(3) D. T. Cromer, *J. Phys. Chem.*, **61**, 1388 (1957).
(4) R. J. Williams, A. C. Larson, and D. T. Cromer, *Acta Crystallogr., Sect. B*, **28**, 858 (1972).
(5) "Gmelins Handbuch der anorganischen Chemie", Cu, Part B, Verlag Chemie, Weinheim/Bergstr., Germany, 1965, p 1006.
(6) H. Basset and A. S. Corbet, *J. Chem. Soc.*, 1660 (1924).
(7) I. N. Plaksin and C. E. Fiskova, *Izv. Akad. Nauk SSSR, Ser. Fiz. Khim.*, **10**, 228 (1938). For example, for a ratio CN:Cu = 2.4, the solubility of copper cyanide, CuCN, in aqueous sodium cyanide is 1.4 mol $l.^{-1}$, vs. 0.60 mol $l.^{-1}$ in the case of potassium cyanide.
(8) The structure of the compound $Na_2Cu(CN)_3\cdot 3H_2O$ is under investigation in our laboratory.
(9) Patterson, Fourier, and block-diagonal least-squares computations were carried out on an IBM 1130 computer with local programs derived from those of M. Laing, *Acta Crystallogr., Sect. B*, **25**, 1674 (1969). Full-matrix least-squares refinements were computed on a UNIVAC 1110 and the following programs were used: SFLS-5 by Prewitt; ORTEP-2 thermal ellipsoid plotting program by Johnson.
(10) F. H. Moore, *Acta Crystallogr.*, **16**, 1170 (1963); "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, pp 213–216.
(11) Changes in the isotropic thermal parameters for the carbon and nitrogen atoms before and after the reversal: C(1), 1.1 to 1.7; N(1), 1.7 to 1.0; C(2), 1.9 to 2.6; N(2), 2.2 to 1.4.
(12) A. F. Wells, "Structural Inorganic Chemistry", 4th ed, Clarendon Press, London, 1975.
(13) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Wiley, New York, N.Y., 1972, p 697.
(14) J. C. Pierrard, C. Kappenstein, and R. Hugel, *Rev. Chim. Miner.*, **8**, 11 (1971).

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Synthesis and Properties of Bis[*N*-R-(5-chloro-α-phenyl-2-hydroxybenzylidene)aminato]copper(II) Complexes and Crystal and Molecular Structures of the Derivatives with R = *n*-Butyl and R = Isobutyl (Two Structural Isomers)

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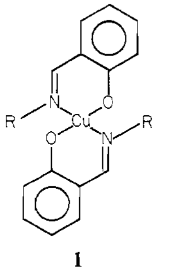
A series of bis[*N*-R-(5-chloro-α-phenyl-2-hydroxybenzylidene)aminato]copper(II) complexes, with R = alkyl (or benzyl), has been prepared and studied using magnetic, spectroscopic, and crystallographic techniques. Unlike the *N*-methyl derivative, the compounds are magnetically normal and are presumed to consist of monomeric distorted planar (R = H, ethyl, *n*-propyl, isobutyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl, benzyl) or distorted tetrahedral (R = isopropyl, *sec*-butyl, cyclohexyl) species, usually having the alkyl groups pointing to *opposite* sides of the approximate O_2N_2 ligand plane ("trans"). The *n*-butyl and isobutyl complexes are exceptional and their crystal structures were determined by single-crystal x-ray diffraction using counter techniques. The isobutyl complex exists in two distinct crystalline forms, green and red. The green isomer has the isobutyl groups pointing to the *same* side of the approximate CuO_2N_2 plane ("cis"). The *n*-butyl complex, which is dark green, has the same arrangement of the *n*-butyl groups. The red isomer of the isobutyl complex contains two crystallographically independent molecules, each having the isobutyl groups trans. The metal environment of the *n*-butyl complex (cis) is much closer to tetrahedral (dihedral angle 31°) than the green isobutyl (also cis) complex (14.5°). Crystal data for the *n*-butyl complex: space group $P2_1/c$, $Z = 4$, $a = 9.026$ (4) Å, $b = 19.52$ (3) Å, $c = 17.88$ (2) Å, $\beta = 94.46$ (7)°, $V = 3142$ Å^3, $R = 3.6\%$, 2624 reflections. Crystal data for the green isomer of the isobutyl complex: space group $P\bar{1}$, $Z = 2$, $a = 10.964$ (5) Å, $b = 11.490$ (5) Å, $c = 12.861$ (7) Å, $\alpha = 99.52$ (5)°, $\beta = 97.07$ (5)°, $\gamma = 97.59$ (6)°, $V = 1566$ Å^3, $R = 3.8\%$, 2309 reflections. Crystal data for red isomer of isobutyl complex: space group $P1$, $Z = 2$, $a = 8.900$ (2) Å, $b = 9.991$ (2) Å, $c = 17.998$ (3) Å, $\alpha = 102.54$ (4)°, $\beta = 94.61$ (4)°, $\gamma = 92.49$ (2)°, $V = 1554$ Å^3, $R = 4.8\%$, 5194 reflections.

Introduction

Copper(II) complexes with bidentate Schiff base ligands such as salicylaldimines can vary from four-coordinated distorted planar[2-10] and distorted tetrahedral[2-4,11,12] monomers, **1**, to square-pyramidal weakly linked dimers,[13] **2**. In all of the four-coordinated species for which definitive studies have been made, the nitrogen substituents have been observed to be on opposite sides of the approximate O_2N_2 plane formed by the four ligand donor atoms.



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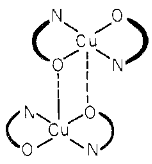

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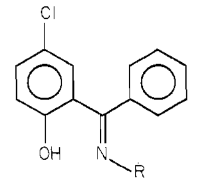

3

The complexes of *N*-R-(5-chloro-α-phenyl-2-hydroxybenzylidene) ligands (5-chloro-2-hydroxybenzophenone imines, cbp, **3**) are expected to have similar structures, but with greater steric constraints in the ligands, as in the bidentate salicylaldimine and related complexes. Structural features should be elucidated by the same physical techniques, such as spectroscopy in the ligand field region for the gross metal geometry and low-temperature magnetic moments for the oxygen-bridged metal dimers. More detailed structural information, such as a new type of isomerism in which both alkyl groups point to the same side of the O_2N_2 plane, are best obtained by x-ray studies. Thus x-ray structural data are given here for the red and green isomers of the (*i*-Bu)cbp complex and of the one form of its closest chemical relative, the *n*-butyl complex. This isomerism is of interest to compare with the monomer–dimer isomerism of the *N*-methylsalicylaldimine complex,[13] the green (known dimeric[14])–red (presumed monomeric) isomerism of the *N*-Me-cbp complex, and the diamagnetic (known planar monomeric)–paramagnetic (presumed polymeric) *N*-Me-cbp complex of nickel(II).[14] The isomerism in the other complexes implies molecular association and hence a change in the magnetic properties, while the absence of any evidence of magnetic exchange interactions in the isobutyl and the *n*-butyl complexes of cbp requires a different isomerization.

Experimental Section

Preparation of Schiff Base Ligands. 5-Chloro-2-hydroxybenzophenone (1 mmol) and the appropriate alkylamine (1.1 mmol) were heated under reflux in methanol (200 ml) for 1 h. On cooling of the mixture, yellow crystals of the Schiff bases precipitated from solution. Microanalytical data are given in Table I.[19]

Preparation of Complexes. (a) General Method. The Schiff base (0.04 mmol) was dissolved in boiling methanol (100 ml). To this solution was added copper(II) acetate monohydrate (0.02 mmol) dissolved in hot methanol (200 ml). The solution was boiled until the complex began to precipitate from solution. With the isobutyl ligand, this method produced a mixture of red and green crystals, the red form being predominant. Addition of piperidine to the hot reaction mixture also produced a mixture, with the green form predominating. Recrystallization from dichloromethane (without heating) now afforded purification of the isomers. When either the red or green isomer is recrystallized from hot benzene, the product is predominantly the red isomer with a smaller proportion of green crystals.

(b) Complexes with R = *n*-Pentyl or Longer Alkyl Chains. The Schiff base ligands were synthesized as before but were reacted with copper acetate without first being isolated from the methanol solution.

Preparation of Crystals for X-Ray Study. Large green crystals were obtained from an unheated dichloromethane solution of the green isomer. The red isobutyl and the *n*-butyl complexes were similarly obtained as large red and large dark green crystals from dichloromethane.

Room-temperature magnetic moments, μ_{RT} (Table I[19]) were determined on a Gouy balance and low-temperature moments (Table II[19]) on a Foner vibrating-sample magnetometer. We thank Professor H. B. Gray for access to the magnetometer and Dr A. Schweizer for assistance with the apparatus.

Reflectance spectra were obtained using a Zeiss PMQII spectrophotometer with an RA3 reflectance attachment.

Infrared spectra were measured on a Perkin-Elmer 521 spectrometer using Nujol and hexachlorobutadiene mulls of the compounds.

Crystal data for the *n*-butyl complex: $CuCl_2O_2N_2C_{34}H_{34}$, mol wt 637, space group $P2_1/c$, $Z = 4$, $a = 9.026$ (4) Å $b = 19.52$ (3) Å, $c = 17.88$ (2) Å, $\beta = 94.46$ (7)°, $V = 3142$ Å^3, $d_{calcd} = 1.35$ g cm^{-3}, $d_{obsd} = 1.36$ g cm^{-3}, μ(Mo Kα) = 9.3 cm^{-1}; crystal dimensions with distances in mm of faces from centroid: $(\bar{1}00)$ 0.32, $(\bar{1}01)$ 0.26, (101) 0.25, $(\bar{1}0\bar{1})$ 0.25, (011) 0.16, $(0\bar{1}\bar{1})$ 0.16, $(01\bar{1})$ 0.145, $(0\bar{1}1)$ 0.145, (001) 0.16.

Crystal data for the isobutyl complex, green isomer: mol wt 637, space group $P\bar{1}$, $Z = 2$, $a = 10.964$ (5) Å, $b = 11.490$ (5) Å, $c = 12.861$ (7) Å, $\alpha = 99.52$ (5)°, $\beta = 97.07$ (5)°, $\gamma = 97.59$ (6)°, $V = 1566$ Å^3, $d_{calcd} = 1.35$ g cm^{-3}, $d_{obsd} = 1.33$ g cm^{-3}, μ(Mo Kα) = 9.3 cm^{-1}; crystal dimensions and mm from centroid: (100) 0.10, $(\bar{1}00)$ 0.10, (010) 0.09, $(0\bar{1}0)$ 0.09, (001) 0.14, $(00\bar{1})$ 0.14.

Crystal data for the isobutyl complex, red isomer: mol wt 637, space group $P1$, $Z = 2$, $a = 8.900$ (2) Å, $b = 9.991$ (2) Å, $c = 17.998$ (3) Å, $\alpha = 102.54$ (4)°, $\beta = 94.61$ (4)°, $\gamma = 92.49$ (2)°, $V = 1554$ Å^3, $d_{calcd} = 1.31$ g cm^{-3}, $d_{obsd} = 1.32$ g cm^{-3}, μ(Mo Kα) = 9.3 cm^{-1}; crystal dimensions and mm from centroid: (100) 0.25, $(\bar{1}00)$ 0.25, (010) 0.20, $(0\bar{1}0)$ 0.20, (011) 0.24, $(0\bar{1}\bar{1})$ 0.24, $(01\bar{1})$ 0.17, $(0\bar{1}1)$ 0.17.

For each crystal, the Enraf–Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and also approximate cell dimensions. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of each crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of Data. Diffraction data were collected at 292 K on an Enraf–Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $0° < 2\theta < 50°$, $0° < 2\theta < 46°$, and $0° < 2\theta < 52°$, respectively, for the *n*-butyl, green isobutyl, and red isobutyl complexes. For the red isobutyl complex, both hkl and $\bar{h}\bar{k}\bar{l}$ data were collected. Scan widths (SW) were calculated from the formula $SW = A + B \tan \theta$ where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1 and Kα_2 splitting. The values of A and B were 0.60 and 0.30°, respectively. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count (NC) is then calculated as NC = TOT − 2(BG1 + BG2) where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on a rapid prescan, such reflections being rejected automatically by the computer.

The intensities of four standard reflections, monitored for each crystal at 100 reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and then for absorption. After averaging of the intensities of equivalent reflections, the data were reduced to 3591 independent intensities for the *n*-butyl complex, 2576 for the green isobutyl complex, and 5625 for the red isobutyl complex, of which 2624 for *n*-butyl, 2309 for green isobutyl, and 5194 for red isobutyl had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[15] These data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structures. The positions of the Cu atoms in the *n*-butyl and green isobutyl complexes and the Cl atoms and one ligand oxygen of the green isobutyl complex were determined from a three-dimensional Patterson function calculated from all intensity data. These positional coordinates were used in the phasing of subsequent electron density maps. The intensities of some positions of the Patterson vectors calculated for the red isobutyl complex did not conform to those expected for space group $P\bar{1}$. The assumption of space group $P1$ permitted determination of the coordinates of two independent Cu and four Cl atoms. The assumption of space group $P1$ is supported by the sparsity of accidentally absent reflections and confirmed by the subsequent solution of the structure and by failure to obtain a solution in space group $P\bar{1}$. The intensity data for each of the crystals were phased sufficiently well by the above-mentioned positional coordinates to permit location of the remaining nonhydrogen atoms.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were taken as $[2F_o/\sigma(F_o)^2]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[16] and those for hydrogen from Stewart et al.[17] The effects of anomalous dispersion for all nonhydrogen atoms were included in F_c using the values of Cromer and Ibers[18] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. To minimize computer time, the initial calculations were carried out on the first 1000 reflections collected.

The high-energy radiation used predetermines that the right and wrong choices for the absolute configuration will not greatly affect the refinement of the red isobutyl complex and therefore that the choice cannot safely be based on the intensities of a few reflections. Both possible configurations were refined on the hkl and $\bar{h}\bar{k}\bar{l}$ data. The absolute configuration was chosen on the basis of slightly better agreement ($R = 5.1$ vs. 5.2%) and the choice confirmed by a detailed comparison of observed and calculated intensities of both weak and strong reflections; this check was repeated after completion of final refinement, but the $\bar{h}\bar{k}\bar{l}$ reflections were not however included in the final refinement.

Anisotropic temperature factors were introduced for all atoms except the nonalkyl carbon atoms of the red isobutyl complex. After convergence, nonmethyl hydrogen atoms were inserted at their calculated positions, included in two cycles of full-matrix least-squares refinement, and then fixed in subsequent cycles. The models converged with $R = 3.6$, $R_w = 3.9\%$; $R = 3.8$, $R_w = 4.6\%$; and $R = 4.8$, $R_w = 6.8\%$ for the *n*-butyl, green isobutyl, and red isobutyl complexes, respectively. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave $R = 4.6$, 4.4, 5.4% for *n*-butyl, green isobutyl, and red isobutyl complexes; on this basis, it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference map was featureless. Tables of the observed structure factors, least-squares planes, microanalyses, melting points, and magnetic moments are available.[19]

Results and Discussion

Final positional and thermal parameters for the *n*-butyl,

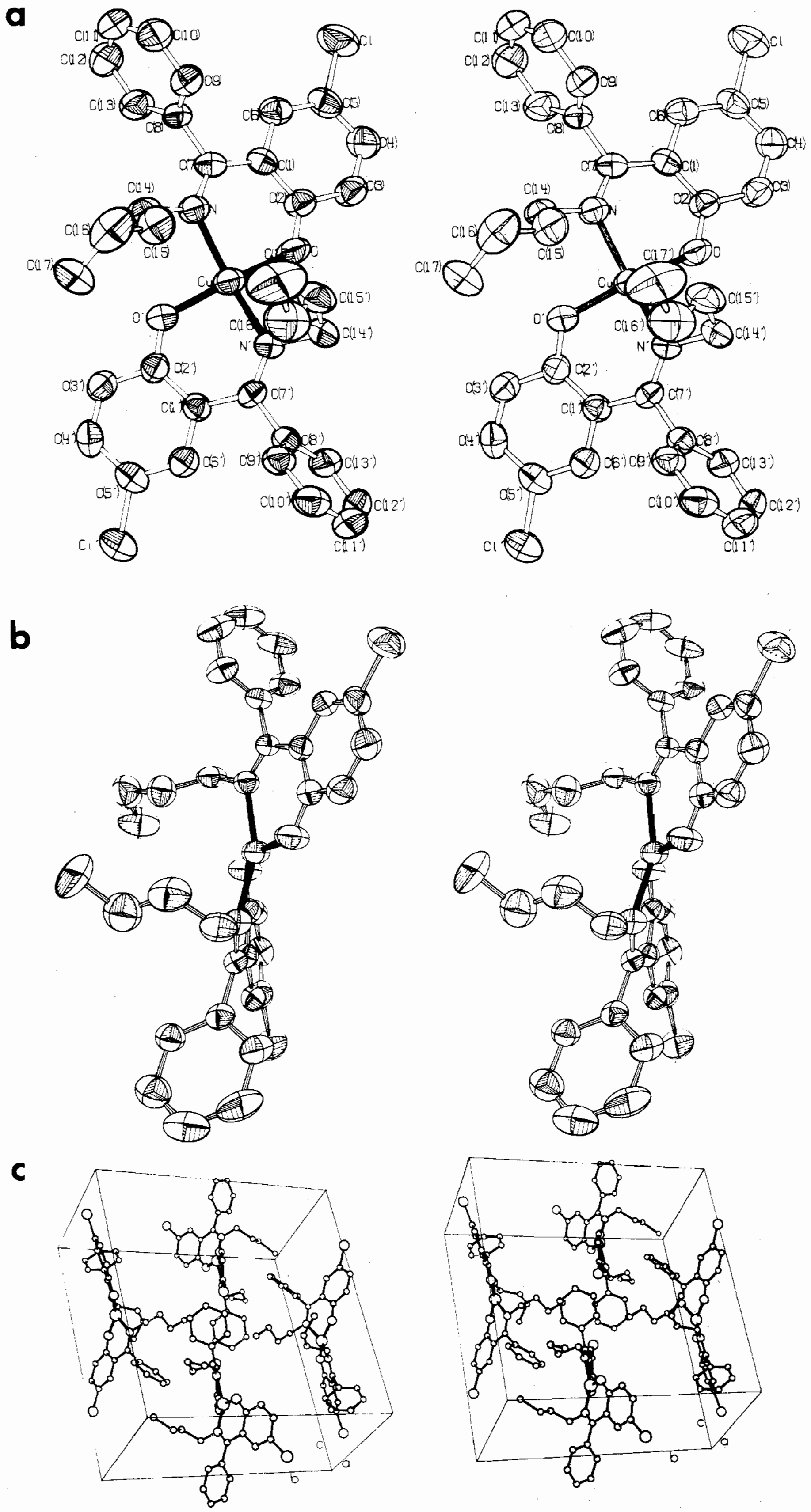

Figure 1. Stereoscopic pair views of Cu((*n*-Bu)cbp)$_2$: (a) top view; (b) side view; (c) molecular packing.

green isobutyl, and red isobutyl complexes are given in Table III. Tables IV and V contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. The atom-labeling systems are analogous for the four different molecules (*n*-butyl, green isobutyl, and the two independent red isobutyl molecules), and in the diagrams (Figures 1–3), only the *n*-butyl molecule is labeled in detail.

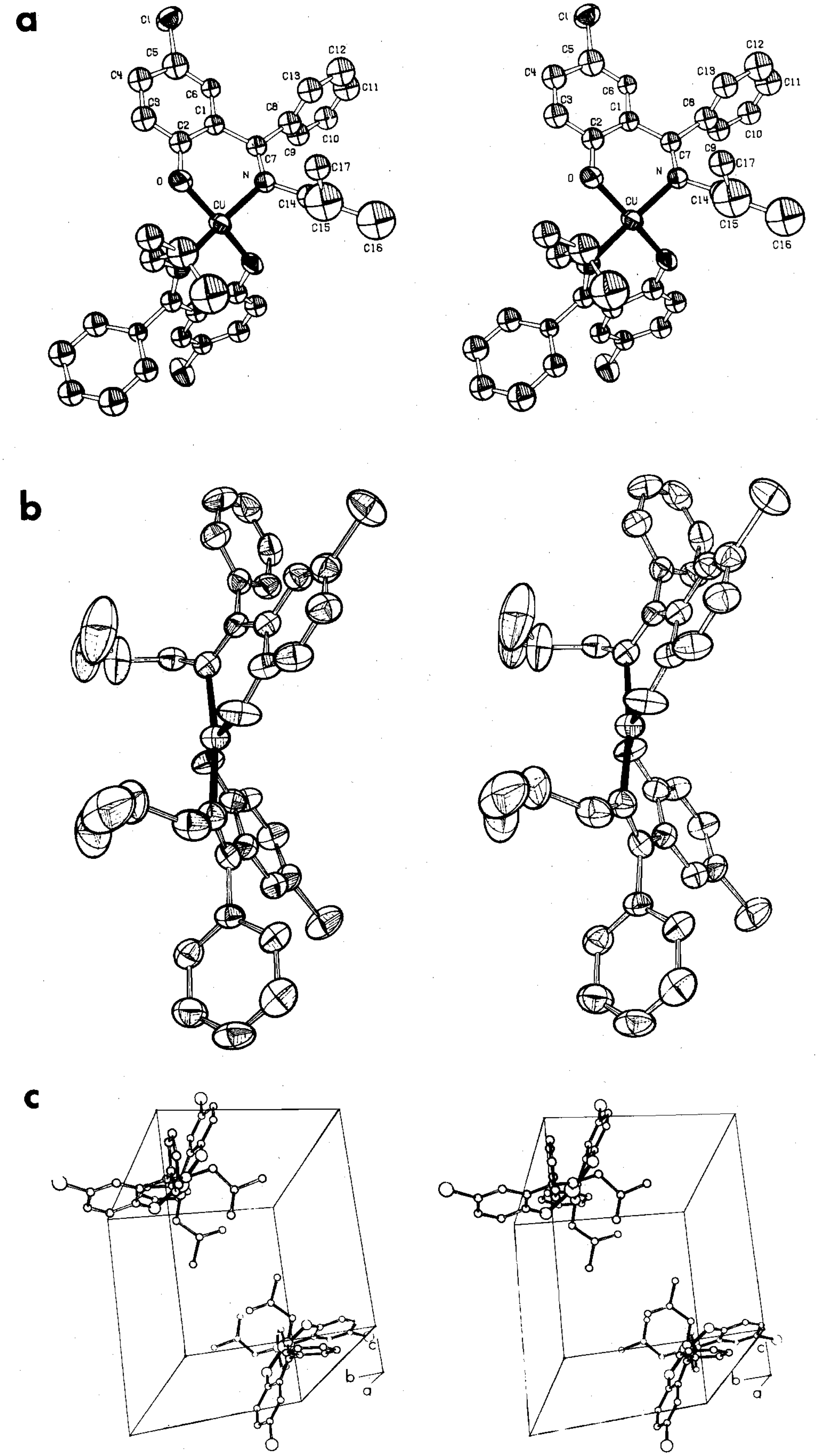

Figure 2. Stereoscopic pair views of the green isomer of Cu((*i*-Bu)cbp)$_2$: (a) top view; (b) side view; (c) molecular packing.

Figure 1a, b shows front and side stereopair views of the *n*-butyl molecule, illustrating the unprecedented arrangement of the *n*-butyl chains on the same side of the O_2N_2 ligand plane (cis). Figure 1c shows the molecular packing in the unit cell. The cis arrangement of the *n*-butyl groups would allow close intermolecular approaches to form an oxygen-bridged dimer,

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

a. Cu((*n*-Bu)cbp)$_2$

Atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.730 14 (9)	0.384 69 (4)	0.128 81 (5)	0.0140 (1)	0.002 06 (2)	0.004 26 (3)	0.000 26 (9)	−0.001 00 (9)	−0.000 25 (5)
Cl	0.284 5 (2)	0.094 6 (1)	−0.006 5 (1)	0.0226 (3)	0.003 80 (6)	0.007 54 (10)	−0.006 8 (2)	−0.003 9 (3)	−0.001 3 (1)
Cl′	1.137 4 (2)	0.687 4 (1)	0.044 4 (1)	0.0193 (3)	0.003 76 (6)	0.006 02 (8)	−0.003 8 (2)	0.005 2 (3)	0.001 8 (1)
O	0.535 7 (5)	0.358 9 (2)	0.093 4 (3)	0.0158 (7)	0.002 3 (1)	0.006 0 (2)	0.001 3 (5)	−0.005 7 (6)	−0.001 0 (3)
O′	0.927 2 (5)	0.415 6 (2)	0.126 1 (3)	0.0142 (7)	0.002 2 (1)	0.006 1 (2)	0.000 3 (5)	0.002 6 (6)	−0.000 5 (3)
N	0.793 4 (6)	0.287 5 (2)	0.144 7 (3)	0.0137 (8)	0.002 3 (1)	0.003 5 (2)	0.000 7 (6)	−0.001 0 (6)	−0.000 1 (3)
N′	0.663 3 (5)	0.477 6 (2)	0.157 7 (3)	0.0113 (7)	0.002 4 (1)	0.004 1 (2)	0.000 1 (5)	0.001 5 (7)	−0.000 2 (3)
C(1)	0.571 6 (7)	0.236 9 (3)	0.083 1 (3)	0.0128 (9)	0.002 2 (2)	0.003 0 (2)	−0.001 4 (7)	0.001 1 (8)	0.000 0 (3)
C(2)	0.486 7 (7)	0.298 1 (3)	0.075 4 (3)	0.0148 (10)	0.002 5 (2)	0.003 0 (2)	−0.000 6 (7)	−0.001 3 (8)	0.000 1 (3)
C(3)	0.337 9 (7)	0.292 5 (3)	0.044 4 (4)	0.0151 (10)	0.002 8 (2)	0.004 7 (3)	0.001 3 (8)	−0.001 8 (9)	0.000 2 (4)
C(4)	0.275 9 (7)	0.232 2 (4)	0.019 6 (4)	0.0140 (10)	0.003 7 (2)	0.004 8 (3)	−0.002 5 (8)	−0.003 8 (10)	0.000 5 (4)
C(5)	0.360 6 (7)	0.173 1 (3)	0.025 8 (4)	0.0151 (11)	0.003 0 (2)	0.004 2 (3)	−0.003 4 (8)	−0.000 3 (9)	−0.000 3 (4)
C(6)	0.503 8 (7)	0.175 1 (3)	0.056 5 (3)	0.0155 (10)	0.002 6 (2)	0.003 0 (2)	−0.000 2 (7)	0.001 8 (8)	0.000 3 (3)
C(7)	0.720 4 (7)	0.233 3 (3)	0.121 4 (3)	0.0146 (9)	0.002 0 (1)	0.002 8 (2)	−0.000 3 (7)	0.000 9 (8)	−0.000 0 (3)
C(8)	0.788 3 (7)	0.163 7 (3)	0.133 1 (3)	0.0124 (9)	0.002 0 (2)	0.003 9 (2)	−0.000 3 (6)	0.000 4 (8)	−0.000 7 (3)
C(9)	0.763 0 (8)	0.125 7 (3)	0.197 3 (4)	0.0167 (11)	0.003 2 (2)	0.004 6 (3)	0.002 0 (8)	0.001 7 (9)	0.001 6 (4)
C(10)	0.829 7 (9)	0.061 4 (4)	0.208 5 (5)	0.0188 (13)	0.003 4 (2)	0.008 1 (4)	0.000 6 (9)	−0.000 2 (12)	0.003 6 (5)
C(11)	0.917 6 (8)	0.035 4 (4)	0.155 3 (5)	0.0170 (12)	0.002 7 (2)	0.009 6 (5)	0.002 2 (9)	0.001 9 (13)	0.000 2 (5)
C(12)	0.944 0 (9)	0.073 2 (4)	0.093 0 (5)	0.0213 (13)	0.003 1 (2)	0.008 8 (4)	0.000 8 (9)	0.009 6 (12)	−0.002 0 (5)
C(13)	0.878 1 (8)	0.137 3 (3)	0.082 6 (4)	0.0197 (12)	0.002 9 (2)	0.004 9 (3)	0.000 3 (8)	0.006 5 (10)	−0.000 7 (4)
C(14)	0.937 2 (7)	0.281 4 (3)	0.190 4 (4)	0.0151 (10)	0.002 1 (2)	0.005 8 (3)	0.001 7 (7)	−0.003 5 (10)	−0.000 2 (4)
C(15)	0.920 5 (8)	0.303 9 (4)	0.270 1 (4)	0.0166 (12)	0.004 7 (3)	0.004 8 (3)	0.000 2 (10)	−0.002 3 (10)	−0.001 1 (5)
C(16)	1.064 6 (10)	0.306 9 (4)	0.318 9 (5)	0.0249 (15)	0.005 2 (3)	0.005 3 (3)	0.003 5 (12)	−0.005 9 (12)	−0.001 5 (6)
C(17)	1.182 5 (10)	0.354 3 (4)	0.290 9 (6)	0.0213 (14)	0.004 5 (3)	0.009 2 (5)	−0.005 4 (11)	0.000 3 (14)	−0.001 0 (7)
C(1′)	0.879 0 (6)	0.536 7 (3)	0.119 3 (3)	0.0116 (8)	0.002 4 (2)	0.002 5 (2)	−0.000 2 (7)	0.001 1 (7)	−0.000 1 (3)
C(2′)	0.967 8 (7)	0.477 5 (3)	0.111 6 (3)	0.0123 (9)	0.002 6 (2)	0.003 2 (2)	0.000 4 (7)	0.000 0 (8)	−0.000 7 (4)
C(3′)	1.113 5 (7)	0.487 1 (3)	0.088 3 (4)	0.0141 (10)	0.002 9 (2)	0.004 0 (3)	0.001 6 (8)	0.000 6 (9)	−0.001 2 (4)
C(4′)	1.164 9 (7)	0.549 6 (3)	0.068 1 (4)	0.0116 (9)	0.004 1 (2)	0.004 0 (3)	−0.001 1 (8)	0.002 5 (8)	−0.001 2 (4)
C(5′)	1.074 5 (7)	0.607 2 (3)	0.072 8 (4)	0.0143 (9)	0.003 0 (2)	0.003 4 (2)	−0.002 4 (8)	0.001 9 (8)	0.000 0 (4)
C(6′)	0.936 6 (7)	0.601 0 (3)	0.098 9 (3)	0.0137 (9)	0.002 4 (2)	0.003 4 (2)	0.000 8 (7)	0.000 5 (8)	−0.000 4 (3)
C(7′)	0.733 5 (6)	0.534 6 (3)	0.149 3 (3)	0.0128 (9)	0.002 0 (2)	0.002 9 (2)	0.000 6 (7)	−0.000 2 (8)	0.000 2 (3)
C(8′)	0.670 6 (6)	0.602 1 (3)	0.173 2 (3)	0.0115 (8)	0.002 2 (2)	0.003 5 (2)	−0.000 3 (6)	0.003 6 (7)	0.000 6 (3)
C(9′)	0.718 9 (7)	0.630 6 (3)	0.242 7 (3)	0.0169 (10)	0.002 5 (2)	0.003 3 (2)	−0.001 0 (7)	0.003 6 (8)	−0.000 6 (3)
C(10′)	0.657 7 (8)	0.691 2 (3)	0.264 5 (4)	0.0202 (12)	0.003 0 (2)	0.004 5 (3)	−0.001 9 (9)	0.006 2 (9)	−0.000 8 (4)
C(11′)	0.553 4 (8)	0.725 0 (3)	0.220 8 (5)	0.0200 (12)	0.002 8 (2)	0.007 9 (4)	−0.000 2 (9)	0.009 5 (11)	−0.001 2 (5)
C(12′)	0.508 7 (8)	0.698 5 (4)	0.152 7 (5)	0.0131 (11)	0.003 3 (2)	0.009 1 (4)	0.002 8 (8)	0.000 7 (11)	0.003 0 (5)
C(13′)	0.565 3 (7)	0.636 4 (3)	0.126 3 (4)	0.0146 (10)	0.002 5 (2)	0.005 6 (3)	0.000 2 (7)	0.000 1 (10)	0.000 4 (4)
C(14′)	0.523 9 (7)	0.475 9 (3)	0.197 2 (4)	0.0131 (10)	0.002 8 (2)	0.006 3 (3)	−0.000 7 (8)	0.003 2 (10)	−0.000 8 (4)
C(15′)	0.541 2 (8)	0.434 8 (4)	0.267 9 (4)	0.0202 (12)	0.003 5 (2)	0.006 8 (4)	−0.003 1 (9)	0.008 2 (11)	0.001 4 (5)
C(16′)	0.647 6 (10)	0.462 6 (5)	0.327 2 (5)	0.0341 (17)	0.005 4 (3)	0.005 9 (3)	−0.002 8 (13)	0.011 4 (13)	0.000 9 (6)
C(17′)	0.672 8 (14)	0.417 3 (5)	0.399 4 (5)	0.0540 (26)	0.006 2 (4)	0.005 1 (4)	0.001 6 (18)	0.009 3 (16)	0.004 8 (6)

Atom	*x*	*y*	*z*	*B*, Å^2	Atom	*x*	*y*	*z*	*B*, Å^2
H(3)	0.280 (5)	0.331 (2)	0.046 (2)	4 (1)	H(3′)	1.166 (6)	0.448 (3)	0.084 (3)	5 (1)
H(4)	0.176 (5)	0.229 (2)	0.001 (3)	4 (1)	H(4′)	1.257 (5)	0.554 (2)	0.055 (3)	4 (1)
H(6)	0.565 (5)	0.133 (2)	0.057 (2)	3 (1)	H(6′)	0.887 (6)	0.640 (3)	0.102 (3)	5 (1)
H(9)	0.700 (6)	0.148 (3)	0.231 (3)	7 (1)	H(9′)	0.806 (6)	0.600 (3)	0.276 (3)	5 (1)
H(10)	0.811 (6)	0.034 (3)	0.261 (3)	8 (2)	H(10′)	0.692 (7)	0.718 (3)	0.316 (3)	8 (2)
H(11)	0.959 (7)	−0.013 (3)	0.156 (4)	10 (2)	H(11′)	0.515 (7)	0.768 (3)	0.243 (4)	8 (2)
H(12)	0.989 (7)	0.051 (3)	0.046 (4)	10 (2)	H(12′)	0.455 (6)	0.715 (3)	0.121 (3)	5 (1)
H(13)	0.890 (5)	0.160 (2)	0.035 (3)	5 (1)	H(13′)	0.531 (6)	0.614 (2)	0.080 (3)	4 (1)
H(14A)	1.020 (6)	0.313 (3)	0.171 (3)	7 (2)	H(14′A)	0.490 (5)	0.516 (2)	0.214 (3)	4 (1)
H(14B)	0.972 (5)	0.240 (2)	0.190 (2)	4 (1)	H(14′B)	0.451 (6)	0.460 (3)	0.162 (3)	5 (1)
H(15A)	0.849 (6)	0.280 (3)	0.296 (3)	6 (2)	H(15′A)	0.572 (6)	0.387 (3)	0.256 (3)	5 (1)
H(15B)	0.881 (7)	0.349 (3)	0.268 (3)	7 (2)	H(15′B)	0.431 (7)	0.431 (3)	0.293 (4)	8 (2)
H(16A)	1.094 (6)	0.270 (3)	0.324 (3)	7 (2)	H(16′A)	0.604 (9)	0.500 (4)	0.337 (5)	11 (3)
H(16B)	1.028 (7)	0.331 (3)	0.370 (4)	8 (2)	H(16′B)	0.730 (6)	0.469 (3)	0.308 (3)	5 (1)

b. Cu((*i*-Bu)cbp)$_2$, Green Isomer

Atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.795 04 (7)	0.151 52 (7)	0.219 86 (6)	0.006 77 (6)	0.006 73 (6)	0.006 45 (5)	0.0029 (1)	0.000 81 (9)	0.003 52 (9)
Cl	0.625 5 (2)	0.379 8 (2)	−0.255 8 (1)	0.012 1 (2)	0.014 9 (2)	0.007 3 (1)	0.0015 (3)	0.002 0 (3)	0.009 7 (2)
Cl(2)	0.874 5 (2)	0.445 4 (1)	0.225 1 (2)	0.011 8 (2)	0.006 1 (1)	0.016 3 (2)	0.0032 (3)	0.006 3 (3)	0.002 1 (3)
O(1)	0.862 5 (4)	0.248 6 (4)	0.130 6 (3)	0.006 9 (4)	0.012 3 (4)	0.010 1 (3)	0.0039 (7)	0.000 5 (6)	0.013 1 (6)
O(2)	0.724 0 (3)	0.028 4 (3)	0.283 6 (3)	0.008 3 (4)	0.007 1 (3)	0.009 5 (3)	0.0063 (6)	0.005 6 (6)	0.006 7 (5)
N(1)	0.629 6 (4)	0.201 4 (4)	0.187 8 (3)	0.007 1 (4)	0.006 3 (4)	0.005 6 (3)	0.0032 (7)	0.002 8 (7)	0.002 1 (6)
N(2)	0.964 0 (4)	0.118 3 (4)	0.270 2 (4)	0.006 7 (5)	0.006 2 (4)	0.006 3 (4)	0.0001 (8)	0.000 2 (7)	0.002 7 (6)
C(1)	0.672 3 (5)	0.265 1 (5)	0.023 2 (4)	0.006 5 (5)	0.005 8 (5)	0.005 5 (4)	0.0026 (9)	0.002 4 (8)	0.002 5 (7)
C(2)	0.803 2 (5)	0.278 5 (5)	0.048 1 (5)	0.007 4 (6)	0.006 4 (5)	0.007 5 (5)	0.0030 (10)	0.002 7 (9)	0.004 1 (8)
C(3)	0.873 4 (5)	0.331 5 (5)	−0.022 0 (5)	0.006 4 (6)	0.009 0 (6)	0.009 6 (5)	0.0037 (10)	0.003 5 (9)	0.007 0 (9)
C(4)	0.821 2 (5)	0.362 8 (5)	−0.112 7 (5)	0.008 2 (6)	0.008 7 (6)	0.008 2 (5)	0.0037 (10)	0.005 8 (9)	0.006 2 (8)
C(5)	0.692 9 (6)	0.343 6 (5)	−0.138 1 (5)	0.010 3 (6)	0.007 2 (5)	0.006 4 (4)	0.0046 (10)	0.004 4 (9)	0.004 0 (8)
C(6)	0.619 9 (5)	0.296 9 (5)	−0.071 4 (4)	0.007 0 (6)	0.007 7 (5)	0.006 0 (4)	0.0028 (9)	0.002 1 (8)	0.002 5 (8)
C(7)	0.589 2 (5)	0.230 0 (5)	0.097 1 (4)	0.006 8 (5)	0.004 9 (5)	0.005 6 (4)	0.0032 (9)	0.000 9 (8)	0.000 6 (7)
C(8)	0.452 2 (5)	0.225 7 (5)	0.065 9 (4)	0.007 3 (5)	0.007 1 (5)	0.004 6 (4)	0.0031 (9)	0.003 1 (8)	0.002 3 (7)

Table III (*Continued*)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(9)	0.377 4 (5)	0.116 1 (5)	0.030 6 (5)	0.007 6 (6)	0.009 6 (6)	0.006 0 (5)	0.0047 (10)	0.002 6 (9)	0.002 3 (9)
C(10)	0.250 1 (6)	0.107 4 (6)	0.001 5 (5)	0.007 6 (6)	0.013 0 (7)	0.006 3 (5)	−0.0001 (12)	0.001 1 (9)	0.001 2 (10)
C(11)	0.198 8 (6)	0.209 6 (7)	0.008 2 (5)	0.007 5 (6)	0.018 9 (9)	0.007 7 (5)	0.0083 (13)	−0.000 9 (10)	0.003 0 (12)
C(12)	0.270 1 (6)	0.318 5 (6)	0.041 6 (6)	0.010 5 (7)	0.012 8 (7)	0.011 4 (6)	0.0140 (11)	0.001 1 (11)	0.004 1 (11)
C(13)	0.397 9 (6)	0.327 7 (5)	0.069 4 (5)	0.010 1 (6)	0.008 5 (6)	0.008 4 (5)	0.0059 (10)	0.000 7 (10)	0.003 0 (9)
C(14)	0.547 2 (5)	0.191 8 (5)	0.268 7 (4)	0.006 8 (6)	0.007 7 (5)	0.005 8 (4)	0.0040 (9)	0.001 3 (8)	0.003 5 (8)
C(15)	0.584 0 (8)	0.292 7 (7)	0.364 9 (6)	0.020 5 (10)	0.012 6 (8)	0.010 2 (6)	0.0017 (16)	0.014 2 (12)	−0.002 9 (12)
C(16)	0.493 3 (9)	0.272 7 (8)	0.446 6 (6)	0.029 6 (12)	0.017 6 (11)	0.010 3 (6)	0.0024 (20)	0.022 2 (13)	−0.000 6 (14)
C(17)	0.611 4 (12)	0.408 2 (9)	0.352 4 (9)	0.049 4 (20)	0.012 9 (10)	0.020 9 (10)	−0.0189 (24)	0.036 7 (21)	−0.010 4 (17)
C(1′)	0.890 5 (5)	−0.088 4 (5)	0.273 1 (4)	0.006 1 (5)	0.005 6 (5)	0.005 3 (4)	0.0024 (9)	0.001 0 (8)	0.001 7 (7)
C(2′)	0.764 6 (5)	−0.074 8 (5)	0.275 4 (4)	0.007 9 (6)	0.006 8 (5)	0.005 4 (4)	0.0029 (9)	0.001 4 (8)	0.003 5 (7)
C(3′)	0.678 3 (5)	−0.179 1 (5)	0.271 4 (5)	0.007 1 (6)	0.008 1 (5)	0.008 3 (5)	0.0048 (9)	0.003 9 (9)	0.005 6 (8)
C(4′)	0.710 9 (5)	−0.290 1 (5)	0.257 9 (5)	0.006 5 (6)	0.007 3 (5)	0.010 0 (5)	0.0002 (10)	0.003 4 (9)	0.004 7 (9)
C(5′)	0.833 6 (5)	−0.301 4 (5)	0.249 7 (5)	0.008 7 (6)	0.004 9 (5)	0.007 2 (5)	0.0024 (9)	0.001 3 (9)	0.000 2 (8)
C(6′)	0.922 3 (5)	−0.204 1 (5)	0.260 1 (4)	0.007 2 (6)	0.007 2 (5)	0.005 9 (4)	0.0021 (9)	0.000 9 (8)	0.001 8 (8)
C(7′)	0.987 9 (5)	0.014 1 (5)	0.285 5 (4)	0.007 2 (5)	0.006 4 (5)	0.004 7 (4)	0.0012 (9)	0.001 7 (8)	0.002 0 (7)
C(8′)	1.119 2 (5)	−0.007 7 (4)	0.315 1 (4)	0.005 5 (5)	0.005 1 (5)	0.005 7 (4)	0.0011 (8)	0.000 8 (8)	0.002 9 (7)
C(9′)	1.162 1 (5)	−0.013 7 (5)	0.419 5 (4)	0.006 5 (5)	0.009 5 (6)	0.006 4 (4)	0.0045 (10)	0.002 5 (8)	0.003 5 (8)
C(10′)	1.280 2 (6)	−0.038 5 (6)	0.446 1 (5)	0.008 5 (6)	0.012 4 (7)	0.007 5 (5)	0.0059 (11)	0.001 4 (9)	0.006 3 (9)
C(11′)	1.354 9 (5)	−0.057 9 (6)	0.369 2 (5)	0.006 3 (6)	0.010 3 (6)	0.010 9 (6)	0.0059 (10)	0.002 0 (10)	0.005 2 (10)
C(12′)	1.313 3 (5)	−0.052 6 (5)	0.265 6 (5)	0.008 0 (6)	0.008 7 (6)	0.008 5 (5)	0.0037 (10)	0.006 6 (9)	0.001 4 (9)
C(13′)	1.195 2 (5)	−0.027 7 (5)	0.238 3 (4)	0.008 8 (6)	0.007 2 (5)	0.005 9 (4)	0.0034 (10)	0.003 4 (8)	0.003 0 (8)
C(14′)	1.063 8 (5)	0.220 8 (5)	0.288 3 (5)	0.007 9 (5)	0.007 1 (5)	0.008 5 (5)	0.0010 (10)	0.000 0 (9)	0.005 7 (8)
C(15′)	1.041 7 (7)	0.323 0 (6)	0.371 6 (6)	0.012 1 (8)	0.007 4 (6)	0.013 4 (7)	0.0010 (12)	−0.001 6 (13)	−0.001 1 (11)
C(16′)	1.035 8 (11)	0.289 3 (8)	0.478 3 (6)	0.036 8 (17)	0.014 2 (9)	0.007 4 (6)	0.0075 (22)	0.001 7 (17)	0.002 1 (13)
C(17′)	1.143 3 (8)	0.431 6 (7)	0.374 4 (9)	0.013 8 (10)	0.007 7 (7)	0.025 5 (12)	−0.0067 (15)	−0.002 0 (18)	0.000 3 (16)

Atom	x	y	z	B, Å	Atom	x	y	z	B, Å
H(3)	0.960 (4)	0.344 (4)	−0.002 (3)	3.4 (10)	H(3′)	0.593 (4)	−0.174 (4)	0.271 (4)	5.0 (13)
H(4)	0.868 (4)	0.393 (4)	−0.161 (4)	4.7 (12)	H(4′)	0.647 (4)	−0.359 (4)	0.252 (3)	3.2 (10)
H(6)	0.534 (4)	0.287 (4)	−0.089 (3)	3.5 (11)	H(6′)	1.010 (4)	−0.218 (4)	0.256 (3)	4.0 (11)
H(9)	0.416 (5)	0.049 (4)	0.032 (4)	5.3 (13)	H(9′)	1.109 (4)	−0.003 (4)	0.474 (4)	5.1 (12)
H(10)	0.198 (4)	0.029 (4)	−0.023 (4)	5.0 (12)	H(10′)	1.306 (4)	−0.043 (4)	0.518 (4)	5.1 (12)
H(11)	0.110 (4)	0.196 (4)	−0.011 (4)	5.1 (13)	H(12′)	1.369 (4)	−0.064 (4)	0.212 (4)	4.6 (12)
H(12)	0.235 (5)	0.381 (4)	0.045 (4)	5.5 (13)	H(13′)	1.163 (4)	−0.022 (4)	0.166 (3)	4.4 (11)
H(13)	0.448 (4)	0.399 (4)	0.089 (3)	4.1 (11)	H(15′)	0.965 (5)	0.341 (4)	0.354 (4)	5.4 (13)
H(141)	0.553 (4)	0.124 (4)	0.298 (4)	4.8 (12)	H(11′)	1.431 (4)	−0.075 (4)	0.389 (4)	5.0 (12)
H(142)	0.461 (4)	0.187 (4)	0.241 (4)	4.4 (12)	H(141′)	1.067 (4)	0.246 (4)	0.223 (3)	3.9 (11)
H(15)	0.691 (4)	0.319 (3)	0.409 (3)	1.9 (9)	H(142′)	1.141 (4)	0.199 (4)	0.310 (4)	4.5 (12)

c. Cu((*i*-Bu)cbp)$_2$, Red Isomer

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	0.2482 (2)	0.2484 (1)	0.249 44 (8)	0.011 84 (6)	0.007 88 (4)	0.002 68 (1)	0.002 13 (9)	0.001 70 (5)	0.002 26 (4)
Cu(2)	0.7476 (2)	0.7485 (1)	0.749 14 (8)	0.008 82 (5)	0.008 29 (4)	0.002 76 (1)	0.002 27 (8)	0.001 21 (5)	0.003 45 (4)
Cl(A)	0.7296 (2)	0.0715 (2)	0.536 5 (1)	0.015 5 (2)	0.015 1 (2)	0.004 66 (6)	0.002 9 (3)	−0.002 2 (2)	0.006 5 (2)
Cl(B)	−0.2297 (2)	0.4267 (2)	−0.037 4 (1)	0.014 8 (2)	0.014 6 (2)	0.005 08 (5)	0.000 0 (3)	−0.002 6 (2)	0.009 7 (1)
Cl(C)	1.2946 (2)	1.1720 (2)	1.020 7 (1)	0.018 9 (3)	0.011 1 (2)	0.004 70 (7)	−0.001 8 (4)	0.000 5 (2)	−0.001 2 (2)
Cl(D)	0.2056 (2)	0.3291 (2)	0.476 6 (1)	0.019 1 (3)	0.013 7 (2)	0.004 24 (6)	−0.003 5 (4)	−0.000 3 (2)	−0.002 0 (2)
O(A)	0.3848 (5)	0.1050 (4)	0.252 2 (2)	0.012 8 (5)	0.009 3 (4)	0.004 0 (1)	0.001 3 (8)	0.001 4 (5)	0.001 9 (4)
O(B)	0.1225 (5)	0.3936 (4)	0.247 9 (2)	0.016 4 (6)	0.009 2 (4)	0.002 6 (1)	0.009 4 (8)	−0.000 8 (5)	−0.000 2 (4)
O(C)	0.8735 (4)	0.9077 (4)	0.756 0 (2)	0.011 2 (5)	0.013 4 (4)	0.003 9 (1)	0.002 4 (8)	−0.000 4 (4)	0.009 0 (3)
O(D)	0.6266 (5)	0.5851 (4)	0.739 8 (3)	0.011 7 (5)	0.007 6 (3)	0.004 7 (1)	−0.002 7 (7)	−0.000 0 (5)	0.004 5 (4)
N(A)	0.4254 (5)	0.3853 (5)	0.301 0 (3)	0.012 3 (6)	0.008 8 (4)	0.003 4 (2)	−0.001 3 (9)	0.003 1 (5)	0.003 4 (4)
N(B)	0.0824 (5)	0.1143 (4)	0.201 1 (2)	0.012 8 (6)	0.007 3 (4)	0.002 4 (1)	0.003 3 (8)	0.001 4 (5)	0.002 5 (4)
N(C)	0.9303 (5)	0.6581 (4)	0.790 0 (2)	0.007 1 (5)	0.009 3 (4)	0.002 9 (1)	0.003 5 (8)	0.002 0 (4)	0.003 2 (4)
N(D)	0.5709 (5)	0.8304 (4)	0.703 8 (2)	0.013 7 (6)	0.005 3 (4)	0.002 4 (1)	0.003 1 (8)	0.001 6 (5)	0.001 5 (4)
C(1A)	0.5280 (6)	0.2222 (5)	0.366 3 (3)	0.009 0 (6)	0.007 6 (5)	0.003 4 (2)	0.002 8 (9)	0.004 6 (5)	0.003 4 (5)
C(2A)	0.4671 (6)	0.1034 (5)	0.315 0 (3)	0.010 3 (6)	0.008 7 (5)	0.003 4 (2)	0.006 0 (10)	0.003 6 (6)	0.002 2 (5)
C(14A)	0.4245 (7)	0.5095 (6)	0.274 3 (4)	0.010 8 (7)	0.010 2 (6)	0.003 6 (2)	0.000 7 (11)	0.001 1 (7)	0.002 1 (6)
C(15A)	0.4270 (5)	0.4985 (5)	0.188 5 (3)	0.005 2 (5)	0.010 7 (6)	0.002 4 (1)	−0.002 6 (9)	−0.001 2 (5)	0.001 6 (5)
C(16A)	0.4643 (19)	0.6382 (8)	0.170 3 (5)	0.099 9 (41)	0.011 0 (8)	0.005 3 (3)	0.012 9 (31)	0.026 9 (15)	0.008 6 (7)
C(17A)	0.5492 (11)	0.4126 (9)	0.159 2 (4)	0.038 6 (15)	0.015 9 (9)	0.005 1 (2)	0.011 7 (20)	0.019 1 (8)	0.007 7 (7)
C(14B)	0.0688 (9)	−0.0244 (5)	0.221 4 (3)	0.027 9 (12)	0.004 8 (4)	0.001 8 (1)	−0.004 3 (12)	0.000 7 (7)	0.002 3 (4)
C(15B)	0.0292 (17)	0.0024 (8)	0.305 2 (4)	0.103 2 (37)	0.008 8 (7)	0.005 9 (2)	0.021 8 (27)	0.034 6 (13)	0.007 6 (7)
C(16B)	−0.0638 (9)	0.0884 (13)	0.339 6 (6)	0.010 6 (10)	0.037 9 (20)	0.006 1 (4)	0.008 8 (23)	0.001 6 (10)	0.002 1 (15)
C(17B)	0.0697 (9)	−0.1452 (7)	0.326 1 (4)	0.022 8 (12)	0.013 8 (7)	0.003 8 (2)	−0.010 3 (16)	−0.005 5 (9)	0.006 5 (6)
C(14C)	0.9310 (6)	0.5125 (5)	0.766 5 (3)	0.010 3 (6)	0.007 3 (5)	0.002 7 (2)	0.000 2 (9)	−0.002 7 (5)	0.002 8 (4)
C(15C)	1.0056 (7)	0.4633 (7)	0.693 1 (3)	0.013 1 (8)	0.012 5 (7)	0.002 9 (2)	0.003 8 (13)	0.003 8 (5)	0.000 3 (6)
C(16C)	0.9314 (8)	0.5187 (8)	0.628 2 (3)	0.012 5 (8)	0.020 6 (10)	0.002 5 (2)	−0.001 2 (15)	−0.000 6 (7)	0.003 2 (7)
C(17C)	1.0098 (10)	0.3159 (8)	0.678 5 (4)	0.029 0 (14)	0.013 8 (8)	0.003 5 (2)	0.016 5 (17)	0.003 6 (10)	0.001 2 (7)
C(14D)	0.5593 (6)	0.9848 (5)	0.726 8 (3)	0.012 2 (7)	0.007 4 (5)	0.002 8 (2)	0.005 1 (10)	0.002 0 (6)	0.001 6 (5)
C(15D)	0.4842 (6)	1.0239 (5)	0.803 5 (3)	0.010 9 (7)	0.006 5 (5)	0.003 5 (2)	0.000 9 (10)	−0.000 7 (6)	0.001 1 (5)
C(16D)	0.4618 (8)	1.1852 (8)	0.820 9 (5)	0.015 0 (9)	0.006 2 (5)	0.007 0 (3)	0.003 0 (12)	0.005 7 (9)	0.000 4 (7)
C(17D)	0.5856 (10)	0.9911 (8)	0.872 7 (4)	0.032 6 (14)	0.015 7 (8)	0.003 1 (2)	0.023 0 (16)	0.005 9 (9)	0.003 9 (7)

Table III (*Continued*)

Atom	*x*	*y*	*z*	*B*, Å^2	Atom	*x*	*y*	*z*	*B*, Å^2
C(3A)	0.4892 (7)	−0.0248 (7)	0.3309 (4)	4.38 (12)	C(11D)	0.1301 (7)	0.9801 (6)	0.5541 (3)	3.64 (10)
C(4A)	0.5759 (6)	−0.0330 (5)	0.4041 (3)	3.22 (9)	C(12D)	0.1007 (7)	0.9409 (6)	0.6170 (4)	4.26 (12)
C(5A)	0.6333 (6)	0.0917 (5)	0.4542 (3)	3.01 (9)	C(13D)	0.2050 (6)	0.8636 (5)	0.6529 (3)	3.36 (9)
C(6A)	0.6105 (6)	0.2062 (6)	0.4315 (3)	3.58 (10)	H(3A)	0.451 (6)	−0.122 (5)	0.293 (3)	3 (1)
C(7A)	0.5195 (6)	0.3559 (5)	0.3456 (3)	3.26 (9)	H(4A)	0.600 (6)	−0.127 (5)	0.407 (3)	3 (1)
C(8A)	0.6504 (6)	0.4605 (5)	0.3821 (3)	3.33 (9)	H(6A)	0.657 (7)	0.268 (6)	0.476 (3)	4 (1)
C(9A)	0.8013 (7)	0.4541 (6)	0.3611 (4)	4.26 (12)	H(9A)	0.824 (6)	0.380 (5)	0.320 (3)	3 (1)
C(10A)	0.9098 (8)	0.5433 (7)	0.3868 (4)	4.66 (12)	H(10A)	0.978 (7)	0.537 (7)	0.367 (4)	5 (1)
C(11A)	0.9007 (7)	0.6424 (6)	0.4504 (4)	4.16 (11)	H(11A)	0.972 (7)	0.691 (6)	0.485 (4)	5 (1)
C(12A)	0.7717 (8)	0.6605 (7)	0.4809 (4)	4.74 (13)	H(12A)	0.752 (9)	0.687 (8)	0.524 (4)	7 (1)
C(13A)	0.6268 (7)	0.5626 (6)	0.4464 (4)	4.31 (12)	H(13A)	0.540 (7)	0.565 (6)	0.473 (3)	4 (1)
C(1B)	−0.0387 (6)	0.2757 (5)	0.1349 (3)	3.29 (9)	H(141)	0.333 (6)	0.565 (5)	0.290 (3)	3 (1)
C(2B)	0.0363 (6)	0.3952 (6)	0.1849 (3)	3.43 (10)	H(142)	0.499 (6)	0.582 (5)	0.310 (3)	3 (1)
C(3B)	0.0045 (7)	0.5226 (6)	0.1653 (3)	3.98 (11)	H(15A)	0.347 (6)	0.442 (5)	0.159 (3)	3 (1)
C(4B)	−0.0717 (8)	0.5352 (7)	0.1074 (4)	4.67 (13)	H(3B)	0.065 (7)	0.574 (6)	0.195 (4)	5 (1)
C(5B)	−0.1299 (7)	0.4246 (6)	0.0533 (3)	3.97 (11)	H(4B)	−0.082 (9)	0.616 (8)	0.095 (4)	7 (1)
C(6B)	−0.1197 (6)	0.2841 (6)	0.0628 (3)	3.57 (10)	H(6B)	−0.171 (6)	0.183 (5)	0.029 (3)	3 (1)
C(7B)	−0.0340 (6)	0.1377 (5)	0.1500 (3)	3.07 (9)	H(9B)	−0.270 (7)	0.127 (6)	0.189 (3)	4 (1)
C(8B)	−0.1549 (6)	0.0340 (6)	0.1110 (3)	3.38 (10)	H(10B)	−0.536 (9)	−0.046 (8)	0.114 (5)	7 (1)
C(9B)	−0.2900 (7)	0.0474 (6)	0.1431 (3)	3.79 (10)	H(11B)	−0.473 (6)	−0.237 (6)	0.014 (3)	3 (1)
C(10B)	−0.4145 (8)	−0.0518 (7)	0.1004 (4)	4.60 (13)	H(12B)	−0.234 (6)	−0.245 (5)	−0.027 (3)	3 (1)
C(11B)	−0.3737 (7)	−0.1604 (7)	0.0384 (4)	4.38 (12)	H(13B)	−0.044 (6)	−0.093 (5)	0.048 (3)	3 (1)
C(12B)	−0.2302 (7)	−0.1622 (6)	0.0164 (3)	3.61 (10)	H(143)	−0.010 (6)	−0.077 (5)	0.201 (3)	3 (1)
C(13B)	−0.1308 (7)	−0.0725 (6)	0.0508 (3)	4.03 (11)	H(144)	0.104 (9)	−0.006 (8)	0.255 (4)	7 (1)
C(1C)	1.0579 (6)	0.8842 (5)	0.8624 (3)	3.09 (9)	H(15B)	0.028 (6)	0.106 (5)	0.352 (3)	3 (1)
C(2C)	0.9726 (6)	0.9656 (6)	0.8208 (3)	3.46 (10)	H(3C)	0.927 (6)	1.159 (5)	0.797 (3)	3 (1)
C(3C)	0.9961 (7)	1.0993 (6)	0.8299 (3)	3.64 (10)	H(4C)	1.122 (6)	1.270 (5)	0.912 (3)	3 (1)
C(4C)	1.0961 (7)	1.1682 (6)	0.9077 (3)	3.63 (10)	H(6C)	1.213 (6)	0.876 (5)	0.943 (3)	3 (1)
C(5C)	1.1694 (6)	1.0960 (6)	0.9379 (3)	3.50 (10)	H(9C)	1.331 (8)	0.704 (7)	0.810 (4)	6 (1)
C(6C)	1.1582 (6)	0.9450 (5)	0.9233 (3)	3.24 (9)	H(10C)	1.493 (9)	0.570 (8)	0.874 (4)	6 (1)
C(7C)	1.0361 (6)	0.7284 (5)	0.8380 (3)	3.02 (9)	H(11C)	1.497 (6)	0.499 (6)	0.992 (3)	4 (1)
C(8C)	1.1614 (6)	0.6617 (5)	0.8790 (3)	3.01 (9)	H(12C)	1.213 (6)	0.504 (5)	1.027 (3)	3 (1)
C(9C)	1.3004 (7)	0.6375 (6)	0.8484 (3)	3.87 (11)	H(13C)	1.017 (6)	0.607 (5)	0.954 (3)	3 (1)
C(10C)	1.4064 (7)	0.5692 (6)	0.0791 (3)	3.53 (10)	H(145)	0.965 (6)	0.473 (6)	0.806 (3)	3 (1)
C(11C)	1.3746 (8)	0.5156 (7)	0.9449 (4)	4.62 (13)	H(146)	0.831 (6)	0.479 (5)	0.753 (3)	3 (1)
C(12C)	1.2340 (7)	0.5482 (6)	0.9782 (3)	3.98 (11)	H(15C)	1.104 (6)	0.504 (5)	0.701 (3)	3 (1)
C(13C)	1.1300 (6)	0.6122 (5)	0.9433 (3)	3.15 (9)	H(3D)	0.619 (9)	0.354 (8)	0.682 (4)	7 (1)
C(1D)	0.4508 (6)	0.6172 (5)	0.6417 (3)	2.97 (9)	H(4D)	0.355 (9)	0.287 (8)	0.661 (4)	7 (1)
C(2D)	0.5322 (6)	0.5385 (5)	0.6866 (3)	3.17 (9)	H(6D)	0.297 (6)	0.569 (5)	0.556 (3)	3 (1)
C(3D)	0.5074 (7)	0.3824 (6)	0.6505 (3)	4.06 (11)	H(9D)	0.446 (6)	0.848 (5)	0.530 (3)	3 (1)
C(4D)	0.4137 (8)	0.3247 (7)	0.6076 (4)	4.66 (13)	H(10D)	0.282 (6)	0.943 (5)	0.462 (3)	3 (1)
C(5D)	0.3254 (7)	0.4142 (6)	0.5520 (3)	3.77 (10)	H(11D)	0.055 (6)	1.059 (5)	0.528 (3)	3 (1)
C(6D)	0.3473 (7)	0.5426 (6)	0.5791 (3)	3.64 (10)	H(12D)	−0.006 (6)	0.968 (5)	0.652 (3)	3 (1)
C(7D)	0.4575 (6)	0.7628 (5)	0.6580 (3)	2.76 (8)	H(13D)	0.195 (6)	0.835 (5)	0.706 (3)	3 (1)
C(8D)	0.3420 (6)	0.8396 (5)	0.6242 (3)	2.90 (9)	H(147)	0.489 (6)	1.029 (5)	0.693 (3)	3 (1)
C(9D)	0.3712 (7)	0.8820 (6)	0.5582 (3)	3.66 (10)	H(148)	0.686 (6)	1.046 (5)	0.734 (3)	3 (1)
C(10D)	0.2615 (6)	0.9607 (6)	0.5250 (3)	3.52 (10)	H(15D)	0.389 (9)	0.944 (7)	0.820 (4)	7 (1)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

but no near approaches occur (Figure 1c, Table VI). Figure 2 shows analogous views of the green isobutyl complex, which has the alkyl groups in the same cis arrangement. As for the *n*-butyl complex, this would permit close intermolecular approach such as required in dimerization, but again no close approaches occur (Figure 2c, Table VI).

Figure 3a, b shows the two molecules of the red isobutyl complex, each of which has the normal trans arrangement of the alkyl groups, emphasized by the side view (Figure 3c) of one of the molecules ("molecule 1"). The main gross structural difference between the two molecules is in the "V" formed by the isopropyl end of the isobutyl groups. In molecule 1 (Figure 3a, c) the V for each ligand points toward the oxygen atom of the other ligand, while in molecule 2 (Figure 3b), each V points away from the oxygen atom. The metal–ligand (CuO_2N_2) planes of the two molecules are at 23.7° to one another.

The geometry of the ligand environment about the metal atom in copper–Schiff base complexes ranges widely between planar and tetrahedral. A crude parameterization of the extent of distortion from planar to tetrahedral geometries is the dihedral angle τ (Figure 4). Values of 0 and 90° of τ are then necessary but not sufficient conditions for planar and tetrahedral environments, respectively. Both molecules of the red isomer of the isobutyl complex are nearly planar, having τ = 0.8 and 3.4° for molecules 1 and 2, respectively. This compares with τ = 14.5° for the green isomer. The *n*-butyl complex exhibits marked tetrahedral distortion (τ = 31.2°) compared to the other structures determined.

From an examination of the structures of the *n*-butyl complex, the green isobutyl complex, and molecules 1 and 2 of the red isobutyl complex and comparisons between them, the observed "cis–trans" isomerism does not appear to be sterically forced. There is no evidence of significant interaction between the alkyl groups and between the adjacent phenyl groups or evidence of the alkyl groups interacting with the phenyls, nor does it appear that there would be any interaction on switching the cis complexes to trans or vice versa. It seems likely that economy of molecular packing permits the formation of the new cis type of structure, in the absence of any other mechanism. The cis–trans isomerism constitutes an additional variation to the well-known distribution between planar and pseudotetrahedral configurations, though whether, and to what extent, the two types of structural variation are independent is unknown at present. Of course for purely tetrahedral (τ = 90°) metal geometry the present definitions

Table IV. Bond Distances (Å)

		$Cu((i\text{-}Bu)cbp)_2$		
			Red isomer	
	$Cu((n\text{-}Bu)cbp)_2$	Green isomer	Molecule 1 (A, B)	Molecule 2 (C, D)
Cu–O	1.887 (4)	1.879 (4)	1.925 (4)	1.881 (4)
Cu–O′	1.882 (4)	1.881 (4)	1.873 (4)	1.885 (4)
Cu–N	1.996 (5)	1.987 (5)	2.060 (5)	2.055 (4)
Cu–N′	1.992 (5)	1.996 (5)	1.961 (5)	2.002 (5)
Cl–C(5)	1.757 (6)	1.738 (6)	1.706 (5)	1.791 (5)
Cl′–C(5′)	1.754 (6)	1.757 (6)	1.800 (5)	1.699 (5)
O–C(2)	1.298 (7)	1.294 (7)	1.301 (7)	1.403 (6)
O′–C(2′)	1.295 (6)	1.309 (7)	1.320 (6)	1.218 (6)
N–C(7)	1.298 (7)	1.306 (7)	1.203 (6)	1.294 (6)
N–C(14)	1.484 (7)	1.469 (7)	1.426 (7)	1.425 (7)
N′–C(7′)	1.296 (7)	1.302 (7)	1.391 (6)	1.311 (7)
N′–C(14′)	1.490 (7)	1.460 (7)	1.510 (6)	1.518 (6)
C(1)–C(2)	1.420 (8)	1.413 (8)	1.394 (8)	1.424 (7)
C(1)–C(6)	1.418 (8)	1.409 (8)	1.377 (7)	1.368 (7)
C(1)–C(7)	1.461 (8)	1.456 (8)	1.466 (7)	1.522 (7)
C(2)–C(3)	1.417 (8)	1.423 (8)	1.390 (8)	1.315 (6)
C(3)–C(4)	1.363 (8)	1.351 (8)	1.492 (7)	1.599 (6)
C(4)–C(5)	1.383 (9)	1.390 (9)	1.417 (6)	1.182 (6)
C(5)–C(6)	1.366 (8)	1.362 (8)	1.314 (7)	1.472 (7)
C(7)–C(8)	1.498 (8)	1.503 (8)	1.534 (7)	1.542 (7)
C(8)–C(9)	1.400 (8)	1.380 (8)	1.424 (8)	1.403 (8)
C(8)–C(13)	1.361 (8)	1.387 (8)	1.403 (8)	1.397 (7)
C(9)–C(10)	1.400 (9)	1.380 (9)	1.270 (8)	1.341 (8)
C(10)–C(11)	1.38 (1)	1.37 (1)	1.352 (7)	1.443 (9)
C(11)–C(12)	1.37 (1)	1.36 (1)	1.314 (7)	1.451 (9)
C(12)–C(13)	1.39 (1)	1.39 (1)	1.582 (8)	1.339 (8)
C(14)–C(15)	1.510 (9)	1.49 (1)	1.525 (7)	1.521 (8)
C(15)–C(16)	1.51 (1)	1.50 (1)	1.530 (8)	1.515 (9)
C(15)–C(17)		1.26 (1)	1.474 (8)	1.442 (9)
C(16)–C(17)	1.53 (1)			
C(1′)–C(2′)	1.418 (8)	1.422 (8)	1.431 (8)	1.424 (7)
C(2′)–C(3′)	1.423 (8)	1.406 (8)	1.428 (8)	1.553 (6)
C(3′)–C(4′)	1.363 (8)	1.365 (8)	1.229 (7)	1.133 (6)
C(4′)–C(5′)	1.397 (8)	1.377 (8)	1.356 (7)	1.657 (7)
C(5′)–C(6′)	1.369 (8)	1.354 (8)	1.456 (7)	1.269 (7)
C(1′)–C(6′)	1.418 (7)	1.407 (8)	1.455 (7)	1.443 (7)
C(1′)–C(7′)	1.458 (8)	1.458 (8)	1.464 (7)	1.418 (7)
C(7′)–C(8′)	1.508 (7)	1.499 (8)	1.480 (7)	1.479 (7)
C(8′)–C(9′)	1.400 (8)	1.378 (8)	1.375 (8)	1.384 (8)
C(8′)–C(13′)	1.390 (8)	1.379 (8)	1.380 (8)	1.373 (7)
C(9′)–C(10′)	1.375 (8)	1.371 (8)	1.496 (8)	1.450 (8)
C(10′)–C(11′)	1.35 (1)	1.38 (1)	1.459 (7)	1.323 (8)
C(11′)–C(12′)	1.36 (1)	1.37 (1)	1.367 (6)	1.317 (8)
C(12′)–C(13′)	1.411 (9)	1.37 (1)	1.254 (7)	1.435 (7)
C(14′)–C(15′)	1.50 (1)	1.51 (1)	1.546 (8)	1.563 (8)
C(15′)–C(16′)	1.48 (1)	1.46 (1)	1.31 (1)	1.598 (7)
C(15′)–C(17′)		1.51 (1)	1.646 (8)	1.580 (9)
C(16′)–C(17′)	1.57 (1)			

Table V. Bond Angles (deg)

		$Cu((i\text{-}Bu)cbp)_2$		
			Red isomer	
	$Cu((n\text{-}Bu)cbp)_2$	Green isomer	Molecule 1	Molecule 2
O–Cu–O′	158.9 (2)	167.6 (2)	177.5 (2)	177.8 (3)
O–Cu–N	92.4 (2)	90.6 (2)	87.0 (2)	88.6 (2)
O–Cu–N′	92.2 (2)	90.4 (2)	91.6 (2)	92.2 (2)
O′–Cu–N	92.8 (2)	90.8 (2)	90.6 (2)	90.2 (2)
O′–Cu–N′	91.2 (2)	89.9 (2)	90.9 (2)	89.0 (2)
N–Cu–N′	156.6 (2)	172.2 (2)	178.5 (3)	176.9 (2)
Cu–O–C(2)	128.1 (4)	126.7 (4)	120.1 (4)	122.9 (4)
Cu–O′–C(2′)	126.0 (4)	121.6 (4)	119.4 (4)	124.3 (4)
Cu–N–C(7)	126.7 (4)	123.6 (4)	121.4 (4)	122.0 (4)
Cu–N–C(14)	112.5 (4)	115.7 (4)	112.2 (4)	116.8 (3)
Cu–N′–C(7′)	126.3 (4)	124.2 (4)	125.0 (3)	126.3 (4)
Cu–N′–C(14′)	112.7 (4)	115.1 (4)	120.5 (4)	118.3 (3)
C(7)–N–C(14)	120.8 (5)	120.3 (5)	126.3 (5)	121.1 (4)
C(7′)–N′–C(14′)	120.8 (5)	120.6 (5)	114.4 (4)	115.3 (5)
C(2)–C(1)–C(6)	117.9 (6)	119.0 (6)	117.3 (5)	120.6 (5)
C(2)–C(1)–C(7)	123.7 (5)	122.5 (5)	120.1 (5)	118.9 (5)
C(6)–C(1)–C(7)	118.2 (5)	118.3 (5)	122.1 (5)	120.5 (5)
O–C(2)–C(1)	125.1 (6)	124.8 (6)	123.1 (5)	122.4 (5)
O–C(2)–C(3)	117.5 (6)	118.4 (6)	116.6 (6)	112.4 (5)
C(1)–C(2)–C(3)	117.4 (6)	116.8 (6)	120.2 (6)	124.2 (5)
C(2)–C(3)–C(4)	123.1 (6)	123.2 (6)	119.1 (5)	112.7 (4)
C(3)–C(4)–C(5)	119.0 (6)	118.9 (6)	117.9 (4)	117.8 (4)
C(4)–C(5)–C(6)	120.5 (6)	120.8 (6)	117.4 (4)	128.2 (5)
Cl–C(5)–C(4)	120.1 (5)	118.7 (5)	114.4 (3)	118.8 (4)
Cl–C(5)–C(6)	119.4 (5)	120.5 (5)	128.3 (4)	112.4 (3)
C(1)–C(6)–C(5)	122.0 (6)	121.3 (6)	127.9 (5)	113.8 (4)
N–C(7)–C(1)	122.4 (5)	122.7 (5)	125.7 (5)	126.8 (5)
N–C(7)–C(8)	120.2 (6)	119.0 (6)	119.7 (5)	123.2 (5)
C(1)–C(7)–C(8)	117.4 (5)	118.3 (5)	114.5 (4)	110.0 (4)
C(7)–C(8)–C(9)	120.2 (6)	119.3 (6)	124.9 (5)	121.1 (5)
C(7)–C(8)–C(13)	120.7 (6)	121.9 (6)	118.7 (5)	119.1 (5)
C(9)–C(8)–C(13)	119.1 (6)	118.8 (6)	116.0 (5)	119.5 (5)
C(8)–C(9)–C(10)	119.8 (7)	121.5 (7)	126.4 (6)	122.4 (6)
C(9)–C(10)–C(11)	119.6 (7)	118.8 (7)	121.2 (6)	118.7 (5)
C(10)–C(11)–C(12)	120.3 (7)	120.9 (7)	120.3 (5)	118.0 (6)
C(11)–C(12)–C(13)	119.6 (7)	120.3 (7)	120.8 (5)	120.3 (6)
C(8)–C(13)–C(12)	121.5 (7)	119.7 (7)	114.1 (5)	120.6 (5)
N–C(14)–C(15)	110.4 (5)	113.0 (5)	117.6 (5)	114.0 (5)
C(14)–C(15)–C(16)	114.3 (6)	111.0 (6)	111.7 (5)	111.1 (5)
C(14)–C(15)–C(17)		123.9 (6)	110.2 (4)	108.8 (5)
C(16)–C(15)–C(17)		114.6 (6)	104.8 (5)	115.2 (6)
C(15)–C(16)–C(17)	115.2 (7)			
C(2′)–C(1′)–C(6′)	118.4 (6)	118.9 (6)	121.0 (5)	117.1 (5)
C(2′)–C(1′)–C(7′)	123.0 (5)	121.7 (5)	123.5 (5)	124.1 (4)
C(6′)–C(1′)–C(7′)	118.5 (5)	119.4 (5)	115.4 (5)	118.6 (4)
O′–C(2′)–C(1′)	124.8 (6)	124.1 (6)	124.4 (5)	125.3 (5)
O′–C(2′)–C(3′)	117.6 (6)	118.8 (6)	120.2 (5)	122.7 (5)
C(1′)–C(2′)–C(3′)	117.6 (6)	117.2 (6)	115.3 (5)	111.1 (4)
C(2′)–C(3′)–C(4′)	122.4 (6)	122.4 (6)	125.3 (6)	129.6 (5)
C(3′)–C(4′)–C(5′)	119.6 (6)	119.2 (6)	121.8 (6)	116.4 (5)
C(4′)–C(5′)–C(6′)	119.9 (6)	121.2 (6)	122.8 (5)	111.6 (4)
Cl′–C(5′)–C(4′)	119.9 (5)	119.0 (5)	126.7 (4)	118.8 (4)
Cl′–C(5′)–C(6′)	120.1 (5)	119.8 (5)	110.5 (4)	129.2 (4)
C(1′)–C(6′)–C(5′)	121.9 (6)	120.8 (6)	113.0 (5)	130.2 (5)
N′–C(7′)–C(1′)	121.9 (5)	122.1 (5)	117.5 (4)	118.6 (5)
N′–C(7′)–C(8′)	121.3 (5)	121.7 (5)	124.8 (4)	119.5 (5)
C(1′)–C(7′)–C(8′)	116.7 (5)	116.2 (5)	117.7 (4)	122.0 (4)
C(7′)–C(8′)–C(9′)	120.1 (6)	120.2 (6)	114.1 (5)	118.0 (5)
C(7′)–C(8′)–C(13′)	120.3 (6)	120.5 (6)	122.8 (5)	122.8 (5)
C(9′)–C(8′)–C(13′)	119.6 (6)	119.3 (6)	123.0 (5)	119.1 (5)
C(8′)–C(9′)–C(10′)	119.4 (6)	120.7 (6)	114.0 (5)	119.0 (5)
C(9′)–C(10′)–C(11′)	122.3 (7)	119.6 (7)	117.1 (5)	119.7 (5)
C(10′)–C(11′)–C(12′)	118.7 (7)	120.3 (7)	120.6 (4)	121.8 (6)
C(11′)–C(12′)–C(13′)	122.5 (7)	119.9 (7)	120.2 (5)	121.0 (6)
C(12′)–C(13′)–C(8′)	117.5 (7)	120.3 (7)	124.6 (6)	119.0 (5)
N′–C(14′)–C(15′)	112.1 (6)	112.5 (6)	106.5 (4)	110.4 (4)
C(14′)–C(15′)–C(16′)	115.5 (6)	112.7 (6)	129.1 (8)	108.1 (5)
C(14′)–C(15′)–C(17′)		109.4 (7)	100.1 (5)	111.9 (5)
C(16′)–C(15′)–C(17′)		111.5 (7)	125.9 (7)	108.5 (5)
C(15′)–C(16′)–C(17′)	115.4 (8)			

of cis and trans become meaningless.

Magnetic Properties. The room-temperature moments all fall within the expected range for distorted square-planar and distorted tetrahedral copper(II) complexes and are not in themselves of diagnostic value for the various structural possibilities.[20] The absence of magnetic exchange interactions in the isobutyl and *n*-butyl complexes is readily rationalized from the molecular structures. If either the cis or the trans form had been dimeric, magnetic interactions would have been observed as in the dimeric form of the *N*-Me-cbp[14] and the *N*-methylsalicylaldimine complexes.

Spectra. The electronic spectra (Figure 5) show a clear difference between the approximately planar and distorted tetrahedral complexes: the tetrahedral complexes show the expected bands at lower energies (approaching 8000 cm^{-1}),[3,4] shifts to higher bond energy being correlated well with a trend from tetrahedral to planar geometry. Thus the cyclohexyl-, isopropyl-, and *sec*-butyl-substituted complexes (Figure 5b) differ markedly from the others, and, of the three, the isopropyl complex is predicted to be nearest to purely tetrahedral geometry (8200 cm^{-1}), somewhat like, but perhaps slightly closer

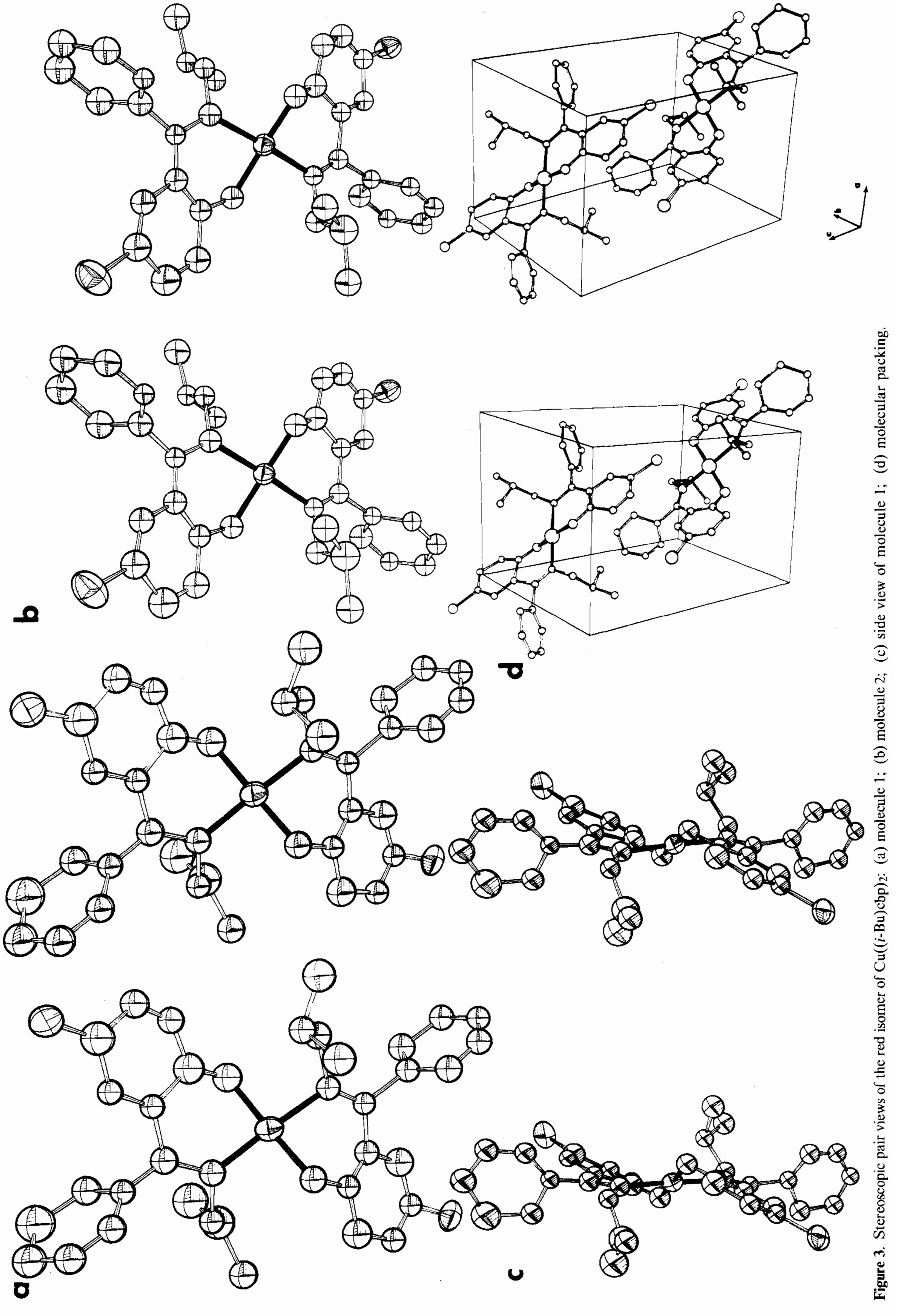

Figure 3. Stereoscopic pair views of the red isomer of Cu((*i*-Bu)cbp)$_2$: (a) molecule 1; (b) molecule 2; (c) side view of molecule 1; (d) molecular packing.

Table VI. Closest Intermolecular Contacts

	Molecule 1	Molecule 2	Dist, Å	Symmetry transformation
n-Butyl	C(17)	C(11′)	3.49	$2-x, y-{}^1/_2, {}^1/_2-z$
	C(2′)	C(4′)	3.38	$2-x, 1-y, -z$
Isobutyl, green	O(2)	C(10′)	3.45	$2-x, -y, 1-z$
	C(5)	C(12)	3.47	$2-x, -y, -z$
Isobutyl, red	O(B)	C(10A)	3.84	$x-1, y, z$
	O(C)	C(12D)	3.40	$x+1, y, z$
	O(D)	C(12C)	3.33	$x-1, y, z$

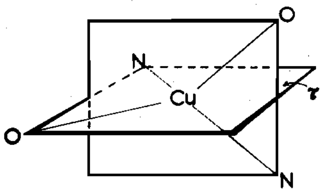

Figure 4. Dihedral angle τ.

Table VII. Observed or Proposed Structures and Relation to Spectra

R	Spectral features	Structure
H	Blue shift	Planar
n-Propyl	Blue shift	Planar
n-Hexyl	Blue shift	Planar
Isobutyl	Blue shift	Planar
Ethyl	Intermediate	Planar-tetrahedral[a]
n-Butyl	Intermediate	Planar-tetrahedral
n-Heptyl	Intermediate	Planar-tetrahedral
n-Octyl	Intermediate	Planar-tetrahedral
Benzyl	Intermediate	Planar-tetrahedral
Cyclohexyl	Red shift	Tetrahedral
Isopropyl	Red shift	Tetrahedral
sec-Butyl	Red shift	Tetrahedral

[a] Planar, but significantly distorted toward tetrahedral.

to tetrahedral than, bis(*N*-isopropylsalicylaldimino)copper(II), Cu(ips)$_2$[21,22] (9000 cm^{-1}). For Cu(ips)$_2$, the dihedral angle τ (Figure 4) is 60.3°, and if we arbitrarily define $\tau = 45°$ the

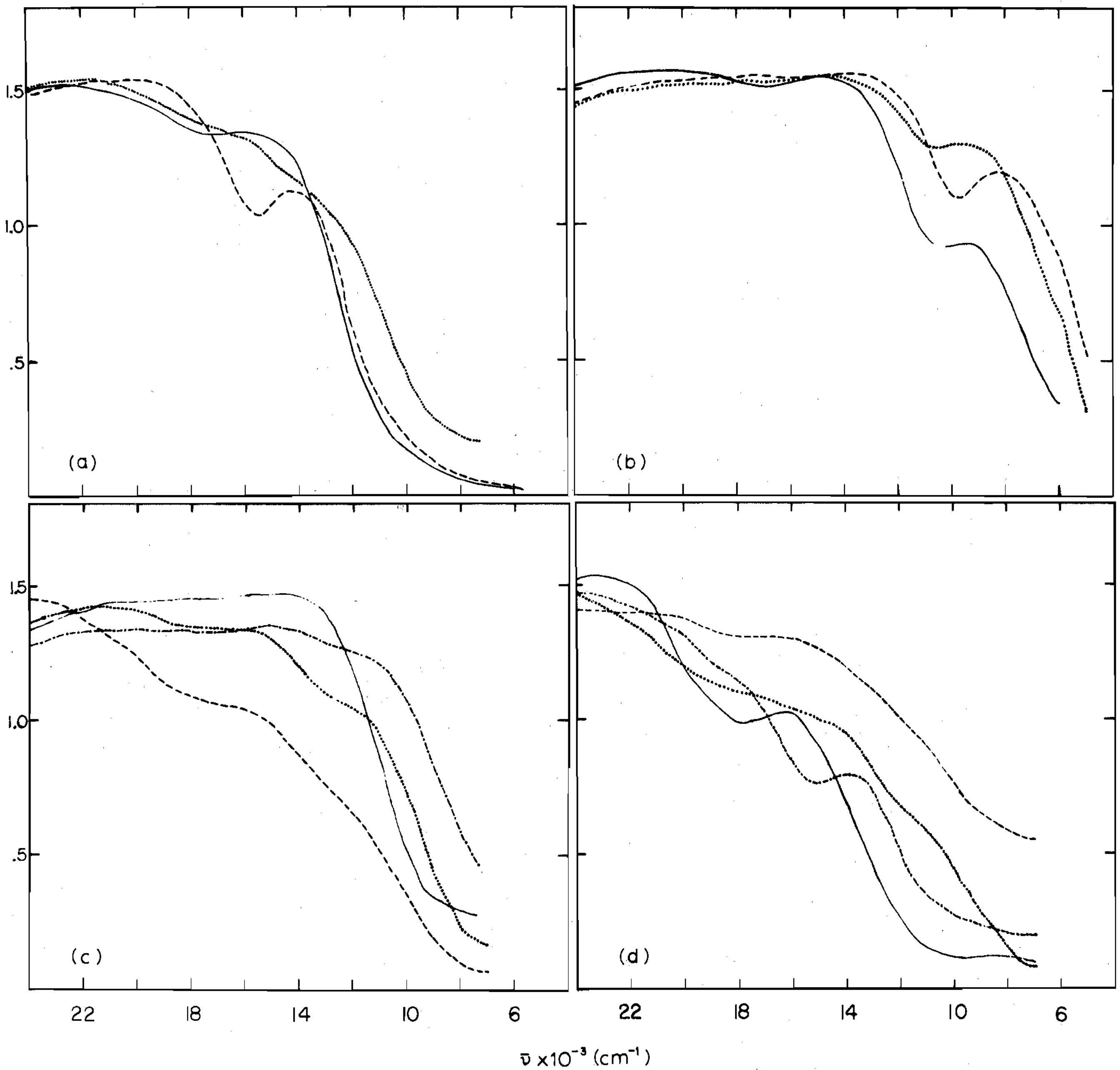

Figure 5. Reflectance spectra of Cu(Rcbp)$_2$ complexes. R groups: (a) –, isobutyl (green isomer); ---, isobutyl (red isomer); ···, *n*-butyl; (b) –, cyclohexyl; ---, isopropyl; ···, *sec*-butyl; (c) –, *n*-pentyl; ---, *n*-hexyl; -·-·, *n*-heptyl; ···, *n*-octyl; (d) –, H; ···, ethyl; -·-·, *n*-propyl; ---, benzyl.

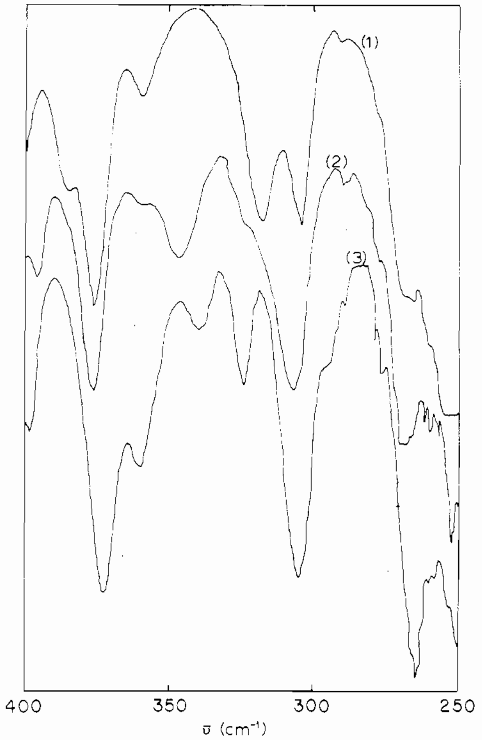

Figure 6. Infrared spectra of Cu(Rcbp)$_2$ complexes, where R is (1) isobutyl (red isomer), (2) isobutyl (green isomer), and (3) *n*-butyl.

crossover between planar and tetrahedral, this complex may be described as a slightly flattened tetrahedron. The metal environments of the cyclohexyl and *sec*-butyl complexes of cbp appear from the spectra to be a little less tetrahedral than the isopropyl analogue but to have geometry similar to that of Cu(ips)$_2$.

Although the red and green isomers of (*i*-Bu)cbp have slightly different spectra, little can be said from this about their relative metal environments, except that both should be close to planar. The colors of the two isomers are far better criteria for distinguishing between them. The (*n*-Bu)cbp complex is expected, correctly, to be somewhat more distorted toward tetrahedral geometry and is distinguishable from the two isobutyl complexes by its electronic spectrum and color (dark green). However, the spectra alone give limited information about the metal environments in the *n*-butyl and isobutyl complexes and none about the ligand configuration. The color and spectroscopic differences between the red and green complexes are due to the copper environment, which in itself does not produce any clues on the orientation of the alkyl groups. Thus x-ray diffraction is the only method of differentiating the cis and trans isomerism observed here.

The structures observed here (*n*-butyl and green isobutyl complexes) are exceptional in that all related complexes for which dipole moment or crystallographic data are available[2,5-14] have been found to be trans in the present definition. The *n*-butyl complex is doubly unusual because in addition to the cis structure, the metal environment has a tetrahedral component which is abnormally large for an *n*-alkyl complex. This feature is reflected in the expected red shift of the optical spectrum in Figure 5a. Because of the rarity of the cis structures, it would be unreasonable to assume at this stage that cis structures occur in many of the other complexes and the electronic spectra are no clear guide. However, in the limited sample of four molecular structures presented here, the cis structures coincide with a greater tetrahedral distortion than closely related trans structures. Thus from the close similarity of the spectra (Figure 5c) to that of the red isobutyl (trans) complex, we would expect the *n*-propyl- and H-substituted complexes to be both very planar and probably trans. Table VII lists the proposed or observed structures and their relationship to the spectra.

The red and green isobutyl and the *n*-butyl complexes have very similar infrared spectra, as expected from the fact that identical or similar ligands are bonded to the same metal atom. For example, in the red isobutyl complex the C–O and C–N regions have bands at 1317 and 1582 cm^{-1} compared with 1320 and 1576 cm^{-1}, respectively, for the green isobutyl complex, while very different frequencies (1285, 1605 cm^{-1}) are observed for the isobutyl ligand. However, some significant differences are observed in the metal–ligand region (Figure 6). Noteworthy is an intense band observed at 308 cm^{-1} for the *n*-butyl and 307.2 cm^{-1} for the green isobutyl complexes but split into two equally intense bands at 304.4 and 317 cm^{-1} for the red isobutyl complex. Such a large shift is only reasonable if the band is predominantly due to a metal–ligand mode. The two equal bands in the red isobutyl complex may be due to the two independent molecules in this complex, whereas the *n*-butyl and green isobutyl complexes contain only a single molecular type. An extensive isotope substitution study[23] on these and related compounds indicates that these bands near 300 cm^{-1} are predominantly Cu–N modes, while Cu–O bands occur at higher energies (387 cm^{-1} in the *n*-butyl complex and 396 cm^{-1} in the green isobutyl complex).

Registry No. Cu((*n*-Bu)cbp)$_2$, 61129-03-1; Cu((*i*-Bu)cbp)$_2$, 61129-02-0; Cu((cyclohexyl)cbp)$_2$, 61176-45-2; Cu((isopropyl)cbp)$_2$, 61216-58-8; Cu((*sec*-butyl)cbp)$_2$, 61129-01-9; Cu((*n*-pentyl)cbp)$_2$, 61129-00-8; Cu((*n*-hexyl)cbp)$_2$, 61008-82-0; Cu((*n*-heptyl)cbp)$_2$, 60949-61-3; Cu((*n*-octyl)cbp)$_2$, 61128-99-2; Cu(Hcbp)$_2$, 61176-44-1; Cu((ethyl)cbp)$_2$, 61176-43-0; Cu((*n*-propyl)cbp)$_2$, 61216-57-7; Cu((benzyl)cbp)$_2$, 61128-98-1.

Supplementary Material Available: Tables I and II containing analyses, melting points, and magnetic moments, a table showing least-squares planes, and tables listing structure factor amplitudes (54 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of New South Wales. (b) University of Virginia. (c) University of Wollongong.
(2) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Prog. Inorg. Chem.*, 7, 83 (1966).
(3) L. Sacconi, M. Ciampolini, and U. Campigli, *Inorg. Chem.*, **4**, 407(1965).
(4) C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 2723 (1968).
(5) E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Sheringer, and C. Freiburg, *Acta Crystallogr.*, **14**, 1222 (1961).
(6) E. N. Baker, G. R. Clark, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 252 (1967).
(7) T. P. Cheeseman, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 694 (1966).
(8) L. Sacconi and I. Bertini, *Inorg. Chem.*, **5**, 1520 (1966).
(9) D. Hall, R. H. Sumner, and T. N. Waters, *J. Chem. Soc. A*, 420 (1969).
(10) C. A. Ghilardi and E. C. Lingafelter, *Acta Crystallogr., Sect. B*, **26**, 1807 (1970).
(11) P. L. Orioli and L. Sacconi, *J. Am. Chem. Soc.*, **88**, 277 (1966).
(12) T. P. Cheeseman, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 685 (1966).
(13) D. Hall, S. V. Sheat, and T. N. Waters, *J. Chem. Soc. A*, 460 (1968).
(14) R. J. Butcher, G. M. Mockler, and E. Sinn, to be submitted for publication.
(15) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(16) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(17) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(18) D. T. Cromer and J. A. Ibers, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(19) Supplementary material.
(20) E. Sinn, *Inorg. Chem.*, in press.
(21) P. L. Orioli and L. Sacconi, *J. Am. Chem. Soc.*, **88**, 227 (1966).
(22) R. J. Butcher and E. Sinn, *Inorg. Chem.*, **15**, 1604 (1976).
(23) E. M. Boge, P. C. Chia, and G. M. Mockler, unpublished work.