Crystal and Molecular Structure of Bis[β-methylmercaptoethylamine]copper(II) Diperchlorate

CHIA CHIH OU,[1a] VINCENT M. MISKOWSKI,[1b] ROGER A. LALANCETTE,[1c] JOSEPH A. POTENZA,*[1a] and HARVEY J. SCHUGAR*[1a]

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The crystal and molecular structure of bis[β-methylmercaptoethylamine]copper(II) diperchlorate, CuC$_6$H$_{18}$N$_2$S$_2$(ClO$_4$)$_2$, have been determined from single-crystal three-dimensional x-ray data collected by counter methods. The compound crystallizes from water as purple prisms in the space group $P2_1/c$ with $Z = 2$, $a = 5.756$ (2) Å, $b = 16.353$ (4) Å, and $c = 8.592$ (3) Å, $\beta = 93.31$ (3)°, $d_{calcd} = 1.826$ g/cm^3, and $d_{obsd} = 1.82$ (1) g/cm^3. Least-squares refinement of 1897 reflections having $F^2 \geq 3\sigma(F^2)$ gave a conventional R factor of 0.037. All atoms in the structure were located. The structure consists of discrete centrosymmetric complexes in which tetragonal Cu(II) ions are bound by two bidentate NH$_2$CH$_2$CH$_2$SCH$_3$ ligands and two monodentate ClO$_4^-$ groups. The equatorial ligand set consists of the strictly planar trans CuN$_2$S$_2$ unit; observed Cu-S and Cu-N bond lengths are 2.366 (1) and 1.977 (2) Å, respectively. The coordination environment is completed by two apical Cu-O bonds (2.599 (2) Å). Both ClO$_4^-$ groups are tilted relative to the CuN$_2$S$_2$ unit. The observed Cu-O-Cl bond angle of 130.1 (1)° is consistent with the valence angle requirements of approximately sp^3-hybridized oxygen. The monodentate perchlorate group in the present structure does not exhibit the T_d symmetry expected of the free ion: the Cl-O bond length involving the coordinated oxygen atom (1.447 (2) Å) is significantly longer than the other three Cl-O bonds (1.416 (3), 1.415 (3), and 1.430 (3) Å).

Introduction

Recent experiments have confirmed that a Cu^{II}-S(cysteine) bond is the chromophore responsible for the intense blue color of various copper proteins.[2] These results have stimulated interest in the electronic structural properties of copper-(II)-sulfur bonding in general and in the nature of copper-(II)-mercaptide bonding in particular. The facile redox chemistry of copper(II)-mercaptide systems has so far frustrated attempts to prepare simple inorganic systems that may serve as models of the blue protein chromophores. Although the reaction of Cu(II) with certain mercaptides may lead to an appropriately intense visible absorption band,[3] the absorbing species are complex cluster molecules. For example, the intense purple color (λ_{max} 530 nm, $\epsilon \simeq 3400$ per Cu(II)) developed in the Cu(II)-HSC(CH$_3$)$_2$CH$_2$NH$_2$ system has been attributed to S → Cu(II) charge transfer within the [Cu$^I_8$Cu$^{II}_6$(-SC(CH$_3$)$_2$CH$_2$NH$_2$)$_{12}$Cl]$^{7+}$ cluster unit.[4] A structurally analogous cluster is responsible for the intense purple color of the Cu(II)-HSC(CH$_3$)$_2$CH(NH$_2$)CO$_2$H system.[5]

Although copper(II)-thioether complexes do not have any obvious biological relevance to the blue copper proteins,[6] they are an attractive vehicle with which to initiate a study of Cu^{II}-S bonding. Aliphatic thioethers are free of electronic absorptions at wavelengths longer than ~230 nm[10] and do not exhibit pronounced redox activity toward Cu(II). Most of the literature dealing with copper(II)-thioether systems has been concerned with the characterization of Cu^{II}-S interactions by various equilibria and NMR line-broadening studies.[11] Structural characterization of copper(II)-thioether bonding has been limited to the crystallographic studies of Cu[S(CH$_2$C(=O)NMe$_2$)$_2$(Cl)$_2$] (I),[12] [CuL(Cl)ClO$_4$]$_2$ (II)[13] where L = 3,4-bis(aminoethylthio)toluene, and CuL'(ClO$_4$)$_2$ (III)[7b] where L' = a macrocyclic thioether. Reports of complexes II and III appeared while this paper was in preparation.

Because of the availability of well-characterized electronic spectral reference compounds such as Cu(NH$_2$CH$_2$CH$_2$N-H$_2$)$_2$(ClO$_4$)$_2$ and related materials, a study of Cu(NH$_2$C-H$_2$CH$_2$SCH$_3$)$_2$(ClO$_4$)$_2$ appeared to be especially attractive. We report here the crystal and molecular structure of Cu(NH$_2$CH$_2$CH$_2$SCH$_3$)$_2$(ClO$_4$)$_2$. A structural study of

Table I. Crystal Data

Space group $P2_1/c$	$d_{obsd} = 1.82$ (1) g/cm^3
$Z = 2$	$d_{calcd} = 1.826$ g/cm^3
$a = 5.756$ (2) A	$V = 807.4$ A^3
$b = 16.353$ (4) A	λ 0.710 69 A
$c = 8.592$ (3) A	$\mu = 20.11$ cm^{-1}
$\beta = 93.31$ (3)°	$T = 25 \pm 1$ °C

[Cu(BuSCH$_2$CH$_2$SBu)(Cl)$_2$]$_2$[14] and a detailed electronic spectral study[9] of these latter two and related Cu(II) complexes will appear elsewhere.

Experimental Section

Preparation of Cu(NH$_2$CH$_2$CH$_2$SCH$_3$)$_2$(ClO$_4$)$_2$. The ligand was prepared by the dropwise addition of CH$_3$I (0.09 mol) to a stirred cold solution of HSCH$_2$CH$_2$NH$_2$·HCl (0.09 mole) and freshly prepared NaOMe (0.18 mol) in dry MeOH. The resulting white suspension was treated with 100 ml of H$_2$O and then extracted several times with 50-ml portions of ether. The ethereal extract was dried with MgSO$_4$, and concentrated to a yellow oil by rotoevaporation at aspirator pressure. The ligand was obtained as a colorless liquid in ~30% yield following a distillation under high vacuum (30-32 °C, ~10^{-2} Torr).

The title complex was precipitated in crude form by adding 1 ml of ligand to a solution of Cu(ClO$_4$)$_2$·6H$_2$O (1.7 gm) in 5 ml of EtOH. After being cooled at 10 °C for 1 day, a filtered solution of the crude product in 20 ml of H$_2$O deposited well-formed purple prisms. The crystals were collected by filtration, washed with dry MeOH, and air-dried. A different preparation of this complex has been described elsewhere.[15]

Anal. Calcd for CuC$_6$H$_{18}$N$_2$O$_8$S$_2$Cl$_2$: C, 16.23; N, 6.31; H, 4.09. Found: C, 16.28; N, 6.27; H, 3.99.

Collection of Diffraction Data. A crystal approximately 0.4 × 0.2 × 0.3 mm was mounted along its a axis in a sealed capillary. Preliminary Weissenberg and precession photographs indicated a monoclinic system and space group $P2_1/c$ by the following systematic absences: $h0l$ absent when l is odd and $0k0$ absent when k is odd.

Unit cell constants were determined by a least-squares fit of 12 moderately intense high-angle reflections accurately centered on a computer-controlled four-circle Syntex $P2_1$ autodiffractometer using graphite-monochromated Mo Kα radiation (λ 0.710 69 Å). A density of 1.826 g/cm^3 was calculated for two Cu(H$_2$NCH$_2$CH$_2$SC-H$_3$)$_2$(ClO$_4$)$_2$ molecules per unit cell and is in good agreement with the value of 1.82 (1) g/cm^3 measured by the density gradient method.[16] The gradient was prepared using tetrabromoethane as the high-density medium and CHCl$_3$ as the low-density medium and calibrated using

Table II. Fractional Atomic Coordinates[a] and Thermal Parameters[b] for $Cu(CH_3SCH_2CH_2NH_2)_2(ClO_4)_2$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0	0.0	0.0	177.5 (10)	17.0 (1)	80.0 (4)	−4.5 (3)	19.3 (6)	−5.0 (2)
Cl	−3230.3 (12)	1398.8 (4)	−2732.3 (8)	224.5 (17)	24.8 (2)	110.3 (7)	−2.0 (5)	3.0 (10)	15.4 (3)
S	2443.8 (12)	999.0 (4)	1232.3 (8)	191.7 (16)	22.8 (2)	117.8 (8)	−6.5 (5)	−8.9 (10)	−8.3 (3)
O(1)	−1024 (5)	1314 (2)	−3340 (3)	322 (8)	64 (1)	175 (4)	14 (3)	65 (5)	37 (2)
O(2)	−5023 (5)	1110 (2)	−3788 (3)	422 (9)	79 (2)	170 (4)	−66 (3)	−68 (5)	18 (2)
O(3)	−3228 (4)	922 (1)	−1313 (3)	319 (7)	41 (1)	134 (3)	8 (2)	30 (4)	29 (1)
O(4)	−3609 (7)	2232 (2)	−2377 (4)	686 (14)	27 (1)	299 (6)	29 (3)	52 (8)	17 (2)
N	−1880 (4)	59 (1)	1851 (3)	205 (6)	30 (1)	89 (2)	−5 (2)	30 (3)	−3 (1)
C(1)	966 (7)	1005 (2)	3030 (4)	333 (10)	54 (1)	115 (4)	−24 (3)	−5 (5)	−34 (2)
C(2)	−1592 (6)	836 (2)	2737 (4)	301 (9)	44 (1)	130 (4)	−4 (3)	55 (5)	−37 (2)
C(3)	1672 (8)	1964 (2)	342 (6)	399 (13)	23 (1)	216 (6)	−10 (3)	−26 (8)	−1 (2)

Atom	x	y	z	B, Å²	Atom	x	y	z	B, Å²
H(C1-1)	116 (9)	157 (3)	352 (5)	3.3 (10)	H(N-2)	−156 (8)	−32 (3)	247 (5)	2.8 (9)
H(C1-2)	157 (11)	54 (4)	383 (6)	5.5 (13)	H(C3-1)	238 (10)	194 (3)	−65 (6)	4.1 (11)
H(C2-1)	−235 (9)	128 (3)	198 (5)	3.5 (10)	H(C3-2)	29 (12)	203 (4)	49 (7)	5.6 (16)
H(C2-2)	−222 (8)	78 (3)	372 (5)	3.0 (9)	H(C3-3)	241 (9)	238 (8)	100 (6)	4.2 (12)
H(N-1)	−332 (9)	0 (3)	154 (6)	2.8 (9)					

[a] Atomic coordinates for nonhydrogen atoms are $\times 10^4$; for hydrogen atoms they are $\times 10^3$. [b] Anisotropic temperature factors are $\times 10^4$ and are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

$Ni(OAc)_2 \cdot 4H_2O$ ($d = 1.744$ g/cm³), $Na_2(tart) \cdot 2H_2O$ ($d = 1.818$ g/cm³), and $CoCl_2 \cdot 6H_2O$ ($d = 1.924$ g/cm³) as standards.[17] See Table I for crystal data.

Intensity data were collected at 25 °C using a θ-2θ scan to a maximum of $2\theta = 60°$. Each scan covered a range from 0.7° below the calculated $K\alpha_1$ position to 0.9° above the calculated $K\alpha_2$ position. All data were collected with a scan rate of 2.55° min⁻¹; stationary-background counts were taken before and after each scan. The total time for background counts equaled the scan time and was equally distributed before and after the peak.

The intensities of three standard reflections were recorded every 47 reflections throughout the data collection; they showed random variations of ±1.5%, but no significant trend. A total of 1933 reflections out of a possible 2658 had $I \geq 3\sigma(I)$. Intensities were calculated from the relationship

$$I = (P - LB - RB) \times SR$$

where P is the peak count, LB is the left background count, RB is the right background count, and SR is the scan rate. These intensities were corrected for any decay by computing average decay factors on the basis of the three standard reflections. Thirty-six peaks were rejected on the basis of a profile scan. The 1897 observed intensities were placed on an arbitrary scale by applying Lorentz and polarization corrections and were used in the structure solution and refinement. The polarization correction for the parallel–parallel mode $P2_1$ diffractometer was chosen assuming the monochromator crystal to be 50% perfect and 50% mosaic.

Initial standard deviations were calculated by

$$\sigma(I) = (P + LB + RB)^{1/2} \times SR$$

To incorporate a 3% instrumental error, $\sigma(F_o^2)$ was calculated from the relationship

$$\sigma(F_o^2) = (1/Lp)(\sigma^2(I) + (0.03I)^2)^{1/2}$$

An estimate of the overall scale factor and overall temperature factor was then obtained using Wilson's method. Absorption corrections were not applied. Absorption factors ranged from 1.464 to 1.808 using a linear absorption coefficient of 20.11 cm⁻¹ for Mo Kα radiation.

Solution and Refinement of the Structure.[18] The structure was solved by the heavy-atom method. Space group $P2_1/c$ has four general positions; the requirement of two molecules per unit cell places the Cu atoms at centers of symmetry. Approximate coordinates for Cu, Cl, and S atoms were obtained readily from a normal sharpened Patterson map. A difference Fourier map based on phases determined by these heavy atoms revealed the positions of all remaining non-hydrogen atoms.

Isotropic refinement was initiated using the atomic scattering factors of Cromer and Waber.[19] All atoms were treated as neutral species. Both real and imaginary parts of the anomalous dispersion corrections were applied to Cu, Cl, and S.[20] Initial refinement was based on F^2

and weights were set according to $w = 1/\sigma^2$. With all nonhydrogen scattering matter present, the initial agreement factor

$$R_F = \frac{\sum \|F_o| - |F_c\|}{\sum |F_o|}$$

was 0.22. Several cycles of full-matrix isotropic refinement reduced R_F to 0.098. Three additional cycles of refinement with anisotropic thermal parameters for all nonhydrogen atoms reduced R_F to 0.049.

Further refinement was based on F and a weighting scheme was chosen by an analysis of variance. This led to the following choices for $\sigma(F_o)$

$$\sigma(F_o) = 3.08 - 0.048|F_o|; \ |F_o| \leq 29.8$$

$$\sigma(F_o) = 1.18 + 0.016|F_o|; \ 29.8 \leq |F_o| \leq 69.5$$

$$\sigma(F_o) = -0.48 + 0.040|F_o|; \ |F_o| > 69.5$$

Two cycles of refinement reduced R_F to 0.046 and $R_{wF} = [\sum w(F_o - F_c)^2/\sum w F_o^2]^{1/2}$ to 0.059. A difference map was computed, and from it, all the hydrogen atoms were located. Three more cycles of refinement with anisotropic thermal parameters for nonhydrogen atoms and isotropic temperature factors for hydrogen atoms gave final values of 0.037 and 0.045 for R_F and R_{wF}, respectively. Hydrogen atom temperature factors were set equal to the final isotropic values of the atoms to which they are attached and were not refined. For the last cycle, all parameter changes were within their estimated standard deviation. A final difference map showed a general background of approximately 0.4 e/Å³ and revealed no significant features. Final atomic parameters, together with their estimated standard deviations, are given in Table II. A view of the structure showing the atomic numbering scheme is given in Figure 1; the packing of the structure is shown in Figure 2. A list of observed and calculated structure factors is available.[21]

Description of the Structure

The complex crystallizes as discrete centrosymmetric species in which tetragonal Cu(II) ions are bound by two bidentate $NH_2CH_2CH_2SCH_3$ ligands and two monodentate ClO_4^- groups. Observed bond distances and angles are presented in Table III. The equatorial ligand set consists of the strictly planar trans CuN_2S_2 unit. The Cu–S bond length (2.366 (1) Å) lies between those reported for the equatorial Cu^{II}–S-(thioether) bonds in complexes I[12] (2.410 (5) Å, square pyramidal), II[13] (2.431 (6) and 2.445 (6) Å, tetragonal and square pyramidal), and III[7b] (2.308 (1) and 2.297 (1) Å, tetragonal). A second type of Cu–S bonding in complex II was considered to be of the axial type; the latter Cu–S bond distances were 2.565 (6) and 2.609 (6) Å.[13] The Cu–N bond length (1.977 (2) Å) is near the short end of the range (1.98–2.04 Å) reported for the normal, covalent, equatorial
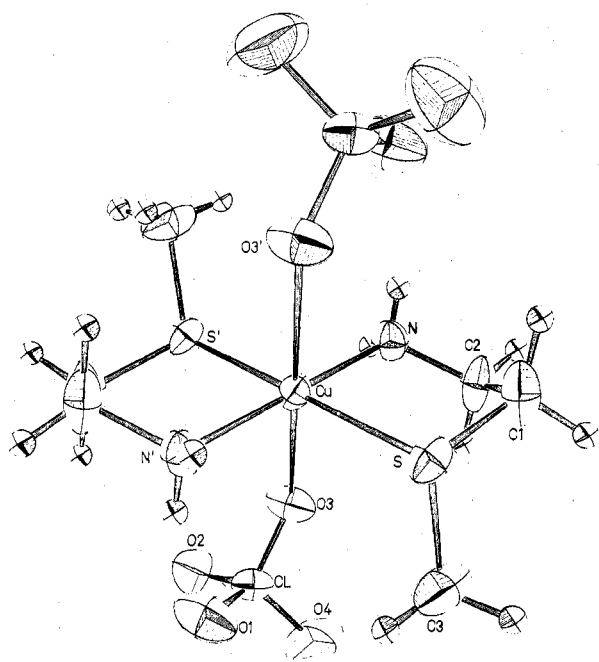
Figure 1. Molecular structure of Cu(H$_2$NCH$_2$CH$_2$SCH$_3$)$_2$(ClO$_4$)$_2$ showing the atom numbering scheme.

Cu–N bonds in complex II (1.991 (14), 2.021 (16) Å), and in a number of Cu(en)$_2$X$_2$ complexes including X$^-$ = ClO$_4$$^-$,[22] NO$_3$$^-$,[23] and BF$_4$$^-$.[24] Further structural similarities between the title complex and the Cu(en)$_2$X$_2$ analogues include the gauche conformation of NH$_2$CH$_2$CH$_2$SCH$_3$ and the S–Cu–N bond angle of 86.8 (1)° which is close to the N–Cu–N angles of 86.2 and 86.4 (5)° reported for Cu(en)$_2$(NO$_3$)$_2$[23] and Cu(en)$_2$(BF$_4$)$_2$,[24] respectively. The five-membered chelate rings are puckered, as indicated by deviations from planarity: C(1) lies 0.35 Å above the best plane defined by the Cu–S–C(1)–C(2)–N fragment while C(2) lies 0.32 Å below this plane.

Both ClO$_4$$^-$ ligands are apical and are weakly bound. The observed Cu–O(3) bond length of 2.599 (2) Å agrees well with the apical Cu–O distances of 2.61 (2), 2.59, and 2.575 (6) Å reported for Cu(en)$_2$(ClO$_4$)$_2$,[22] Cu(en)$_2$(NO$_3$)$_2$,[23] and Cu(CH$_3$NHCH$_2$CH$_2$NH$_2$)$_2$(ClO$_4$)$_2$;[25] it is ca. 0.1–0.3 Å

Table III. Bond Distances (Å) and Angles (deg) in Cu(CH$_3$SCH$_2$CH$_2$NH$_2$)$_2$(ClO$_4$)$_2$

	Distances		
Cu–S	2.366 (1)	H(C1-1)–C(1)	1.02 (5)
Cu–N	1.977 (2)	H(C1-2)–C(1)	1.06 (6)
Cu–O(3)	2.599 (2)	H(C2-1)–C(2)	1.04 (5)
S–C(3)	1.799 (4)	H(C2-2)–C(2)	0.94 (5)
S–C(1)	1.806 (4)	H(N-1)–N	0.87 (5)
C(1)–C(2)	1.505 (5)	H(N-2)–N	0.82 (4)
C(2)–N	1.484 (4)	H(C3-1)–C(3)	0.97 (5)
Cl–O(1)	1.430 (3)	H(C3-2)–C(3)	0.82 (6)
Cl–O(2)	1.415 (3)	H(C3-3)–C(3)	0.97 (5)
Cl–O(3)	1.447 (2)		
Cl–O(4)	1.416 (3)		

	Angles		
S–Cu–N	86.8 (1)	O(3)–Cl–O(1)	109.2 (2)
Cu–S–C(1)	95.1 (1)	O(3)–Cl–O(2)	109.0 (2)
S–C(1)–C(2)	111.2 (2)	O(3)–Cl–O(4)	109.3 (2)
C(1)–C(2)–N	108.8 (3)	O(1)–Cl–O(2)	110.0 (2)
C(2)–N–Cu	113.9 (2)	O(1)–Cl–O(4)	109.3 (2)
Cu–S–C(3)	106.9 (1)	O(2)–Cl–O(4)	110.1 (2)
C(3)–S–C(1)	104.0 (2)		
O(3)–Cu–N	84.8 (1)		
O(3)–Cu–S	100.7 (1)		
Cl–O(3)–Cu	130.1 (1)		

longer than the Cu^{II}–O(apical) distances observed with stronger oxygen donor ligands such as H$_2$O (e.g., 2.23 (1) Å in Cu(O$_2$CCH$_2$CH$_2$S–)$_2$·2C$_5$H$_5$N·H$_2$O,[26] 2.38 (3) and 2.48 (3) Å in bis[copper(II) D-penicillamine disulfide] nonahydrate,[27] and 2.277 (11) Å in Cu$_2$(citrate)·2H$_2$O[28]). Presumably, both the electronic structural properties of Cu(II) and the poorly ligating nature of ClO$_4$$^-$ contribute to this weak apical bonding. Comparison with the structure[29] of Co(CH$_3$SCH$_2$CH$_2$SCH$_3$)$_2$(ClO$_4$)$_2$ is interesting in this respect since octahedral Co(II) does not exhibit Jahn–Teller distortion. With the Co complex, the Co–O(ClO$_4$) bond distance (2.34 (2) Å) was also found to be 0.1–0.3 Å longer than corresponding distances in complexes with stronger oxygen donors. Thus the difference of ~0.25 Å in the M^{II}–O(ClO$_4$) lengths (M = Cu, Co) may be ascribed crudely to electronic structural differences between d^7 and d^9 divalent metal ions.

As indicated by the Cu–O–Cl angle of 130.1 (1)°, the ClO$_4$$^-$ group is tilted significantly relative to the planar CuN$_2$S$_2$ unit. This effect may arise from a combination of (a) intramolecular hydrogen bonding of ClO$_4$$^-$ to the NH$_2$ fragments (Table IV), (b) steric interaction between the ClO$_4$$^-$ and CH$_3$ groups
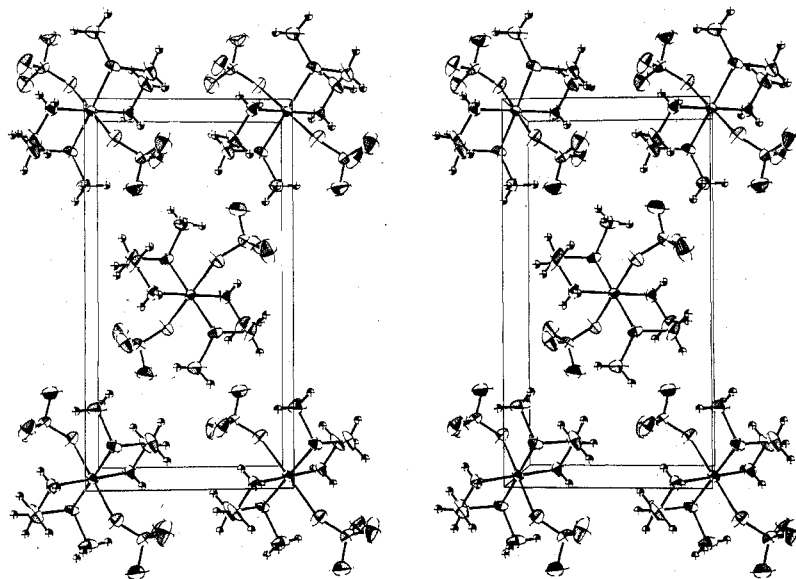

Figure 2. Stereoscopic packing diagram for Cu(H$_2$NCH$_2$CH$_2$SCH$_3$)(ClO$_4$)$_2$ viewed along the a* axis; the b axis is vertical. The box delineates one unit cell.

Table IV. Hydrogen-Bonding Contacts in $Cu(CH_3SCH_2CH_2NH_2)_2(ClO_4)_2$

Donor (D)	Hydrogen (H)	Acceptor (A)^a	D–H⋯A, deg	D⋯A, Å	H⋯A, Å
N	H(N-2)	O(1) (ii)	150 (4)	3.058 (4)	2.32 (5)
N	H(N-1)	O(2) (iii)	102 (3)	3.154 (4)	2.86 (5)
N	H(N-1)	O(3) (iii)	147 (4)	3.251 (4)	2.49 (5)
N	H(N-1)	O(3) (i)	98 (3)	3.120 (3)	2.88 (5)
N	H(N-2)	O(2) (iii)	119 (4)	3.154 (4)	2.67 (5)

^{a} i $= x, y, z$; ii $= \bar{x}, \bar{y}, \bar{z}$; iii $= -1 - x, \bar{y}, \bar{z}$.

(Figure 1), (c) the valence angle preference of approximately sp^3-hybridized oxygen, and (d) crystal packing forces. In the $Co(CH_3SCH_2CH_2SCH_3)_2(ClO_4)_2$ structure, the ClO_4^- groups are also tilted (by an unspecified amount) relative to the CoS_4 unit; hydrogen-bonding interactions cannot play a significant role in this structure. Moreover, hydrogen-bonding interactions cannot play a significant role in the structure of complex III for which a Cu–O–Cl angle of 130.3 (2)° was observed.[7b] A smaller Cu–O–Cl angle of 121.0 (3)° was observed for the $Cu(CH_3NHCH_2CH_2NH_2)_2(ClO_4)_2$ complex.[25] In all three structures, the ClO_4^- groups are tilted away from the CH_3 fragments in the $NH_2CH_2CH_2SCH_3$, $CH_3SCH_2CH_2SCH_3$, and $CH_3NHCH_2CH_2NH_2$ ligands. However, the Cu–F–B angle of 116.3° observed[24] for $Cu(en)_2(BF_4)_2$ suggests that substantial tilting may occur in the absence of significant steric interactions. Thus, it seems likely that the above structural feature arises predominantly from the valence preference of sp^3 oxygen (and fluorine).

For the ClO_4^- group, the various O–Cl–O angles are equivalent to within 3σ (Table III), while the Cl–O(3) bond length (1.447 (2) Å) is significantly larger than the remaining three. Although the differences are not large, the Cl–O(1) distance is also significantly longer than the Cl–O(2) and Cl–O(3) distances; thus, the ClO_4^- group exhibits, at best, only approximate C_{3v} symmetry. As noted elsewhere, the lower symmetry of monodentate ClO_4^- relative to "free" ClO_4^- may be detected readily by infrared spectral measurements.[30-32] The results of such studies indicate that monodentate ClO_4^- effectively has C_{3v} symmetry. Since the differences in Cl–O bond lengths are small, the present structural results do not contradict this conclusion. The effect of hydrogen bonding on the infrared spectral properties of the ligand ClO_4^- was considered responsible for the apparent C_{2v} symmetry observed for the ClO_4^- group of 1-aminopyridinium perchlorate.[33] In the present structure, the effect of hydrogen bonding on the Cl–O bond lengths is difficult to quantify, although it does appear to be small. For example, O(4) and O(2) experience two and zero hydrogen-bonding interactions, respectively (Table IV), while the Cl–O(4) and Cl–O(2) bond lengths (1.416 (3), 1.415 (3) Å) are identical within experimental error. A similar lack of correlation between hydrogen-bonding interactions and Cl–O distances has been observed[34] in the structure of $HClO_4 \cdot 2.5H_2O$.

The ClO_4^- structural parameters agree well (± 0.02 Å) with those reported for the structurally similar complex $Cu(CH_3NHCH_2CH_2NH_2)_2(ClO_4)_2$ for which the ClO_4^- oxygen atom coordinated to Cu also exhibited the longest Cl–O bond distance (1.431 (6) Å). The remaining Cl–O lengths were 1.414 (7), 1.407 (9), and 1.418 (6) Å. However, lengthening of the Cl–O bond involving the coordinated oxygen atom was not observed with di-μ-hydroxo-bis[2-(2-ethylamino)pyridine]dicopper(II) diperchlorate.[35] While the observed Cu–O(apical) distances (2.618 (9), 2.562 (10) Å) are comparable to those of the title complex, seven of the eight bond distances had lengths of 1.401 ± 0.007 Å. Only one Cl–O bond was significantly larger (1.464 (10) Å), and this was not explained. The Cl–O distances reported for the perchlorate groups in

complex III fell in the range 1.421 (4)–1.443 (4) Å; the bond involving the coordinated oxygen atom was not uniquely long.[7b] A final structure of relevance here is that of di-μ-hydroxo-bis[bipyridylcopper(II)] diperchlorate.[36] Both ClO_4^- ions were viewed as bidentate bridging groups. Although a long Cu–O distance was observed (2.797 (4) Å) relative to the above complexes, the Cl–O bond distances were equivalent and fell in the range 1.444 ± 0.002 Å.

With one exception, bond distances within the $CH_3SCH_2CH_2NH_2$ ligand compare favorably to those observed for coordinated en and $CH_3SCH_2CH_2SCH_3$. The C–C bond distance (1.30 ± 0.05 Å) reported for $Co(CH_3SCH_2CH_2SCH_3)_2(ClO_4)_2$ appears to be too short. The value of 1.505 (5) Å observed for the C–C bond in the title complex is in better agreement with the values of 1.56 and 1.545 ± 0.027 Å reported, respectively, for the corresponding distances in $Cu(en)_2(BF_4)_2$ and $Cu(en)_2(NO_3)_2$.

References and Notes

(1) (a) School of Chemistry, Rutgers, The State University, New Brunswick, N.J. 08903. (b) Division of Natural Sciences, University of California, Santa Cruz, Calif. 95064. (c) Department of Chemistry, Rutgers, The State University, Newark, N.J. 07102.
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Notes

Contribution from the Department of Chemistry,
University of Nevada, Reno, Reno, Nevada 89557,
and the Life Sciences Division, Stanford Research Institute,
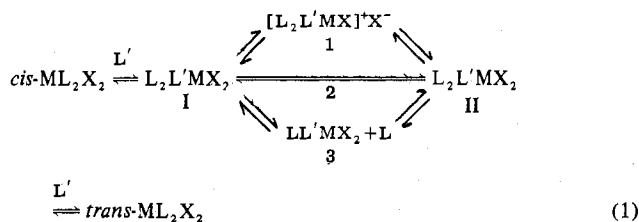Menlo Park, California 94025

Palladium (II)–Cyanide–Phosphine Complexes[1]

Allen W. Verstuyft,[2a] Lewis W. Cary,[2b] and John H. Nelson*[2a]

Recent investigations[3-14] of the geometrical isomerization of complexes of the type L_2PdX_2 have indicated that the isomerization process is associative, proceeding through pentacoordinate transition states (I and II) according to eq 1. Each of the three pathways (1, 2, and 3) occurs under

$$cis\text{-}ML_2X_2 \underset{I}{\overset{L'}{\rightleftharpoons}} L_2L'MX_2 \begin{array}{c} \overset{[L_2L'MX]^+X^-}{\overbrace{}} \\ 1 \\ \underset{2}{\rightleftharpoons} \\ \underset{\underset{3}{LL'MX_2+L}}{\diagdown\diagup} \end{array} \overset{L_2L'MX_2}{II}$$

$$\overset{L'}{\rightleftharpoons} trans\text{-}ML_2X_2 \qquad (1)$$

various conditions and the conditions favoring each have been delineated.[9] The least studied pathway is fluxional rotation[15] (pathway 2) and it should dominate in nonpolar solvents when L and L′ are small and have nearly the same basicity, with X being a strongly coordinating anion. In some investigations[3-5] of catalyzed isomerizations the lack of L and L′ interchange was taken to imply that any mechanistically important pentacoordinate species cannot have a regular geometry but must be distorted in such a way that L and L′ can never become equivalent. It is apparent then that more information is needed regarding the solution behavior of pentacoordinate palladium complexes.

To date there have been few pentacoordinate complexes of palladium(II) with monodentate ligands reported.[16-21] Except for the ligand[21] $C_6H_5CH_2P(CH_3)_2$, these all involve the sterically undemanding phosphole type ligands,[16-20] and still, each of these complexes is extensively dissociated in solution. Numerous studies with pentacoordinate nickel complexes have shown that pentacoordination is stabilized by strong field ligands.[22] The exact reasons are not yet clear but evidence is emerging which suggests that the relative stabilities of ML_2X_2 and ML_3X_2 complexes depend upon a subtle interplay of steric and electronic effects.[23]

Thus there are two possible approaches in seeking to stabilize pentacoordinate heteroleptic palladium(II) complexes of the type PdL_3X_2. One approach is to seek sterically undemanding
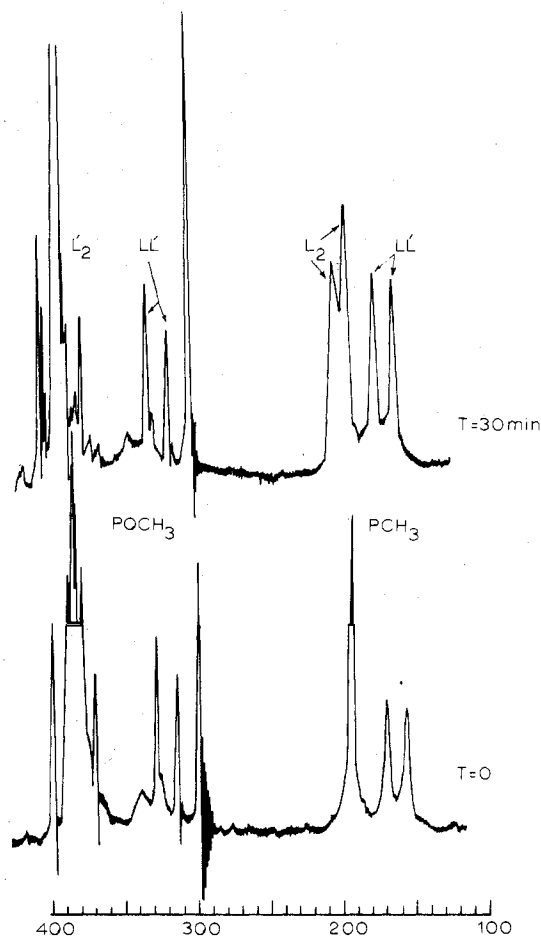

Figure 1. The 100-MHz ^{1}H NMR spectra in the methyl and methoxy regions for a $CDCl_3$ solution containing an equimolar (1.25×10^{-4} M each) mixture of $[(CH_3)_2PC_6H_5]_2Pd(CN)_2$ and $(CH_3O)_3P$ as a function of time. The numbers are chemical shifts in Hz from internal TMS. $L'_2 = [(CH_3O)_3P]_2Pd(CN)_2$, $LL' = [\{(CH_3O)_3P\}\{(CH_3)_2PC_6H_5\}]Pd(CN)_2$, and $L_2 = [(CH_3)_2PC_6H_5]_2Pd(CN)_2$.

ligands L and the other is to study strong-field anions X. The latter approach has been undertaken in this work by utilizing cyanide as the strong-field anion with a variety of phosphorus ligands L.

Experimental Section

Chemicals used were reagent grade and used as received. All solvents, when necessary, were dried by standard procedures and stored over Linde 4-Å molecular sieves for at least 2 days prior to use. All reactions involving phosphines were conducted in a prepurified nitrogen