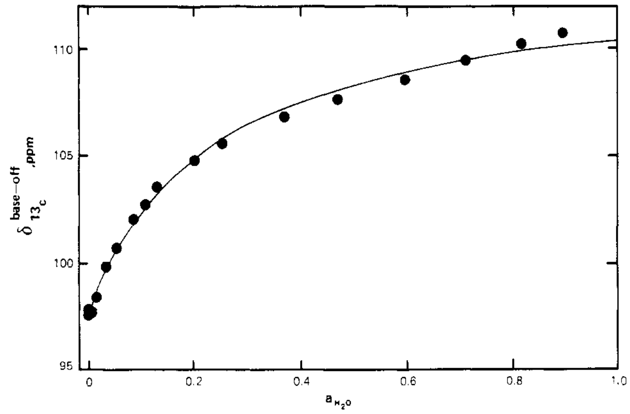
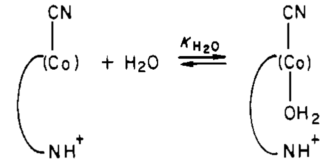


Figure 8. Plot of $\delta_{^{13}C}{}^{\text{base-off}}$ for ^{13}CNCbl at 25 °C vs. the activity of water in the aqueous sulfuric acid solvent. The solid line is a least-squares fit to eq 34 from which the values of $K_{H_2O} = 4.13$, $\delta_{^{13}C}{}^{(III)} = 97.60$, and $\delta_{^{13}C}{}^{(IV)} = 113.58$ were obtained.

shift due to phosphodiester hydrolysis).

An alternative explanation for the changes in base-off ^{13}C chemical shift of ^{13}CNCbl at H_0 below −0.5 involves the reversible formation of a pentacoordinate cyanocobalt corrin species (eq 33, 34) due to the reduced activity of water in such acidic mixtures.[49,62] Spectroscopic evidence of various kinds has previously been presented for the existence of such 5-coordinate–6-coordinate equilibria in cobalt corrins.[63-66] A fit of these data to eq 34 (Figure 8) yields the values $K_{H_2O} = 4.13$, $\delta_{^{13}C}{}^{(III)} = 97.60$, and $\delta_{^{13}C}{}^{(IV)} = 113.58$. It should be pointed out that although this fit is clearly trended, the fit of these data to eq 31 (Figure 7) is similarly trended although it is more difficult to see due to the plot vs. logarithm of titrant concentration. In either case, some trending of these fits must be expected since it seems unlikely that either K_a in eq 30 or K_{H_2O} in eq 33 would be completely independent of the phosphodiester protonations occurring in this same acidity range. Nonetheless, the value of K_{H_2O} (4.13) is surprisingly low and implies that, at 25 °C in unit activity water, base-off CNCbl is some 20% 5-coordinate. While it is difficult to believe this assignment, it cannot be ruled out a priori on the basis of the evidence at hand. Additional experimentation with other cobalamins in aqueous sulfuric acid is currently in progress to attempt to resolve this question.



III IV (33)

$$\delta_{^{13}C}{}^{\text{base-off}} = \frac{\delta_{^{13}C}{}^{(III)} + \delta_{^{13}C}{}^{(IV)} K_{H_2O} a_{H_2O}}{1 + K_{H_2O} a_{H_2O}} \tag{34}$$

Acknowledgment. This research was supported by the Robert A. Welch Foundation, Houston, TX (Grant No. Y-749), and the Organized Research Fund of The University of Texas at Arlington. The authors are extremely grateful to Prof. Dennis S. Marynick (UTA) for supplying the nonlinear least-squares routine and assisting in its use.

Registry No. ^{13}CNCbl (base-on), 89975-17-7; ^{13}CNCbl (base-off), 89959-47-7; ($^{1}\beta$-^{13}CN)(α-H_2O)Cbi, 90026-99-6; (β-H_2O)(α-^{13}CN)Cbi, 89959-48-8; (^{13}CN)$_2$Cbl, 89959-49-9; (^{13}CN)$_2$Cbi, 89959-50-2; CH_3Cbl, 13422-55-4; (H_2O)$_2$Cbi, 15259-55-9.

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Contribution from the Department of Chemistry,
University of California at Davis, Davis, California 95616

Influence of Ligand Structure on the Mechanism of Oxidation of Dithioethers by Copper(II). X-ray Crystal Structure of Bis(3-hydroxy-1,5-dithiacyclooctane)copper(II) Perchlorate

W. K. MUSKER,* M. M. OLMSTEAD, and R. M. KESSLER

Received August 16, 1983

Although 1,5-dithiacyclooctane (1,5-DTCO) rapidly reduces copper(II) perchlorate, substitution of a hydroxyl group at the 3-position of the eight-membered ring (3-hydroxy-1,5-dithiacyclooctane, 3-OH-1,5-DTCO) gives a facially coordinating ligand that completely inhibits reduction of copper(II). The crystal structure of Cu(3-OH-1,5-DTCO)$_2$(ClO_4)$_2$ is also reported: space group $P2_1/c$, $a = 6.811$ (3) Å, $b = 9.225$ (4) Å, $c = 16.575$ (5) Å, $\beta = 90.54$ (3)°, $Z = 2$. On the basis of these and other observations a mechanism that accounts for the differences in the ability of various thioether ligands to reduce copper(II) perchlorate is proposed. This mechanism depends on a linear Cu–S···S arrangement of orbitals, which facilitates ligand to metal electron transfer and leads, in turn, to metal–ligand bond cleavage.

Introduction

Our interest in the coordination and redox chemistry of copper complexes of dithioethers arose from the observation that the eight-membered ring dithioether 1,5-dithiacyclooctane (1,5-DTCO) causes a rapid reduction of copper(II) perchlorate in methanol at room temperature, whereas the six-membered ring dithioether 1,4-dithiane (1,4-DT) causes *no* reduction of copper(II) perchlorate even in refluxing methanol. This facile reduction is not due to any destabilization of a planar copper(II) complex as noted for 2,9-dimethyl-*o*-phenanthroline complexes[1] since planar bis complexes of eight-membered mesocycles are well-known.[2,3] Because of the behavior of

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(1) James, B. R.; Williams, R. J. P. *J. Chem. Soc.* **1961**, 2007.

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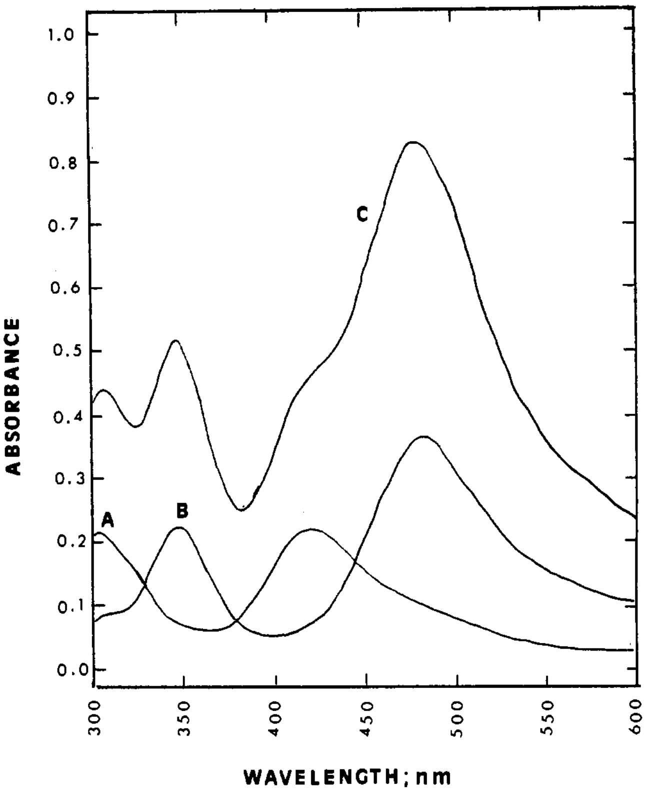

Figure 1. Ultraviolet and visible spectra of copper(II) perchlorate with 3-OH-1,5-DTCO in methanol: (A) 90% Cu(II); 10% 3-OH-1,5-DTCO; (B) 50% Cu(II), 50% 3-OH-1,5-DTCO; (C) 10% Cu(II), 90% 3-OH-1,5-DTCO.

unsubstituted 1,5-DTCO, we wondered whether substitution of a nucleophile at the 3-position would lead to similar redox behavior. In this initial effort it was discovered that the placement of a hydroxyl group at the 3-position *completely inhibits* the reduction of copper(II) perchlorate in methanol. An X-ray crystal structure of bis(3-hydroxy-1,5-dithiacyclooctane) copper(II) perchlorate ($Cu(3\text{-}OH\text{-}1,5\text{-}DTCO)_2(ClO_4)_2$) reveals that the ligand exhibits facial coordination.

On the basis of these and other observations, a mechanistic scheme for the oxidation of dithioethers by copper(II) has been developed.

Experimental Section

Preparation of Compounds. Reagents. The following reagents were obtained from the indicated sources: 3-hydroxy-1,5-dithiacyclooctane (1,5-dithiacyclooctan-3-ol) from Aldrich Chemical Co., Milwaukee, WI; $Cu(BF_4)_2 \cdot xH_2O$ from Ventron, Alfa Division, Danvers, MA; $Cu(ClO_4)_2 \cdot 6H_2O$ from G. Frederick Smith Chemical Co., Columbus, OH; $CuCl_2$ from Allied Chemical Co., General Chemical Division, Morristown, NJ; anhydrous (200 proof) ethanol from Gold Shield Chemical Co., Hayward, CA. 1,5-Dithiacyclooctane was prepared in the usual way.[4]

$Cu(3\text{-}OH\text{-}1,5\text{-}DTCO)_2(ClO_4)_2$. A 5-mL portion of a 0.100 M methanol solution of $Cu(ClO_4)_2$ was added to a 10-mL portion of a 0.102 M methanol solution of 3-OH-1,5-DTCO. The mixture turned dark immediately and showed the start of precipitation after a few minutes. The mixture was placed at −5 °C overnight and then gravity filtered. The dark purple microcrystals were air-dried. A total of 0.229 g (77.4% yield) of product was recovered.

The complex dissociates when dissolved in methanol. However, with use of Job's method two species are shown to be present, a mono complex that absorbs at 308 and 422 nm and a bis complex that absorbs at 346 and 480 nm (Figure 1).

Table I. Crystal Data for Bis(3-hydroxy-1,5-dithiacyclooctane)copper(II) Perchlorate

formula	$Cu(S_2C_6OH_{12})_2(ClO_4)_2$
fw	591.02
color and habit	dark purple microcrystals
space group	$P2_1/c$
a, Å	6.811 (3)
b, Å	9.225 (4)
c, Å	16.575 (5)
β, deg	90.54 (3)
T, K	140
Z	2
cryst dimens, mm	0.175 × 0.175 × 0.50
d_{calcd}(140 K), g cm^{-3}	1.88
radiation	Mo Kα (λ = 0.710 69 Å) graphite monochromator
μ(Mo Kα), cm^{-1}	17.4
diffractometer	$P2_1$
scan method	ω scans
2θ range, deg	0–55
hkl	0–9, 0–12, −22 to +22
scan speed, deg min^{-1}	8–60, variable
no. of unique data	2294
no. of data with $F > 3\sigma(F)$	2034
no. of parameters refined	142
R^a	0.027
$R_w{}^b$	0.027

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_w = [\Sigma ||F_o| - |F_c||^2 / \Sigma w |F_o|^2]^{1/2}$.

Table II. Positional Parameters (×10^4) for $[Cu(3\text{-}OH\text{-}1,5\text{-}DTCO)_2](ClO_4)_2$

atom	x	y	z
Cu	5000	0	0
Cl	9960 (1)	1416 (1)	3379 (1)
S(1)	6909 (1)	1177 (1)	976 (1)
S(2)	2250 (1)	1358 (1)	359 (1)
O(1)	4111 (2)	−1311 (2)	1156 (1)
O(2)	9108 (3)	2341 (2)	2772 (1)
O(3)	9655 (3)	−68 (2)	3158 (1)
O(4)	12012 (3)	1696 (3)	3457 (1)
O(5)	8995 (3)	1705 (2)	4140 (1)
C(1)	5634 (3)	598 (3)	1879 (1)
C(2)	3702 (3)	−159 (3)	1713 (1)
C(3)	2011 (3)	765 (3)	1400 (1)
C(4)	2949 (4)	3253 (3)	425 (2)
C(5)	4458 (4)	3666 (3)	1062 (2)
C(6)	6532 (4)	3121 (3)	938 (1)
HO(1)	3051 (48)	−1834 (33)	1166 (19)

$Cu(3\text{-}OH\text{-}1,5\text{-}DTCO)Cl_2$. A 10-mL portion of a 0.100 M methanol solution of $CuCl_2$ was added to a 10-mL portion of a 0.102 M methanol solution of 3-OH-1,5-DTCO. The mixture immediately turned dark and showed the start of precipitation. The mixture was placed at −5 °C overnight and then gravity filtered. The dark red-brown crystals were air-dried; yield 0.226 g (75.6%).

Physical Measurements. The ultraviolet/visible spectra of solutions were recorded on a Hewlett-Packard 8450A spectrophotometer. Nujol mull spectra were recorded on a Varian Cary 17 ultraviolet/visible spectrophotometer.

X-ray Crystallography. Crystals of $Cu(3\text{-}OH\text{-}1,5\text{-}DTCO)_2(ClO_4)_2$ suitable for X-ray data collection were obtained from a cooled methanol solution. The crystal selected was mounted in the cold stream with its needle axis parallel to the ϕ axis of the $P2_1$ diffractometer. Since the range of absorption correction factors (1.29–1.44) is small, no absorption correction was applied. From systematic absences, the space group was uniquely determined to be $P2_1/c$. On the basis of the computed density and $Z = 2$, Cu was expected to lie on a center of symmetry. Solution of the structure followed from arbitrary placement of Cu at ($^1/_2$, 0, 0),[5,6] subsequent difference Fourier maps,

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(6) All calculations were performed with use of SHELXTL, Version 3, July 1981, by G. M. Sheldrick, installed on a Data General Eclipse computer.

Table III. Bond Lengths (Å) and Bond Angles (deg) for $[Cu(3\text{-}OH\text{-}1,5\text{-}DTCO)_2][ClO_4]_2$

Cu–S(1)	2.333 (1)	C(1)–C(2)	1.513 (3)
Cu–S(2)	2.335 (1)	C(2)–C(3)	1.520 (3)
Cu–O(1)	2.350 (1)	C(4)–C(5)	1.515 (3)
S(1)–C(1)	1.818 (2)	C(5)–C(6)	1.515 (3)
S(1)–C(6)	1.813 (2)	Cl–O(2)	1.437 (2)
S(2)–C(3)	1.819 (2)	Cl–O(3)	1.432 (2)
S(2)–C(4)	1.815 (2)	Cl–O(4)	1.426 (2)
O(1)–C(2)	1.437 (3)	Cl–O(5)	1.453 (2)
O(1)–HO(1)	0.87 (3)		
S(1)–Cu–S(2)	91.0 (1)	C(1)–S(1)–C(6)	104.5 (1)
S(1)–Cu–O(1)	79.7 (1)	C(3)–S(2)–C(4)	104.9 (1)
S(2)–Cu–O(1)	81.6 (1)	C(1)–C(2)–C(3)	117.2 (2)
Cu–S(1)–C(1)	99.6 (1)	C(4)–C(5)–C(6)	116.7 (2)
Cu–S(1)–C(6)	111.0 (1)	O(1)–C(2)–C(3)	110.3 (2)
Cu–S(2)–C(3)	99.2 (1)	O(1)–C(2)–C(1)	106.6 (2)
Cu–S(2)–C(4)	108.8 (1)	C(2)–O(1)–HO(1)	103.0 (2)
Cu–O(1)–C(2)	101.3 (1)	O(2)–Cl–O(3)	109.3 (1)
Cu–O(1)–HO(1)	121.0 (2)	O(2)–Cl–O(4)	110.2 (1)
S(1)–C(1)–C(2)	114.0 (2)	O(2)–Cl–O(5)	108.4 (1)
S(1)–C(6)–C(5)	117.1 (2)	O(3)–Cl–O(4)	109.7 (1)
S(2)–C(3)–C(2)	114.7 (2)	O(3)–Cl–O(5)	109.4 (1)
S(2)–C(4)–C(5)	117.4 (2)	O(4)–Cl–O(5)	109.8 (1)

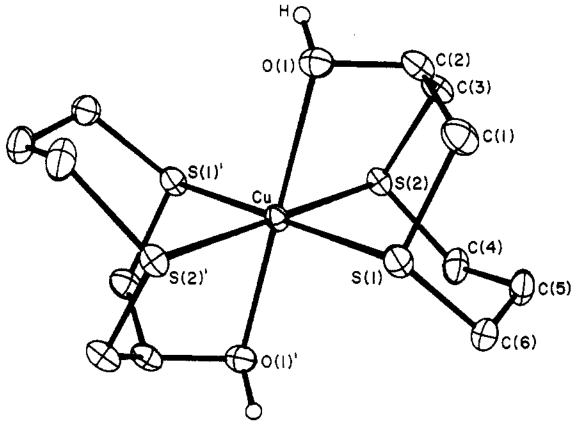

Figure 2. Perspective drawing of $Cu(3\text{-}OH\text{-}1,5\text{-}DTCO)_2(ClO_4)_2$ showing thermal ellipsoids at the 50% probability level and the atom-numbering scheme.

and blocked-cascade least-squares refinement. The hydroxyl hydrogen was located on a difference Fourier map and allowed to refine. The remaining hydrogen atoms were refined at computed positions riding on the bonded carbon atom. Anisotropic thermal parameters were used for non-hydrogen atoms in the final cycles of refinement. The largest shift/esd in the final cycle was 0.09 for the x coordinate of O(4). A final difference map was featureless, with maximum and minimum peak values of 0.37 and -0.28 e Å^{-3}, respectively. Positional parameters and selected bond distances and angles are presented in Tables II and III, respectively. Calculated hydrogen atom coordinates, anisotropic thermal parameters for non-hydrogen atoms, and a listing of structure factor amplitudes are available as supplementary material.

Results and Discussion

Description of Structure. The crystal structure consists of centrosymmetric cations of $Cu(3\text{-}OH\text{-}1,5\text{-}DTCO)_2^{2+}$, weakly hydrogen bonded via the 3-OH group to uncoordinated perchlorate anions. The cation geometry is depicted in Figure 2. As can be seen in the drawing, the donor set for copper is S_4O_2. The O atoms are tilted 13.6° off the axial direction due to the constraints imposed by the coordination of the eight-membered dithioether ring. Nevertheless, the coordination around copper is best described as tetragonal (4 + 2) since the Cu–O distances are typical for axial ligation. The eight-membered ring is in a boat–chair conformation.

Bond distances and angles (Table III) appear normal for a copper(II)–thioether complex. The Cu–O distance of 2.350 (2) Å is shorter than previous Cu^{II}–OH distances observed: 2.528 (9) and 2.483 (8) Å in a tetrameric thiodiethanol complex[7] and 2.510 (3),[8a] 2.419 (3), and 2.518 (3) Å[8b] in (2-hydroxyethyl)ethylenediamine complexes. The one Cl–O distance that is somewhat longer than the others (1.453 (2) Å vs. an average for three others of 1.431 (4) Å) is probably a consequence of hydrogen bonding between this perchlorate oxygen and the hydroxyl hydrogen (HO(1)···O(5) = 2.00 (3) Å).

Mechanism of Oxidation of Dithioethers. The unsubstituted 1,5-DTCO ring system is oxidized rapidly by $Cu(ClO_4)_2$ or $Cu(BF_4)_2$ in methanol whereas 3-OH-1,5-DTCO is not oxidized at all. Thioethers that function as monodentate ligands (e.g. tetrahydrothiophene (THT), 1,4-dithiane (1,4-DT) are oxidized extremely slowly[9] whereas some bidentate acyclic dithioethers (e.g. 2,5-dithiahexane (2,5-DTH), 3,6-dithiaoctane (3,6-DTO) are oxidized at intermediate rates such that both copper(I) and copper(II) complexes can easily be isolated.[10,11] Explanations of the enhanced reactivity of 1,5-DTCO could be based on its unusually low oxidation potential, its coordination ability, or its ability to undergo a facile electron-transfer process. A cyclic voltammetric study of the oxidation of a series of thioethers in acetonitrile has shown that monothioethers have high peak potentials (1.2–1.3 V relative to Ag/0.1 M $AgNO_3$) and acyclic dithioethers have intermediate potentials (0.6–1.0 V) but *both* mesocyclic dithioethers have low potentials (~0.3–0.5 V).[9b,12] Thus, a correlation of peak potentials and the ease of oxidation by $Cu(ClO_4)_2$ is consistent except for 3-OH-1,5-DTCO.

The oxidation abilities of $Cu(ClO_4)_2$ and $Cu(BF_4)_2$ toward thioethers differ markedly from that of $CuCl_2$. For example, reaction of $CuCl_2$ with 1,5-DTCO or 3-OH-1,5-DTCO gives a stable chloride-bridged dimer,[9c] and oxidation can be achieved only if the complex is refluxed in methanol. The organic oxidation product from the oxidation of these and other thioethers with $CuCl_2$ is the monosulfoxide whereas only traces of sulfoxide are found when $Cu(ClO_4)_2$ or $Cu(BF_4)_2$ are used.[14] These observations, together with our results on the oxidation of thioethers with other oxidizing agents, suggest that $CuCl_2$ reacts via a direct two-electron oxidation to give the sulfoxide whereas $Cu(ClO_4)_2$ reacts via a one-electron oxidation to give a cation radical.[15] Thus, the enhanced rate of oxidation of 1,5-DTCO by $Cu(ClO_4)_2$ may be attributable to the facile formation of the long-lived 1,5-DTCO cation radical. This radical has previously been observed by ESR on treatment of 1,5-DTCO with either $Cu(CH_3CN)_4^{2+}$ or $NOBF_4$ in acetonitrile.[16] Its stability is due to a 1,5-transannular interaction between the two sulfur atoms.

The sequential formation of a bis complex of copper(II) with two 1,5-DTCO ligands would be expected since bis complexes of the corresponding mesocyclic diamine (1,5-diazacyclooctane) with copper(II)[2] and $Ni(1,5\text{-}DTCO)_2^{2+}$ are well-known.[3] With other dithioethers that reduce copper(II) more slowly (2,5-DTH, 3,6-DTO), Job's plots reveal that reduction does

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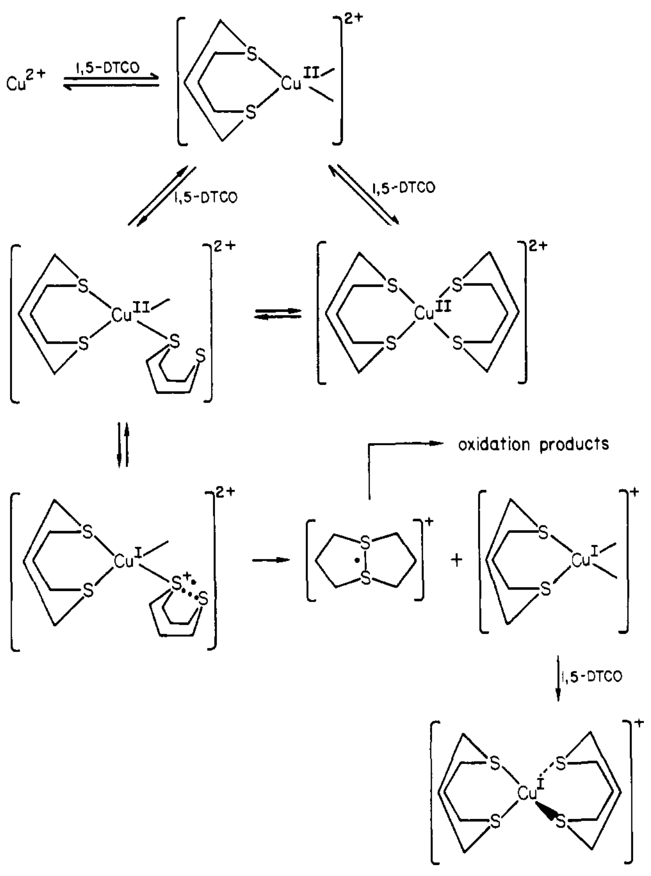
Scheme I



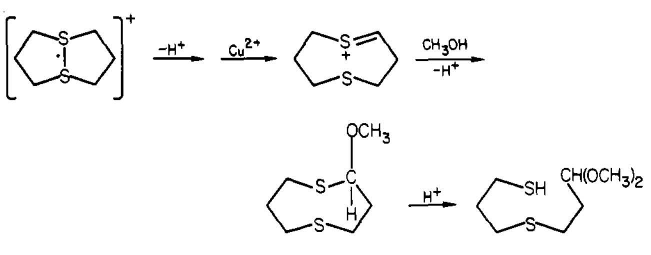
not proceed significantly until the ligand to metal ratio is greater than 1.[17]

A possible path for the facile oxidation of 1,5-DTCO by $Cu(ClO_4)_2$ in methanol is given by Scheme I.

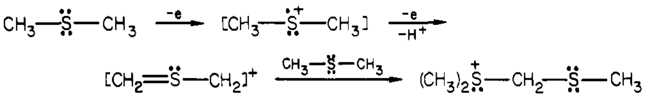
On the basis of its low oxidation peak potential 3-OH-1,5-DTCO should also form a cation radical easily but, just as water and alcohols destroy cation radicals, the 3-hydroxyl substituent in the molecule will prevent the observation of a cation radical.[15] However, both 1,5-DTCO and 3-OH-1,5-DTCO undergo rapid two-electron oxidations with aqueous iodine to give the corresponding sulfoxides.[18] Since both 1,5-DTCO and 3-OH-1,5-DTCO would be expected to react rapidly with copper(II), specific coordination factors must contribute to the enormous difference in reactivity.

It might be suggested that if 3-OH-1,5-DTCO forms a stable octahedral bis complex, facile reduction of copper(II) would be prevented. However, $Cu(3\text{-}OH\text{-}1,5\text{-}DTCO)_2^{2+}$ readily dissociates in solution, as indicated by absorbances due to both mono and bis complexes in the ultraviolet and visible spectra. A Job plot of bands at 308 and 422 nm reveals the presence of the mono complex: the bands at 346 and 480 nm are due to the bis complex.

Scheme II



Scheme III



A number of studies of the structure and reactivity of derivatives of thioethers reveal that nucleophiles interact with the sulfur atom along the direction of the lowest unoccupied molecular orbital (i.e. σ^*).[19] For example, the structure of a monocoordinated 1,5-DTCO complex, $SnCl_4(1,5\text{-}DTCO)_2$, exhibits an Sn–S···S angle near 180°.[20] In another complex that involves monocoordinated 1,5-DTCO, $(NH_3)_5Ru(1,5\text{-}DTCO)^{2+}$, Stein and Taube[21] reported the observation of two ligand-to-metal charge-transfer bands in the visible spectrum, which they attributed to a splitting of the sulfur lone pairs of the ligand and subsequent transfer of σ and σ^* electrons to the metal. In studies of concomitant electrophilic/nucleophilic cleavage reactions of disulfides the incoming nucleophile attacks sulfur along an extension of the S–S bond (i.e. at the σ^* orbital).[22]

If a linear Cu–S···S arrangement of orbitals is required for facile oxidative-cleavage reactions, one sulfur atom of the dithioether must be coordinated to copper(II) while an orbital of the other must interact with the Cu–S σ^* orbital to cause homolytic cleavage of the Cu–S bond. When 3-OH-1,5-DTCO is the ligand, a linear arrangement of Cu–S···S orbitals in the activated complex of the electron transfer reaction is difficult to achieve because of the affinity of the hydroxyl group for a coordination site on copper(II). In this regard, it should be noted that another facial tridentate ligand, 1,4,7-trithiacyclononane, forms a stable bis complex with copper(II) perchlorate.[23] Likewise, complexes of copper(II) with macrocyclic tetrathioethers are stable and the ligand is not oxidized.[24] However, acyclic dithioethers with either three or four methylene groups between the two sulfur atoms (2,6-dithiaheptane and 2,7-dithiaoctane) also undergo a facile oxidation whereas acylic dithioesters with only two methylene groups (2,5-DTH, 3,6-DTO) between the two sulfur atoms undergo slow oxidation.[9a] The lack of reduction of copper(II) by 1,4-dithiane is based on the inability of the activated complex to attain the appropriate alignment and overlap of orbitals required for facile electron transfer. Thus, only those dithioethers that can easily adopt a linear metal–S···S arrangement of orbitals seem particularly susceptible to oxidation by copper(II). This orientation may be a common path for ligand oxidation reactions at other metal centers.

As mentioned previously, the product of the decomposition of the 1,5-DTCO cation radical in methanol is not the sulfoxide. Radicals of this type undergo rapid α-deprotonation followed by further oxidation to give alkylidene sulfonium salts. Subsequent solvolysis of this salt in methanol causes ring opening to give an acyclic thiol aldehyde or its acetal, and these functional groups are susceptible to further decomposition during workup (Scheme II). Because of complicated decompostion processes it would be quite unlikely to isolate and characterize the organic products resulting from the one-electron oxidation of 1,5-DTCO.

A similar decomposition scheme (Scheme III) was reported for the electrochemical oxidation of dimethyl sulfide in ace-

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tonitrile.[25] In acetonitrile, solvolysis is minimized and the product can be isolated.

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Registry No. 1,5-DTCO, 6572-95-8; 3-OH-1,5-DTCO, 86944-00-5; $Cu(3\text{-}OH\text{-}1,5\text{-}DTCO)_2(ClO_4)_2$, 89959-19-3; $Cu(ClO_4)_2$, 13770-18-8.

Supplementary Material Available: Tables of anisotropic temperature factors, hydrogen coordinates, and observed and calculated structure factors for $Cu(C_{12}H_{24}S_4O_2)(ClO_4)_2$ (13 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Canada S7N 0W0,
and Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Bereich Strahlenchemie,
D-1000 Berlin 39, Federal Republic of Germany

Pulsed-Laser Conductivity and Emission Study of Some Chromium(III) Amine Complex Ions in Acidic and Alkaline Aqueous Media

WILLIAM L. WALTZ,*[1a] JOCHEN LILIE,[1b] and SANG H. LEE[1a]

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The photochemistry and photophysics of $Cr(tn)_3^{3+}$, *trans*-$Cr(en)_2F_2^+$, $Cr(en)_3^{3+}$, $Cr(NH_3)_6^{3+}$, $Cr(NH_3)_5(CN)^{2+}$, and $Cr(NH_3)_5(NCS)^{2+}$, where en and tn designate ethylenediamine and 1,3-propanediamine ligands, respectively, have been studied in acidic aqueous media with use of conductivity and emission detection methods in conjunction with pulsed-laser excitation at 347 nm and at 530 nm. The last five complex ions have also been investigated in alkaline solutions. For acidic conditions, the conductivity decreases in two distinct stages with the exception of only one stage for *trans*-$Cr(en)_2F_2^+$. The longer term stage has the same lifetime as that for emission decay, and it represents the major component to photochemical reaction (67–100%). In this regard, the issue of direct chemical reaction from doublet electronically excited states vs. one of thermal back intersystem crossing from the doublet to low-lying quartet levels, followed by ligand substitution, is discussed. The initial short-term decreases in conductivity are attributed to protonation of released ammonia and of the monodentate en and tn ligands ($k_{H^+} = (0.3\text{–}2) \times 10^{10}\ M^{-1}\ s^{-1}$) subsequent to their prompt formation from short-lived quartet states. In basic media, both the emission intensities and the lifetimes decrease with increasing hydroxide ion concentration, except for *trans*-$Cr(en)_2F_2^+$. The rate constants for emission quenching range from about 0.2×10^{10} to $2 \times 10^{10}\ M^{-1}\ s^{-1}$. The conductivity results indicate that, with the possible exception of $Cr(NH_3)_5(NCS)^{2+}$, hydroxide ion quenching of emission and chemical reaction does not induce net chemical change.

Introduction

The photochemistry and photophysics of chromium(III) amine type complex ions in aqueous and nonaqueous media have been for many years the focus of a large number of both experimental and theoretical studies.[2-9] In part, this intense activity is made feasible by the availability of six-coordinate chromium(III) complex ions, having a wide variety of different ligand systems. In contrast to the relatively inert thermal behavior of the complexes toward substitution reactions, irradiation in the UV–visible region of the quartet and doublet ligand field bands gives rise to substantial levels of photochemical reaction, generally that of photosolvolysis or photoanation, and this is frequently accompanied by emission, usually from the lower energy and spin-forbidden doublet states. The situation is exemplified by the numerous studies of $Cr(NH_3)_6^{3+}$, $Cr(NH_3)_5(CN)^{2+}$, $Cr(NH_3)_5(NCS)^{2+}$, *trans*-$Cr(en)_2F_2^+$, $Cr(en)_3^{3+}$, and $Cr(tn)_3^{3+}$, where en and tn are ethylenediamine and 1,3-propanediamine, respectively, which are the subject of this report.[2,5,6,9,10-38]

While the photochemical and photophysical investigations on these and related systems have contributed very significantly

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