_6H_5CH_2$) (mp 91–93 °C) from CH_2Cl_2/C_5H_{12}.

Chiral iminoalkoxy complexes were prepared from resolved primary amines (supplied by Norse Laboratories, Santa Barbara, CA) by using the same procedure. Use of (+)-(*S*)-2-aminobutane gave **6** (R = $CH(CH_3)C_2H_5$) (mp 113–116 °C) from $CH_2Cl_2/EtOH$, while (+)-(*R*)-α-phenylamine gave **6** (R = $CH(CH_3)C_6H_5$) (mp 132–135 °C) from EtOH, and (−)-(1*R*,2*S*,5*R*)-menthylamine gave **6** (R = $C_6H_9(CH_3)(C_3H_7)$) (mp 172–173 °C).

The bidentate amino alcohols, **7**, were prepared by reduction of the iminoalkoxy complexes. Use of sulfide treatment to remove Cu^{2+} was not necessary in these preparations, as the copper complexes were less stable than those of the tridentate ligands and could be decomposed by acidification to give the ligand hydrochlorides. In a typical preparation, **6** (R = *n*-C_4H_9) (3.1 g, 5 mmol) in anhydrous Et_2O (250 mL) was added dropwise to $LiAlH_4$ (2.3 g, 30 mmol) suspended in Et_2O (15 mL) over 2 h, followed by stirring for 1 h. The resulting yellow suspension was treated with 95% EtOH to destroy excess hydride, when a black precipitate formed. After being stirred for 12 h with a continuous flow of air, the solution became light purple, and the precipitate gray-white. Filtration followed by solvent removal gave a light purple oil, which was dissolved in Et_2O (300 mL) and dried over $MgSO_4$. Passage of gaseous HCl precipitated the ligand **7** (R = *n*-Bu) as its hydrochloride, which was recrystallized from $(CH_3)_2CO/Et_2O$ to give 2.26 g of product (71%; mp 125 °C).

The other type **7** ligands were prepared similarly giving **7** (R = C_6H_{11}) (mp 206–210 °C) from $(CH_3)_2CO/Et_2O$ and **7** (R = $C_6H_5CH_2$) (mp 194–197 °C) from $(CH_3)_2CO$. In the case of the ligands derived from optically active primary amines, the diastereomeric reduction product was recrystallized to constant optical rotation: **7** (R = $CH(CH_3)C_2H_5$) (mp 185–186 °C) from $(CH_3)_2CO/Et_2O$, $[\alpha]_D^{24} = -16.1$; **7** (R = $CH(CH_3)C_6H_5$) (mp 193–195 °C) from $(CH_3)_2CO$, $[\alpha]_D^{24} = +0.9°$; **7** (R = $C_6H_9(CH_3)(C_3H_7)$) (mp 202–204 °C) from $(CH_3)_2CO$; $[\alpha]_D^{24} = -58.7°$.

Aminoalkoxy Cu^{2+} complexes of type **8** were prepared by the reaction of $CuCl_2$ with the ligand hydrochloride in EtOH. In a typical preparation, anhydrous $CuCl_2$ (0.34 g, 2.5 mmol) in warm EtOH was added to the hydrochloride of ligand **7** (R = *n*-C_4H_9) (1.59 g, 5 mmol) followed by ethanolic KOH (0.65 g, 11.5 mmol). After being stirred for 2 h at 25 °C, the solution was cooled to 0 °C and filtered to give a purple solution. Evaporation followed by recrystallization from ethanol gave **8** (R = *n*-C_4H_9) (1.37 g, 88%); mp 109–111 °C). Other type **8** complexes were prepared by the same route.

Table I. Visible Absorption Spectra (in Dichloromethane) of Copper Complexes of Tridentate Ligands

compd	R substituent	λ_{max}, nm	ε
1a	H	640	178
3a	CH_3	638	167
3b	C_2H_5	634	163
3c	C_6H_5	620	149
3d	$CH(CH_3)_2$	614	80
2a	H	659	175
5a	CH_3	667	186
5b	C_2H_5	670	176
5c	C_6H_5	663	212
5d	$CH(CH_3)_2$	675	189

Table II. Visible Absorption Spectra (in Dichloromethane) of Copper Complexes of Bidentate Ligands

compd	R substituent	λ_{max}, nm	ε
6	*n*-C_4H_9	552	123
6	C_6H_{11}	565	135
6	$C_6H_5CH_2$	558	126
6	$CH(CH_3)C_2H_5$	545	84
6	$CH(CH_3)C_6H_5$	558	144
6	$C_6H_9(CH_3)(CH(CH_3)_2)$	587	155
8	*n*-C_4H_9	516	111
8	C_6H_{11}	518	129
8	$C_6H_5CH_2$	512	111
8	$CH(CH_3)C_2H_5$	514	126
8	$CH(CH_3)C_6H_5$	508	119
8	$C_6H_9(CH_3)(CH(CH_3)_2)$	519	176

Characterization

All new compounds were characterized by elemental analysis and mass spectra (Table S-I) and by infrared and UV–visible spectra, which were in all cases consistent with the proposed structures. Iminoalkoxy complexes of types **3** and **6** showed a strong absorption associated with the C=N bond at 1630–1670 cm^{-1}, while the aminoalkoxy complexes **5** and **8** showed NH absorption at 3120–3200 cm^{-1}. Hydrochlorides of the free tridentate aminoalkoxy ligands, **4**, showed –OH absorptions at 3205–3245 and 3405–3415 cm^{-1} and two NH absorptions in the region 2370–2710 cm^{-1}. Hydrochlorides of the bidentate ligands, **7**, showed only one –OH absorption, at 3090–3190 cm^{-1}, together with NH absorptions at 2390–2460 and 2500–2710 cm^{-1}. All compounds showed

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Table III. Summary of Crystal Data, Intensity Collection, and Structure Refinement

fw	$CuC_{26}H_{52}F_{12}N_2O_2$ (788.31)
a, A	16.225 (5)
b, A	18.021 (5)
c, A	13.248 (4)
cryst syst	orthorhombic
space group	$P2_12_12_1$
V, A^3	3873.6 (1)
d(obsd), g cm^{-3}	1.38
d(calcd), g cm^{-3}	1.371
Z	4
cryst dimens, mm	0.55 × 0.65 × 0.60
cryst faces	(110), (1$\bar{1}$0), ($\bar{1}\bar{1}$0), {111}, {110}, {010}, {011}
μ (abs coeff), cm^{-1}	6.10
radiation (λ, A)	Mo K$\bar{\alpha}$ (λ = 0.710 73)
scan speed, deg min^{-1}	θ–2θ, 1
scan range, deg	0.90, corrected for dispersion dispersion
receiving aperture, mm	5.0 × 5.0, 31 cm from crystal
bkgd	10-s stationary counts
data collecd	$+h,+k,+l$; 3.0° < 2θ < 50°
unique data ($F^2 > 3\sigma(F^2)$)	2665
no. of variables	282
data/variable ratio	9.5
final *R*	0.076
final R_w	0.057

strong C–F absorptions in the region 1150–1200 cm^{-1}.

Copper complexes gave blue solutions with one maximum absorption in the visible region, as shown in Tables I and II.

Structural Determination

Deep purple crystals of the copper complex **8** (R = menthyl) were grown slowly from dichloromethane/ethanol. An extensive preliminary photographic investigation, employing Weissenberg and precession technique,[9] indicated orthorhombic symmetry and uniquely defined the space group as $P2_12_12_1$[10] (systematic absences: $h00$ for h odd, $0k0$ for k odd, $00l$ for l odd). Crystal data are summarized in Table III.

Intensity data were collected on a Picker FACS-1 computer-controlled diffractometer with graphite-monochromatized Mo K$\bar{\alpha}$ radiation (λ = 0.710 73 Å). Accurate cell constants and an orientation matrix were obtained from a least-squares refinement of 28 intense, carefully centered reflections with 25° < 2θ < 28°.

The ω-scans of several intense, low-angle reflections, recorded as a check on crystal mosaicity, had an average width at half-height of 0.20°. Five standard reflections were recorded every 200 reflections. Their intensities showed no statistically significant change over the duration of the data collection. The raw data were corrected for background and Lorentz–polarization effects. A series of absorption correction trials[11] showed transmission factors varying from 0.975 to 0.977, so no absorption correction was applied. A total of 2665 reflections with $F^2 > 3\sigma(F^2)$ were used in preliminary solution and structure refinement. Data collection parameters are summarized in Table III.

The Cu atom and 16 of the 49 non-hydrogen atoms were located from an *E* map phased by direct methods (MULTAN). The remaining non-hydrogen atoms were found through a series of least-squares refinement and Fourier map calculations. The neutral-atom scattering factors of Cu, F, N, O, and C were taken from Cromer and Waber[12] and those for H from Stewart, Davidson, and Simpson.[13] Anomalous contributions were included for Cu and F atoms.[14] Refinement of all 49 atoms with isotropic thermal parameters and the correct model

Table IV. Atomic Positional Parameters (×10^4)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu	−69.2 (9)	−397.3 (8)	−103.0 (12)	C(1)	1537 (9)	−711 (8)	−843 (11)	C(17)	−1453 (8)	−1340 (7)	50 (12)
F(1)	3047 (5)	−735 (5)	−812 (9)	C(2)	2401 (11)	−283 (11)	−800 (14)	C(18)	−2397 (9)	−1288 (9)	308 (12)
F(2)	2463 (5)	145 (5)	24 (8)	C(3)	1462 (13)	−1196 (11)	−1843 (15)	C(19)	−1163 (9)	−2124 (8)	326 (12)
F(3)	2473 (6)	175 (6)	−1609 (7)	C(4)	1532 (7)	−1278 (7)	17 (12)	C(20)	−1398 (8)	−1317 (8)	−1203 (10)
F(4)	756 (6)	−1482 (5)	−1897 (7)	C(5)	1417 (8)	−959 (7)	1105 (9)	C(21)	−1442 (8)	−527 (8)	−1651 (10)
F(5)	2068 (6)	−1678 (6)	−1921 (8)	C(6)	1540 (10)	−1644 (8)	1874 (11)	C(22)	−1509 (11)	−595 (10)	−2791 (13)
F(6)	1559 (8)	−753 (6)	−2639 (7)	C(7)	536 (8)	5 (7)	2003 (10)	C(23)	−957 (9)	782 (8)	−1414 (11)
F(7)	−2676 (4)	−598 (4)	139 (7)	C(8)	−295 (8)	53 (8)	2562 (10)	C(24)	−187 (9)	1282 (8)	−1633 (11)
F(8)	−2887 (4)	−1750 (5)	−197 (8)	C(9)	−537 (8)	−634 (8)	3141 (11)	C(25)	340 (11)	1036 (10)	−2542 (16)
F(9)	−2514 (5)	−1397 (6)	1261 (7)	C(10)	17 (11)	−771 (8)	4074 (12)	C(26)	1184 (12)	1470 (10)	−2543 (14)
F(10)	−1553 (5)	−2676 (4)	−162 (8)	C(11)	−1441 (12)	−654 (10)	3380 (13)	C(27)	−133 (12)	1136 (9)	−3608 (14)
F(11)	−367 (4)	−2202 (4)	129 (8)	C(12)	−288 (8)	805 (8)	3150 (11)	C(28)	−452 (9)	2089 (9)	−1654 (12)
F(12)	−1227 (5)	−2229 (4)	1300 (6)	C(13)	−68 (10)	1474 (7)	2550 (10)	C(29)	−923 (10)	2310 (9)	−742 (12)
O(1)	935 (5)	−196 (5)	−841 (7)	C(14)	719 (9)	1424 (8)	2072 (11)	C(30)	−1679 (10)	1874 (9)	−490 (12)
O(2)	−1021 (5)	−815 (4)	522 (6)	C(15)	998 (10)	2108 (9)	1443 (13)	C(31)	−2164 (10)	2024 (9)	−421 (13)
N(1)	546 (5)	−615 (5)	1211 (7)	C(16)	773 (8)	732 (7)	1376 (11)	C(32)	−1397 (8)	1016 (7)	−475 (10)
N(2)	−715 (6)	−23 (6)	−1355 (8)								

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(13) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
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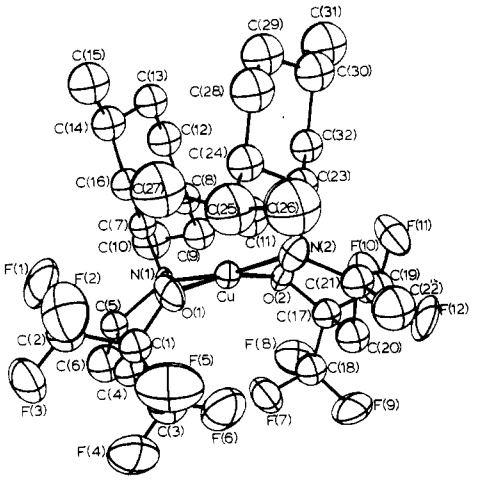

Figure 1. Perspective view of the structure of compound **8** (R = menthyl), showing the atom-numbering scheme.

absolute configuration (*R,R,S,S*)[15] gave agreement factors of R = 0.118 and R_w = 0.100.

All 52 H atoms were located in a difference Fourier synthesis, at densities ranging from 0.340 to 0.562 e Å^{-3}, and their contributions were included with idealized geometry assumed: N–H and C–H bond lengths = 1.00 Å. Isotropic thermal parameters 10% greater than those of the atoms to which they are attached were used. Several cycles of refinement, with concomitant idealization of H atom positions, were required before the model converged at R_1 = 0.0761 and R_2 = 0.0573 (282 variables, 2537 observations). The largest parameter shift in the final cycle was 0.103 esd, in the y coordinate of C(6). The error in an observation of unit weight is 4.18 e. A difference Fourier synthesis was essentially featureless; the highest peak, 0.5 (1) e Å^{-3} (−0.190, 0.240, −0.010), associated with C(30) was of no chemical significance.

Structure Description

A perspective ORTEP drawing of the molecule with the atom-numbering scheme is presented in Figure 1 and a stereoview shown in Figure 2 (supplementary material). The coordination of the Cu atom is essentially square with identical trans ligands, each containing a secondary amino nitrogen atom and an anionic alkoxy oxygen atom. The two ligands make "bite" angles at the Cu center of 93.1 (7) and 93.8 (4)°. A slight tetrahedral distortion is evident, the N(1)–Cu–N(2) and O(1)–Cu–O(2) angles being 171.7 (4) and 167.3 (4)°, respectively. The oxygen atoms O(1) and O(2) are respectively 0.25 and 0.16 Å above the weighted least-squares plane through Cu, N(1), N(2), O(1), and O(2), while the nitrogen atoms N(1) and N(2) are 0.13 and 0.19 Å below the plane.

Bond lengths and bond angles are summarized in Table V. The Cu–O bond lengths of 1.934 (8) and 1.906 (8) Å are longer than those that we determined previously[16] in the only other published structure in which a fluorinated alkoxy group is coordinated to copper(II). These values are, however, in the upper portion of the usual range for Cu–O bonds (1.85–1.96 Å). Cu–N bonds of 2.045 (9) and 2.075 (11) Å agree with those usually observed for square-planar copper(II) complexes.

Both chelates of this bis copper(II) complex have the same ring conformations and absolute configurations. Since the absolute configuration of the (−)-menthyl group is known to be 1*R*,2*S*,5*R*, the unknown site of chirality may be identified as having the *S* absolute configuration without performing the Bijvöet experiment. The secondary nitrogen of each ligand is an enantiotropic donor atom since these interconverting centers of stereoisomerism can be stabilized upon coordination, and the resulting absolute configuration assumed by the nitrogen atoms is *S*.

Table V. Selected Intramolecular Dimensions

Bond Lengths, Å			
Cu–O(1)	1.934 (8)	N(1)–C(5)	1.55 (2)
Cu–O(2)	1.906 (8)	N(1)–C(7)	1.53 (1)
Cu–N(1)	2.045 (9)	O(2)–C(17)	1.33 (1)
Cu–N(2)	2.075 (11)	C(17)–C(18)	1.57 (2)
O(1)–C(1)	1.35 (2)	C(17)–C(19)	1.53 (2)
C(1)–C(2)	1.59 (2)	C(17)–C(20)	1.66 (2)
C(1)–C(3)	1.60 (2)	C(20)–C(21)	1.54 (2)
C(1)–C(4)	1.53 (2)	C(21)–C(22)	1.52 (2)
C(4)–C(5)	1.56 (2)	N(2)–C(21)	1.54 (2)
C(5)–C(6)	1.61 (2)	N(2)–C(23)	1.50 (1)
Bond Angles, deg			
C(1)–Cu–O(2)	167.3 (4)	O(1)–C(1)–C(3)	108.9 (13)
N(1)–Cu–N(2)	171.7 (4)	O(1)–C(1)–C(4)	117.0 (12)
O(1)–Cu–N(1)	93.1 (4)	C(1)–C(4)–C(5)	116.2 (11)
O(1)–Cu–N(2)	87.7 (4)	C(4)–C(5)–C(6)	106.6 (11)
O(2)–Cu–N(1)	87.1 (3)	C(4)–C(5)–N(1)	109.9 (10)
O(2)–Cu–N(2)	93.8 (4)	N(1)–C(7)–C(8)	112.3 (10)
Cu–O(1)–C(1)	118.8 (8)	N(1)–C(7)–C(16)	103.9 (9)
Cu–O(2)–C(17)	120.2 (8)	O(2)–C(17)–C(18)	111.5 (12)
Cu–N(1)–C(5)	116.4 (8)	O(2)–C(17)–C(19)	112.4 (12)
Cu–N(1)–C(7)	115.9 (7)	O(2)–C(17)–C(20)	115.0 (12)
C(5)–N(1)–C(7)	111.3 (9)	C(17)–C(20)–C(21)	113.8 (11)
Cu–N(2)–C(21)	113.6 (9)	C(20)–C(21)–C(22)	108.1 (13)
Cu–N(2)–C(23)	119.2 (9)	C(20)–C(21)–N(2)	114.2 (11)
C(21)–N(2)–C(23)	110.8 (10)	N(2)–C(23)–C(24)	110.9 (11)
O(1)–C(1)–C(2)	107.6 (12)	N(2)–C(23)–C(32)	110.7 (13)

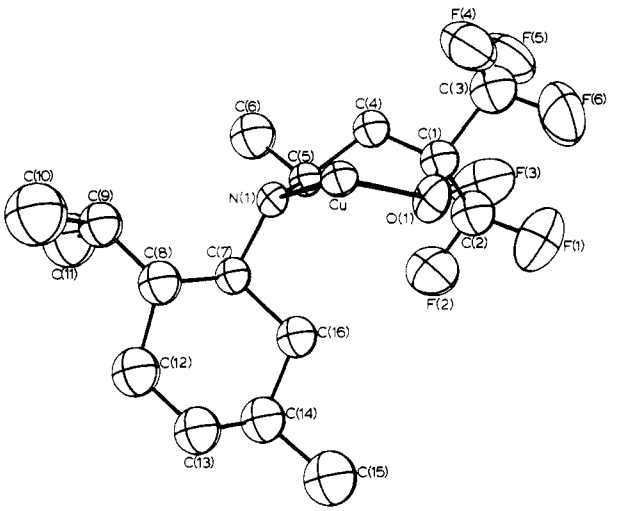

Figure 3. Conformation of the six-membered chelate ring.

The fluorinated amino alcohol ligand forms a six-membered chelate ring when coordinated to the copper center. In general, six-membered chelate rings are conformationally similar to cyclohexane except that the ligand–metal–ligand bond angle is usually near 90°, and there are three possible conformations for this type of chelate ring: a rigid chair with mirror symmetry, two enantiomeric twist-boats (λ or δ) with a 2-fold axis, and a boat with mirror symmetry.[17] In this compound, the chelate rings are in δ-skew-boat conformation, illustrated in Figure 3. This allows the methyl group on the ring to adopt a pseudoequatorial position, since a chair conformation with an equatorial methyl group is impossible because of the *S* absolute configuration at the new chiral center. The menthyl substituent on the nitrogen adopts a pseudoaxial position and an *S* absolute configuration, presumably to avoid interaction with the methyl group of the chelate ring. One of the trifluoromethyl groups attached to the chelate ring is in a

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Table VI. Circular Dichroism Spectra[a,b] for Copper(II) Complexes of Bidentate Ligands

compd (R)	λ_{max}, nm	$\Delta\epsilon$
	Imino Alcohols	
6 (*sec*-butyl)	686; 506	+2.04; −1.61
6 (phenethyl)	584; 472	−1.98; +0.14
6 (menthyl)	594; 470; 414	−4.20; +0.08; −0.11
	Amino Alcohols	
8 (*sec*-butyl)	674; 504	+6.71; −4.48
8 (phenethyl)	672; 498	+4.00; −3.47
8 (menthyl)	690; 514	+7.97; −4.04

[a] All spectra are recorded in dichloromethane. [b] Calibration was with (+)-*d*-10-camphorsulfonic acid; dichloromethane was taken as a base line.

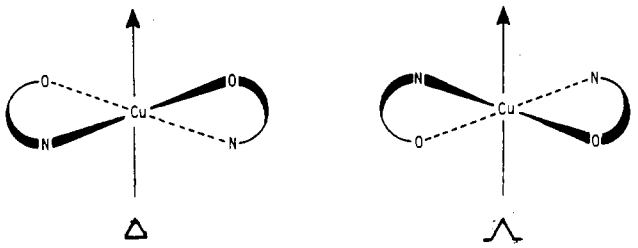


Figure 4. Two possible configurations at the metal center.

pseudoequatorial and the other in a pseudoaxial position.

CD Spectra and Configurations of Complexes

Circular dichroism (CD) spectra were recorded for the 14 copper(II) complexes discussed in this study where the ligand was chiral and optically pure. (In type **2** amino complexes, a chiral center is introduced during the hydrogenation, but no attempt was made to resolve these enantiomeric mixtures.) Complete absolute configurations are known for eight of this series: the seven imino complexes prepared from amino alcohols or amines of known structure and the amino complex derived from menthylamine, whose structure was discussed in the preceding section. We have therefore used the CD spectra to correlate the configurations of all the complexes and, in this way, to deduce the absolute configurations at the chiral centers introduced during the hydrogenation step.

The complexes fall into two groups, those of bidentate ligands and those of tridentate ligands, and CD data for the first group are given in Table VI. In each of these, there will be a vicinal effect because of the chiral center in the organic substituent. However, the magnitude of the observed CD is much too large to be completely attributed to a vicinal C* effect. Because of the planarity of the imino group, there can be no chelate ring conformational effect, so the unusually large CD must be attributed to tetrahedral distortion of the Cu^{2+} square coordination plane and the imposition of a preferred configuration at the metal center. This dominating configurational effect combined with the smaller vincinal effect of R* accounts for the observed CD spectra. Figure 4 shows the two possible configurations at the metal center, Δ and Λ.

Figure 5 shows how a difference in the absolute configuration at the α-carbon of R* may result in different configurations at the metal center.

The difference between the CD spectrum of the *sec*-butyl derivative and those of the imino complexes of the other two compounds may then be accounted for in terms of the different configuration at the C atom joined to nitrogen. Whereas the *sec*-butylamine had an *S* configuration, which would favor a α conformation for the chelate rings in the complex, the phenethyl- and menthylamines had *R* configurations and the Λ conformation would be expected in their imino complexes.

With the amino complexes of the bidentate ligands, the CD spectra (Table VI) were very similar. The hydrogenation of

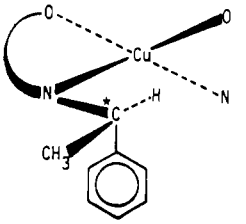


Figure 5. Differences in configuration at a metal center resulting from different absolute configurations of a substituent group.

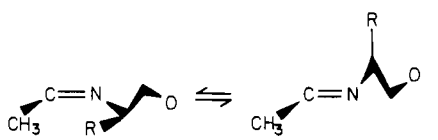
Table VII. CD Spectra for Copper(II) Complexes of Chiral Tridentate Ligands

compd (R)	λ_{max}, nm	$\Delta\epsilon$
	Imino Diol Complexes	
3a (CH_3)	695; 568	−0.93; +0.73
3b (C_2H_5)	678; 560	+0.92; −0.69
3c (C_6H_5)	674; 542	+1.60; −0.02
3d ($CH(CH_3)_2$)	672; 562	−1.66; +0.54
	Amino Diol Complexes	
5a (CH_3)	568	+0.48
5b (C_2H_5)	578	−0.60
5c (C_6H_5)	582	−0.51
5d ($CH(CH_3)_2$)	594	+0.35

the C=N bond has removed the requirement for the ring to be planar, and we would therefore expect the conformational chelate effect to be dominant in determining these spectra. By analogy with the known absolute configuration of the menthyl complex therefore, we may assign a Λ conformation to the chelate ring in each amino complex, with *S* configurations at both the new chiral C atom and the coordinated N atom.

Table VII summarizes the CD data for copper(II) complexes of the tridentate ligands. The magnitudes of the CD spectra for these complexes are much less than those observed for the bidentate chelates. This can be attributed to a lack of configurational dissymmetry at the Cu^{2+} center because of the planar environment imposed by the bridging system in these complexes, and the dissymmetry is almost certainly restricted to the conformation of the five-membered chelate ring and its asymmetric center.

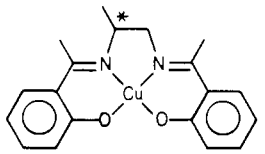
The particular ring conformation present will depend upon the absolute configuration at the asymmetric center and should dictate the sign of the CD spectra.[18] A good example of this is the observation that the CD spectra for complexes **3a** (R = CH_3) and **3b** (R = C_2H_5) are of opposite sign, while their absolute configurations are known to be *S* and *R*, respectively. However, although these complexes have opposite CD curves and we can attribute this to different chelate ring conformations, it is important to note that the two conformations, δ and λ, are interchangeable depending upon whether the R substituent is axial or equatorial.[18-20]



The relationship between these two possibilities is diastereomeric, and one should predominate in solution. Although it is well-known that the *R* equatorial conformation is preferred, inspection of molecular models shows a significant "in-plane 1,3-interaction" between the ring R substituent and the methyl group on the imine carbon atom.

Previous studies[18-20] on chiral Schiff base type complexes

(18) Downing, R. S.; Urbach, F. L. *J. Am. Chem. Soc.* **1969**, *91*, 5977.
(19) Downing, R. S.; Urbach, F. L. *J. Am. Chem. Soc.* **1968**, *90*, 5344.
(20) Farmer, R. L.; Urbach, F. L. *Inorg. Chem.* **1970**, *9*, 2562.



have proved that indeed the axial conformation predominates when this type of interaction is important. The sign of the CD curve in these analogous complexes is the same as it is in the complexes described in this work, provided that the absolute configurations of the asymmetric centers are identical. Thus, assuming an axial disposition of the R substituent on the five-membered chelate ring, we can obtain the following configurational and conformational assignments for the iminoalkoxy type **3** complexes:

complex	chelate ring conformation	abs confign at C atom
3a ($R = CH_3$)	λ	*S*
3b ($R = C_2H_5$)	δ	*R*
3c ($R = C_6H_5$)	δ	*R*
3d ($R = CH(CH_3)_2$)	λ	*S*

The situation is more complicated with the reduced, type 5, complexes, because of the presence of new chiral centers at carbon and coordinated nitrogen. One would expect the largest contribution to the CD spectra to come from the conformational effects of the five- and six-membered chelate rings, with smaller contributions from the vicinal effects of the chiral –NH*–, C*–R, and C*–CH_3. As the data in Table VII show, the sign and general shape of the CD curves in each amino diol complex are similar to those of its imino diol predecessor and we attribute this to the dominant effect of the conformation of the five-membered chelate ring. This would imply that the substituent R group is still axial.

However, the actual magnitude of the CD effect is less in each amino diol complex than in its imino diol precursor, and this may be attributed to an opposite contribution from the six-membered chelate ring. It is established that five- and six-membered chelate rings of the same conformation produce CD spectra of the same sign, with the former having the stronger effect.[21] The amino nitrogen may adopt either an *R* or *S* absolute configuration on coordination to Cu^{2+}, but one would expect the geometry with the adjacent methyl group equatorial to predominate.

A combination of the above arguments leads to the following conformational and configurational assignments in the amino diol complexes:

complex	chelate ring conformation: five	chelate ring conformation: six	abs confign: C*–R	abs confign: C*–CH_3
5a ($R = CH_3$)	λ	δ	*S*	*S*
5b ($R = C_2H_5$)	δ	λ	*R*	*R*
5c ($R = C_6H_5$)	δ	λ	*R*	*R*
5d ($R = CH(CH_3)_2$	λ	δ	*S*	*S*

Stereospecificity of Hydrogenation

The conversion of imino- to aminoalkoxy ligands produces in each case a new chiral center in the molecule, and the stereochemical course of the reaction may therefore be influenced by the presence of an adjacent chiral center. For the tridentate ligands studied, where the hydrogenation produces a type **4** ligand from a type **3** complex, we find that the reaction proceeds with a high degree of stereospecificity. Yields of the reduced ligands **4** after initial workup were in the region

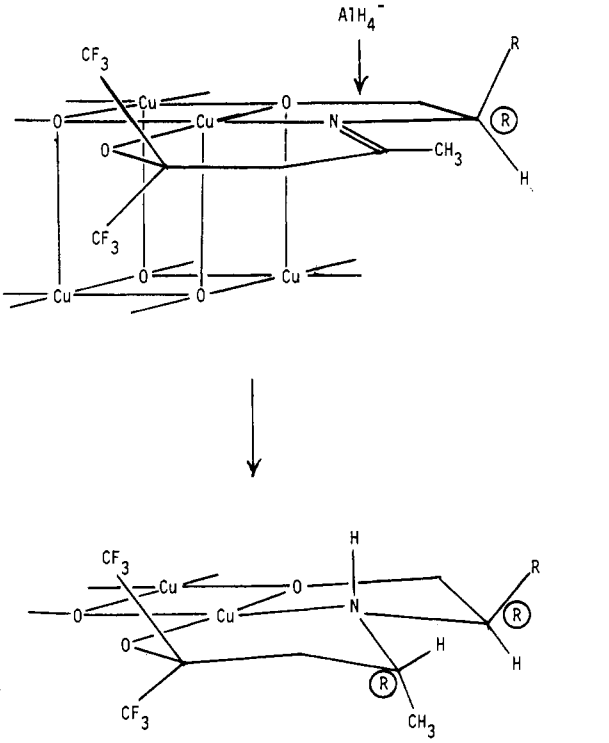


Figure 6. Attack on the C=N bond in a tetranuclear iminoalkoxy complex.

70–90%, and attempts at further purification by recrystallization showed no evidence of the separation of diastereomers. The possibility of some fortuitous fractionation of product isomers during initial workup cannot, of course, be excluded, but we feel confident that, in each case, the hydrogenation process gives a high yield of one diastereomer.

As discussed in the preceding section, the new chiral center in the tridentate amino ligands **4** has the same chirality (*R* or *S*) as that present in its iminoalkoxy precursor and this may readily be rationalized in terms of the established structures of the latter. We have previously demonstrated, on the basis of molecular weight and magnetic studies,[5] that the substituted type **3** iminoalkoxy complexes exist as associated tetranuclear units with a Cu_4O_4 "cubane" type core. Provided that these remain undissociated during the initial stages of the hydrogenation, this would clearly provide a preferred direction of attack, leading to a product in which the chirality of the new center was related to that originally present. The most sterically favorable configuration for the tetranuclear unit, shown in Figure 6, has the substituent R group directed outward from the Cu_4O_4 core, such that attack by the incoming AlH_4^- nucleophile occurs on the same side of the complex as the R group. The chirality of both centers in the product will then be the same, either *R*,*R* or *S*,*S*. If the tetranuclear unit had dissociated into dinuclear units before reaction, a predominance of the other diastereomer would be expected, since the AlH_4^- should then attack from the side of the molecule opposite to that occupied by the bulk of the substituent group.

With the complexes of chiral bidentate ligands, **6**, where aggregation into polynuclear units does not occur, a lower degree of stereospecificity in the hydrogenation would be expected. This we find to be the case, with the relative proportions of the two diastereomers varying according to the bulk of the substituent group, as has been found in other imine systems,[22] and a more detailed account of this process will be published elsewhere.

(21) Urbach, F. L.; et al. *Inorg. Chem.* **1973**, *12*, 1836, and 1840; **1974**, *13*, 587.

(22) Charles, J. P.; Christol, H.; Solladie, G. *Bull. Chim. Fr. Soc.* **1970**, *12*, 4439.

Table VIII. Calculated Parameters from Best Fit to the Bleaney–Bowers Equation for Magnetic Susceptibility

R	g	$-2J$	s^a
H	2.07	202.0	0.26
CH_3	2.00	163.9	2.3
C_2H_5	2.00	154.8	15.4
$(CH_3)_2CH$	2.04	137.0	0.03
C_6H_5	2.04	110.0	0.06

^{a} $s = [\Sigma(\chi_{calcd} - \chi_{obsd})^2] \times 10^7$.

Magnetic Properties

The type **5** dinuclear aminoalkoxy complexes of copper(II) prepared in this work form an interesting extension to the series of complexes whose magnetic properties were summarized in the Introduction. In contrast to the case of their iminoalkoxy analogues, we find no evidence for association into tetranuclear units, and magnetic properties were rationalized on dinuclear models.

Each compound studied showed a maximum value in magnetic susceptibility over the temperature range 77–300 K. Copper–copper interactions were determined from the χ_A vs. temperature data by employing the Heisenberg–Dirac–VanVleck model for the effective Hamiltonian with total spin S:

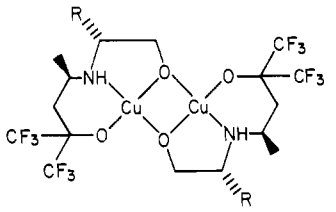
$$\mathcal{H} = 2\sum_{i>j} J_{ij} S_i S_j \qquad (1)$$

All complexes were fitted to the Bleaney–Bowers equation for a dinuclear system

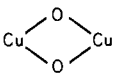
$$\chi_A = \frac{N\beta^2 g^2}{3kT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} + N_\alpha \qquad (2)$$

suggesting that a dinuclear structure exists similar to that found for complexes **2a–c**, which contain the various sized bridging chelate rings.

Each ligand in the type **4** complexes contains two chiral centers, and the positions of the substituents attached to these chiral centers will be of importance in determining ring conformations and hence magnetic properties of the complexes. It is therefore important to ensure, for comparative purposes, that each complex is of the same structural type. Since we have shown that each of the ligands contains two chiral centers of the same absolute configuration (*R,R* or *S,S*), there exists only one structural possibility for the dinuclear copper(II) complexes. The substituents can be positioned either above or below the Cu_2O_2 plane, but their relative positionings will be identical for each ligand. Thus, the complexes may form different structures with positions dictated by the absolute configuration of the ligand, but only two possibilities exist, (*R,R*:*R,R*) and *S,S*:*S,S*):



Exchange parameters for this series of compounds (Table VIII) show a general trend in which the bulkier substituents on the bridging chelate ring produce a reduction in the degree of antiferromagnetic coupling. A similar trend was previously observed[3] in the variation of bridging chelate ring size. As the ring size was reduced from seven to six to five members, the value of the isotropic exchange parameter, $|2J|$, dropped from 492 to 352 to 202 cm^{-1}. Structurally, the degree of superexchange, in these types of systems, is usually correlated to the planarity of the



bridging system. It is well-known that, if an exchange pathway involving the Cu^{2+} $d_{x^2-y^2}$ and oxygen p_x orbitals is important, distortion from planarity toward tetrahedral geometry would reduce overlap and weaken antiferromagnetic interaction. It can thus be rationalized that, as the chelate ring becomes smaller, a greater amount of torsional strain is placed on the Cu_2O_2 core and the orbital overlap producing exchange is decreased. In this series of complexes with substituted five-membered bridging chelates, the different R groups cause systematic changes in the observed magnetism, a bulkier group being associated with a weaker antiferromagnetic interaction and therefore a larger distortion of the planar geometry.

It is accepted that, for copper(II), a shift in the visible absorption band (500–800 nm) to lower energy indicates an increase in tetrahedral distortion at the metal center. Table I shows that, as the bulkier group is introduced, there is an increase in λ_{max} for these complexes. Indeed, the visible spectra parallel the trends observed in the magnetic properties and support the overall assertion that it is the metal center geometry in the Cu_2O_2 core that is of greatest importance in determining the magnetic properties of the complexes.

The most significant result of this magnetic study is to show that small systematic variations in structure produce changes in magnetic properties consistent with those found for other dinuclear complexes in which the size of the bridging chelate ring is varied.

Acknowledgment. Financial support of this work was provided by the Natural Sciences and Engineering Research Council of Canada. X-ray structural determination was made possible by the kind cooperation of Dr. N. C. Payne, of this department, in making available experimental facilities and computer programs. Variable-temperature magnetic moments were determined by Dr. A. B. P. Lever, York University.

Registry No. **1a**, 77744-95-7; **2a**, 71328-77-3; **3a**, 86350-29-0; **3b**, 86350-30-3; **3c**, 86350-31-4; **3d**, 86350-32-5; **4a**, 86335-78-6; **4b**, 86335-79-7; **4c**, 86335-80-0; **4d**, 86335-81-1; **5a**, 86350-33-6; **5b**, 86350-34-7; **5c**, 86350-35-8; **5d**, 86350-36-9; **6** (R = *n*-C_4H_9), 86350-37-0; **6** (R = C_6H_{11}), 86350-38-1; **6** (R = $CH_2C_6H_5$), 86350-39-2; **6** (R = $CH(CH_3)C_2H_5$), 86350-40-5; **6** (R = $CH(CH_3)C_6H_5$), 86350-41-6; **6** (R = $C_6H_9(CH_3)(C_3H_7)$), 86350-42-7; **7** (R = *n*-C_4H_9), 86335-82-2; **7** (R = C_6H_{11}), 86335-83-3; **7** (R = $CH_2C_6H_5$), 86335-84-4; **7** (R = $CH(CH_3)C_2H_5$), 86335-85-5; **7** (R = $CH(CH_3)C_6H_5$), 86350-14-3; **7** (R = $C_6H_9(CH_3)(C_3H_7)$), 86335-86-6; **8** (R = *n*-C_4H_9), 86364-00-3; **8** (R = C_6H_{11}), 86363-98-6; **8** (R = $CH_2C_6H_5$), 86350-43-8; **8** (R = $CH(CH_3)C_2H_5$), 86350-44-9; **8** (R = $CH(CH_3)C_6H_5$), 86350-45-0; **8** (R = $C_6H_9(CH_3)(C_3H_7)$), 86350-46-1; HFDA, 10487-10-2; 1-amino-*n*-butane, 109-73-9; aminocyclohexane, 108-91-8; benzylamine, 100-46-9; (+)-(*S*)-2-aminobutane, 513-49-5; (+)-(*R*)-2-phenethylamine, 3886-69-9; (−)-(1*R*,2*S*,5*R*)-menthylamine, 2216-54-8.

Supplementary Material Available: Listings of analytical data and mass spectra on new compounds (Table S-I), magnetic susceptibility vs. temperature data (Table S-II), nonessential bond lengths and bond angles (Table S-III), derived hydrogen atom parameters (Table S-IV), anisotropic thermal parameters (Table S-V), and structure amplitudes, as $10|F_o|$ vs. $10|F_c|$ in electrons (Table S-VI), and a stereoview of the molecule (Figure 2) (17 pages). Ordering information is given on any current masthead page.