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Crystal and Molecular Structures of (1,8-Diamino-3,6-dithiaoctane)(1-methylimidazole)copper(II) Perchlorate

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The crystal and molecular structures of (1,8-diamino-3,6-dithiaoctane)(1-methylimidazole)copper(II) perchlorate have been determined from three-dimensional X-ray data. The compound crystallizes in the monoclinic space group $P2_1/c$ with four formula units in a cell of dimensions a = 8.996 (2) Å, b = 18.435 (4) Å, c = 13.687 (3) Å, and β = 116.84 (1)°. The structure has been refined by full-matrix least-squares techniques on F, using 3725 unique reflections for which $F^2 > 0$, to a final agreement factor of 0.088. The coordination geometry at the Cu atom is that of a distorted square pyramid. The imidazole ligand, two N atoms, and one S atom of the tetradentate ligand form the square plane, while the second S atom occupies the apical site. A perchlorate ion is weakly bonded (Cu–O = 2.845 (5) Å) in the remaining octahedral coordination site. The structure observed in the solid state suggests that a distorted square-pyramidal geometry is probable in solution, which, supported by spectral evidence, indicates that this complex models the coordination geometry of the Cu atom in the enzyme galactose oxidase.

Introduction

The geometry of the metal-binding site is thought to play a significant role in copper protein chemistry.[1,2] The "blue" or "type I" copper site has been studied extensively with a number of structural models having been proposed.[3] However, to date there has been less speculation concerning the "nonblue" or "type II" copper site. Type II copper is usually found in combination with types I and III, but it occurs alone in the enzyme galactose oxidase. This enzyme catalyzes the oxidation of D-galactose to galactohexodialdose concomitant with the reduction of molecular oxygen to hydrogen peroxide.[5] Chemical studies on the enzyme and the apoenzyme suggest coordination of R–S$^-$ ligands to the Cu atom;[6] however, the number of cysteines present and the nature of the remaining ligands are not known.

The title compound was prepared by Bosnich and coworkers, as one of a series of Cu(II) complexes with varying geometries and donor ligands.[7] The visible absorption spectrum of the title compound was found to be similar to that of galactose oxidase in the region of the d–d transitions. The general profile of the d–d manifold suggested a distorted five-coordinate environment for the Cu(II) atom. We, therefore, undertook a single-crystal structural analysis of the complex, in order to study the coordination geometry of the copper atom in detail.

Experimental Section

Deep blue crystals of (1,8-diamino-3,6-dithiaoctane)(1-methylimidazole)copper(II) perchlorate, [Cu(EEE)(1-MeIm)](ClO_4)$_2$, were kindly supplied by Bosnich and Amundsen.[7] A photographic study using Weissenberg and precession cameras indicated monoclinic symmetry. Preliminary cell constants were obtained. The systematic absences observed, l odd for $h0l$ and k odd for $0k0$, uniquely define the space group as $P2_1/c$, C_{2h}^5, No. 14.[8] The density of the crystals was measured by flotation in a mixture of carbon tetrachloride and 1,2-dibromoethane. These data indicated four formula units per cell.

The crystal chosen for data collection was of approximate dimensions 0.16 × 0.16 × 0.23 mm^3. It was carefully measured on a microscope fitted with a filar eyepiece. Nine faces, the forms {100}, {010}, and {011}, and a fractured face (30$\bar{4}$) were identified by optical goniometry. The crystal was mounted on a Picker FACS-1 computer-controlled diffractometer with [100] offset approximately 30° from coincidence with the spindle axis. Cell constants and an orientation matrix were obtained at 23 °C from a least-squares refinement of the angular settings for 26 intense, carefully centered reflections with $21 < 2\theta < 46°$. ω scans recorded for several intense, low-angle reflections, using a narrow source and a wide-open counter, had an average width at half-height of 0.08°, indicating a suitable mosaicity.

Table I. Crystal Data and Experimental Conditions

$C_{10}H_{22}Cl_2CuN_4O_8S_2$	fw 524.89
a = 8.996 (2) Å	space group $P2_1/c$
b = 18.435 (4) Å	Z = 4
c = 13.687 (3) Å	density (obsd) = 1.70 g cm^{-3}
β = 116.84 (1)°	density (calcd) = 1.72 g cm^{-3}

radiation	Mo(λ(Kα_1) 0.709 26 Å), prefiltered with 0.018-mm Nb foil
receiving aperture	5.0 × 5.0 mm, 31 cm from crystal
takeoff angle	2.0° (90% of maximum Bragg intensity)
scan	θ–2θ, at 1° min^{-1}
scan range	1.2° symmetric, corrected for dispersion
background	10 s stationary counter, stationary crystal at scan limits
standards	040, 100, 122, 0$\bar{4}$0, 004

Crystal data and the conditions for data collection are summarized in Table I. Intensity data were recorded over a period of 8 days for a total of 4263 reflections. Five standard reflections were recorded every 200 reflections. Of these standards four were found to decrease by less than 3.5%, and one showed an increase of 11.0% during data collection. No correction was made for this. The raw data were corrected for background and Lorentz–polarization effects, and standard deviations were assigned according to the expression

$$\sigma(I) = [\mathrm{TC} + {}^1/_4(t_c/t_b)^2(B_h + B_l) + (pI)^2]^{1/2}$$

where TC is the integrated count over the scan range, measured in time t_c, and B_h and B_l are background counts, each measured in times t_b. I, the corrected intensity, is given by TC – ${}^1/_2(t_c/t_b)(B_h + B_l)$. A series of absorption correction trials (μ = 14.90 cm^{-1} for Mo Kα), showed transmission factors varying from 0.798 to 0.862, so an absorption correction was applied employing the analytical method of de Meulenaer and Tompa.[9] Of the total number of reflections collected, 2655 had $F^2 > 3\sigma(F^2)$ and these were used in the solution and preliminary refinement of the structure.

Structure Solution and Refinement

The Cu atom was located from a three-dimensional Patterson synthesis. Structure factor and difference Fourier synthesis calculations revealed the positions of the remaining 26 nonhydrogen atoms. Refinement of atomic parameters was carried out by full-matrix least-squares techniques on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The weighting factor w is defined as $4F_o^2/\sigma^2(F_o^2)$.

The atomic scattering factors for the Cu, S, Cl, O, N, and C atoms were those of Cromer and Waber,[10] while those for the H atom were taken from Stewart et al.[11] Anomalous dispersion contributions to the scattering factor were included for Cu, Cl, and S atoms and were taken from Cromer and Liberman.[12] One cycle of least-squares refinement with the two perchlorate ions constrained as rigid groups (T_d symmetry, Cl–O = 1.42 Å[13]) and with the positional and anisotropic thermal parameters for the Cu, S, N, and C atoms varied led to the agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.105$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.122$.

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Table II. Final Atomic Positional and Thermal Parameters[a]

atom	x	y	z	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	−533.5 (9)	3260.5 (4)	−317.1 (6)	270 (4)	329 (4)	338 (4)	13 (4)	109 (3)	−33 (4)
Cl(1)	1191 (2)	4024 (1)	−2248 (1)	519 (11)	573 (11)	447 (10)	−4 (9)	260 (9)	26 (9)
Cl(2)	−4493 (2)	3823 (1)	3098 (2)	381 (10)	516 (11)	716 (13)	0 (9)	244 (10)	−84 (10)
S(1)	−2082 (2)	4382 (1)	−842 (1)	375 (9)	279 (8)	443 (10)	6 (7)	160 (8)	22 (7)
S(2)	−2100 (2)	3007 (1)	811 (1)	473 (11)	482 (10)	456 (11)	−101 (8)	248 (9)	51 (8)
O(1)	1255 (8)	4092 (3)	−1188 (4)	1234 (49)	709 (35)	587 (34)	−100 (35)	569 (35)	−73 (28)
O(2)	2662 (8)	3783 (5)	−2192 (6)	728 (45)	2509 (92)	990 (51)	581 (55)	534 (42)	250 (55)
O(3)	774 (14)	4665 (4)	−2785 (7)	3425 (134)	1172 (59)	1487 (71)	1180 (76)	1645 (85)	849 (54)
O(4)	−1 (10)	3511 (5)	−2833 (6)	1475 (68)	2495 (102)	1044 (54)	−1272 (70)	753 (52)	−901 (60)
O(5)	−4997 (9)	4254 (3)	3702 (7)	1551 (67)	803 (43)	2040 (78)	−389 (44)	1447 (66)	−511 (47)
O(6)	−2815 (7)	3727 (4)	3497 (6)	471 (38)	1354 (61)	1778 (74)	182 (40)	239 (44)	79 (54)
O(7)	−5373 (8)	3157 (3)	2871 (6)	915 (48)	419 (35)	2114 (81)	−84 (33)	335 (52)	−347 (41)
O(8)	−5085 (10)	4202 (4)	2069 (6)	1416 (68)	1486 (68)	1184 (59)	293 (56)	529 (54)	533 (51)
N(1)	−2143 (6)	2916 (3)	−1803 (4)	380 (31)	428 (30)	351 (30)	21 (25)	97 (25)	−46 (24)
N(2)	1178 (6)	3697 (3)	1072 (4)	339 (30)	476 (32)	394 (32)	−3 (26)	108 (26)	−35 (25)
N(3)	960 (6)	2412 (3)	−164 (4)	314 (29)	393 (31)	360 (29)	69 (24)	150 (25)	62 (24)
N(4)	1926 (7)	1311 (3)	−19 (4)	529 (37)	463 (34)	324 (31)	160 (30)	105 (28)	16 (25)
C(1)	−3729 (8)	3320 (4)	−2357 (5)	400 (38)	477 (40)	389 (37)	−43 (34)	38 (32)	−99 (33)
C(2)	−3427 (9)	4120 (4)	−2238 (5)	540 (46)	467 (41)	367 (38)	87 (36)	113 (35)	66 (32)
C(3)	−3435 (8)	4367 (4)	−198 (6)	448 (43)	601 (47)	602 (47)	147 (37)	243 (39)	−25 (38)
C(4)	−3786 (8)	3643 (4)	184 (6)	390 (41)	882 (56)	581 (49)	44 (40)	291 (39)	61 (42)
C(5)	−558 (9)	3475 (4)	1996 (5)	622 (48)	626 (48)	340 (38)	−66 (39)	186 (36)	27 (33)
C(6)	529 (9)	4005 (4)	1789 (5)	476 (44)	597 (46)	400 (41)	−93 (37)	134 (36)	−118 (35)
C(11)	2361 (8)	2431 (4)	−328 (6)	310 (36)	574 (46)	596 (45)	62 (34)	218 (35)	47 (37)
C(12)	2954 (8)	1746 (4)	−232 (6)	401 (41)	763 (53)	481 (43)	130 (42)	198 (35)	20 (41)
C(13)	747 (8)	1729 (4)	25 (5)	474 (40)	422 (38)	388 (37)	35 (35)	209 (32)	76 (32)
C(14)	2089 (11)	517 (4)	137 (7)	990 (69)	405 (44)	789 (58)	262 (45)	270 (53)	34 (40)

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. All parameters have been multiplied by 10^4. [b] $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$ Å^2. The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

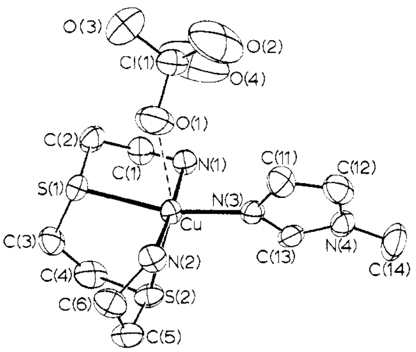

Figure 1. Perspective view of the Cu(EEE)(1-MeIm)(ClO$_4$) cation, showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Idealized positional coordinates for the 22 H atoms were computed assuming sp^2 and sp^3 coordination geometries about the C and N atoms and C–H and N–H bond distances of 1.00 Å. All were found to lie on regions of positive electron density (0.4 (1)–0.8 (1) e Å^{-3}) in a difference Fourier synthesis. Two further cycles of refinement, with the group restraints removed and the Cl and O atoms refined as individual atoms assigned anisotropic thermal parameters and the H atom contributions included, resulted in R_1 and R_2 values of 0.053 and 0.058, respectively.

After recalculation of the H atom positions, the model was refined for two further cycles and, with 244 variables and 3725 observations for which $I > 0$, converged at $R_1 = 0.0884$ and $R_2 = 0.0677$. No parameter shift exceeded 1.06 of its estimated standard deviation. A statistical analysis of R_2 in terms of $|F_o|$, indices, $\lambda^{-1} \sin \theta$, and the diffractometer setting angles χ and ϕ showed no unusual trends. The standard deviation on an observation of unit weight is 1.62 electrons. A final difference Fourier synthesis was calculated and showed no residual electron density of chemical significance. The largest peak, 0.8 (2) e Å^{-3} at (−0.363, 0.391, 0.450), was associated with O(6) of the uncoordinated perchlorate ion. No evidence was found for secondary extinction. Final atomic positional and thermal parameters for nonhydrogen atoms are given in Table II. H parameters are presented in Table III. Structure amplitudes are listed in Table IV, as $10F_o$ vs. $10F_c$ in electrons.[14]

Table III. Derived Hydrogen Atom Positional (×10^4) and Thermal Parameters

atom[a]	x	y	z	B, Å^2
H1N(1)	−1572	2943	−2282	4.23
H2N(1)	−2417	2400	−1733	4.23
H1N(2)	2000	3310	1488	4.38
H2N(2)	1758	4091	876	4.38
H1C(1)	−4279	3189	−3153	4.75
H2C(1)	−4477	3177	−2026	4.75
H1C(2)	−4522	4373	−2484	5.06
H2C(2)	−2901	4273	−2708	5.06
H1C(3)	−2925	4688	465	5.24
H2C(3)	−4531	4572	−725	5.24
H1C(4)	−4668	3396	−471	5.65
H2C(4)	−4214	3743	727	5.65
H1C(5)	−1166	3746	2339	5.28
H2C(5)	172	3100	2517	5.28
H1C(6)	1492	4138	2504	5.12
H2C(6)	−126	4450	1438	5.12
H1C(13)	−172	1550	185	4.30
H1C(12)	3954	1594	−313	5.31
H1C(11)	2856	2875	−487	4.82
H1C(14)	2092	393	853	7.20
H2C(14)	1125	275	−473	7.20
H3C(14)	3153	355	150	7.20

[a] H atoms are numbered according to the atom to which they are bonded; thus, H1N(1) is bonded to N(1) etc.

Structure Description

The structure consists of discrete [Cu(EEE)(1-MeIm)(ClO$_4$)] cations and perchlorate anions. The shortest cation–cation distance of approach is 2.42 Å between H atoms bonded to C(11) and C(4). Selected interatomic distances and bond angles are given in Table V. A perspective view of the cation, including the weakly coordinated perchlorate ion, shows the atom labeling scheme in Figure 1. A stereoview of the contents of the unit cell is given in Figure 2.

The Cu atom is strongly bonded to three N atoms and two S atoms, a coordination geometry closely approaching square pyramidal. The sixth site of a distorted octahedron is occupied

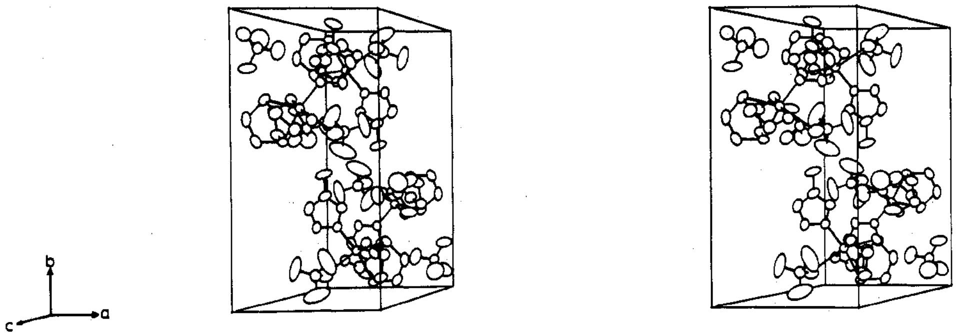

Figure 2. Stereoview of the unit cell contents.

Table V.

(a) Selected Bond Distances, Å

Cu-S(1)	2.414 (2)	N(3)-C(11)	1.377 (7)
Cu-S(2)	2.560 (2)	N(3)-C(13)	1.317 (7)
Cu-N(1)	1.994 (5)	N(4)-C(12)	1.353 (9)
Cu-N(2)	1.998 (5)	N(4)-C(13)	1.334 (8)
Cu-N(3)	2.011 (5)	N(4)-C(14)	1.477 (8)
Cu-O(1)	2.845 (5)	C(11)-C(12)	1.353 (9)
N(1)-C(1)	1.480 (8)	Cl(1)-O(1)	1.430 (5)
N(2)-C(6)	1.464 (8)	Cl(1)-O(2)	1.364 (6)
S(1)-C(2)	1.805 (7)	Cl(1)-O(3)	1.352 (6)
S(1)-C(3)	1.797 (7)	Cl(1)-O(4)	1.383 (7)
S(2)-C(4)	1.799 (7)		
S(2)-C(5)	1.807 (7)	Cl(2)-O(5)	1.363 (6)
C(1)-C(2)	1.494 (9)	Cl(2)-O(6)	1.365 (6)
C(3)-C(4)	1.517 (10)	Cl(2)-O(7)	1.418 (6)
C(5)-C(6)	1.497 (9)	Cl(2)-O(8)	1.442 (7)

(b) Selected Bond Angles, Deg

N(1)-Cu-S(1)	85.0 (1)	Cu-N(3)-C(11)	125.5 (4)
S(1)-Cu-N(2)	91.8 (2)	Cu-N(3)-C(13)	128.0 (4)
N(2)-Cu-N(3)	91.3 (2)	C(11)-N(3)-C(13)	106.4 (5)
N(3)-Cu-N(1)	90.1 (2)	N(3)-C(11)-C(12)	108.0 (6)
S(2)-Cu-S(1)	86.3 (1)	C(11)-C(12)-N(4)	107.3 (6)
S(2)-Cu-N(1)	102.3 (2)	C(12)-N(4)-C(13)	107.5 (5)
S(2)-Cu-N(2)	84.1 (2)	N(4)-C(13)-N(3)	110.8 (6)
S(2)-Cu-N(3)	108.6 (1)	C(12)-N(4)-C(14)	125.9 (7)
S(2)-Cu-O(1)	157.0 (1)	C(13)-N(4)-C(14)	126.5 (7)
Cu-N(1)-C(1)	116.8 (4)	Cu-O(1)-Cl(1)	127.3 (3)
N(1)-C(1)-C(2)	110.8 (5)	O(1)-Cl(1)-O(2)	112.2 (4)
C(1)-C(2)-S(1)	112.5 (4)	O(1)-Cl(1)-O(3)	110.4 (4)
C(2)-S(1)-Cu	96.1 (2)	O(1)-Cl(1)-O(4)	108.3 (4)
C(2)-S(1)-C(3)	103.7 (3)	O(2)-Cl(1)-O(3)	109.8 (6)
C(3)-S(1)-Cu	105.6 (2)	O(2)-Cl(1)-O(4)	106.7 (5)
S(1)-C(3)-C(4)	118.4 (5)	O(3)-Cl(1)-O(4)	109.3 (6)
C(3)-C(4)-S(2)	118.4 (5)	O(5)-Cl(2)-O(6)	116.4 (5)
C(4)-S(2)-Cu	99.7 (2)	O(5)-Cl(2)-O(7)	109.3 (4)
C(4)-S(2)-C(5)	104.9 (3)	O(5)-Cl(2)-O(8)	103.5 (5)
C(5)-S(2)-Cu	92.6 (2)	O(6)-Cl(2)-O(7)	112.4 (4)
S(2)-C(5)-C(6)	116.4 (5)	O(6)-Cl(2)-O(8)	107.9 (5)
C(5)-C(6)-N(2)	111.5 (5)	O(7)-Cl(2)-O(8)	106.4 (5)
C(6)-N(2)-Cu	115.2 (4)		

by the oxygen atom of one perchlorate ion. The equatorial atoms form a distorted square plane, with an average angle at the Cu of 89.6 (3)°. A weighted least-squares plane was calculated using the Hamilton method and results are shown in Table VI. The largest deviation from the plane is that of N(3), 0.431 (5) Å. The Cu–N distances of 1.994 (5), 1.998 (5), and 2.011 (5) Å may be considered statistically equivalent with the mean value (2.001 (5) Å) falling well within the range (1.98–2.04 Å) reported for equatorial bonds in a number of previous studies.[15,16] The axial Cu–S bond is 0.146 (3) Å longer than the equatorial bond. The values of 2.414 (2) and 2.560 (2) Å for the equatorial and axial bonds, respectively, compare favorably with the equatorial distances of 2.431 (6) and 2.445 (6) Å and the axial distances of 2.565 (6) and 2.609 (6) Å reported for $[CuL(Cl)ClO_4]_2$, where L = 3,4-bis(aminoethylthio)toluene.[17] They are rather long, however, in comparison with distances ranging from 2.17 to 2.32 Å in complexes containing cysteine-type S ligands[18] and different thioethers.[19]

Table VI. Weighted Least-Squares Planes and Atom Distances (Å) from the Planes

Plane 1: $7.590x + 6.165y - 10.342z = 1.954$

Cu	−0.0211 (7)	N(2)	0.110 (5)
S(1)	0.038 (2)	N(3)	0.431 (5)
N(1)	0.082 (5)		

Plane 2: $1.269x + 2.543y + 11.100z = 0.5559$

N(3)	−0.003 (5)	C(12)	0.005 (7)
N(4)	0.001 (5)	C(13)	0.006 (6)
C(11)	−0.002 (7)	C(14)	−0.008 (8)

The dimensions of the EEE ligand show no major differences from those previously reported for β-(methylmercapto)ethylamine.[15] Each unit cell contains two pairs of cations, related by centers of symmetry. Coordinates are reported for the cations in which the two five-membered rings formed by the $NH_2CH_2CH_2S$ entities of gauche conformations have absolute configurations λ and in which the SCH_2CH_2S part of the ligand forms a five-membered ring, also of gauche conformation but of δ absolute configuration.

The 1-methylimidazole ligand is planar within experimental error (Table VI). The internal geometry is in excellent agreement with that found in imidazole at −150 °C[20] and those reported for the neutral ligand in other complexes.[21]

An examination of the final difference Fourier synthesis and the range of Cl–O distances within the "free" perchlorate ion suggests that there might be some slight disorder in the crystal packing. Bond distances vary from 1.363 (6) to 1.442 (7) Å, while the angles at Cl (2) range from 103.5 (5) to 116.4 (5)°. The present model is the best that can be achieved, however, in the present study. There is a definite trend within the coordinated perchlorate ion which indicates a lengthening of the Cl–O bond involving O(1), which is weakly coordinated to the Cu atom (Cu–O(1) = 2.845 (5) Å). The Cl–O bond length of 1.430 (5) Å is significantly longer than the mean of the other three Cl–O bonds, 1.366 (9) Å. Such a lengthening is not normally observed in complexes of this type[15,22] but is strongly suggested in this study. It is surprising perhaps that the Cu–O bond length is slightly longer in the present study than values found in other complexes showing this type of interaction which has been termed "semicoordination".[23] The Cu–O(1)–Cl(1) angle of 127.3 (3)° indicates a significant tilting of the anion relative to the S(1), N(1), N(2), N(3) plane. This structural feature is typical of semicocordination.[23]

Both O(1) and O(4) of the coordinated perchlorate ion are so positioned as to form hydrogen bonds within the cation. H1N(1) approaches O(4) at 2.15 Å and H2N(2) is 2.65 Å distant from O(1). The interaction between O(4) and H1N(1) could possibly be contributing to the tilting of the perchlorate ion. The free perchlorate anion also forms several hydrogen bonds, the most notable being 2.16 Å between O(6) and

H2N(1) on the cation at x, $^1/_2 - y$, $^1/_2 + z$ and 2.28 Å between O(7) and H1N(2) on the cation at $x - 1$, y, z.

Discussion

The Cu–S bonds observed in this analysis are rather long in comparison to those determined for other types of S donor ligands. It has been suggested[17] that thioethers do not have a high affinity for Cu(II), and the bond lengths determined here support this contention. It is probable that the perchlorate ion will be lost from the Cu atom coordination sphere in solution, to be replaced by a solvent molecule. The resultant species would be expected to adopt a similar configuration to that found in the solid state. The similarity between the absorption spectrum of the title complex in solution[7] and that of galactose oxidase in the region of the d–d transitions[4] is indicative of a similar environment for the metal atom in each system.

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Registry No. [Cu(EEE)(1-MeIm)](ClO$_4$)$_2$, 64692-43-9.

Supplementary Material Available: Table IV listing structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. A. Fee, *Struct. Bonding (Berlin)*, **23**, 1 (1975).
(2) B. L. Vallee and R. J. P. Williams, *Proc. Natl. Acad. Sci. U.S.A.*, **59**, 498 (1968); H. A. Henriksson, B. Sjoberg, and R. Osterberg, *J. Chem. Soc., Chem. Commun.*, 130 (1976).
(3) J. S. Thompson, T. J. Marks, and J. A. Ibers, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 3114 (1977), and references cited therein; R. R. Gagné, J. L. Allison, R. S. Gall, and C. A. Koval, *J. Am. Chem. Soc.*, **99**, 7170 (1977).
(4) M. J. Ettinger, *Biochemistry*, **13**, 1242 (1974).
(5) D. J. Kosman, M. J. Ettinger, R. E. Weiner, and E. J. Massaro, *Arch. Biochem. Biophys.*, **165**, 456 (1974).
(6) F. Kelly-Falcoz, H. Greenberg, and B. L. Horecker, *J. Biol. Chem.*, **240**, 2966 (1965).
(7) A. R. Amundsen, J. Whelan, and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6730 (1977).
(8) "International Tables for X-Ray Crystallography", Vol. 1, Kynoch Press, Birmingham, England, 1962.
(9) Computing was performed on the CDC Cyber 73-14 at the University of Western Ontario. Programs used include local modifications of the following: cell refinement and orientation matrix, from W. C. Hamilton's MODE 1; absorption correction, AGNOST, as modified by D. Cahen and J. A. Ibers; Patterson and Fourier syntheses, A. Zalkin's FORDAP; full-matrix least-squares, J. A. Ibers' NUCLS; error calculations, ORFFE, by W. R. Busing, K. O. Martin, and H. A. Levy; and molecular illustrations, ORTEP, by C. K. Johnson.
(10) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(12) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(13) F. S. Lee and G. B. Carpenter, *J. Phys. Chem.*, **63**, 279 (1959).
(14) Supplementary material.
(15) C. C. Ou, V. M. Miskowski, R. A. Lalancette, J. A. Potenza, and H. J. Schugar, *Inorg. Chem.*, **15**, 3157 (1976).
(16) J. J. Bonnet and Y. Jeannin, *Acta Crystallogr., Sect. B*, **26**, 318 (1970); M. H. Meyer, P. Singh, W. E. Hatfield, and D. J. Hodgson, *ibid.*, **28**, 1607 (1972).
(17) A. C. Braithwaite, C. E. F. Rickard, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1817 (1975).
(18) R. Eisenberg, *Prog. Inorg. Chem.*, **12**, 295 (1970); L. E. Warren, S. M. Horner, and W. E. Hatfield, *J. Am. Chem. Soc.*, **94**, 6392 (1972).
(19) M. D. Glick, D. P. Gavel, L. L. Diaddario, and D. B. Rorabacher, *Inorg. Chem.*, **15**, 1190 (1976).
(20) S. Martinez-Carrera, *Acta Crystallogr.*, **20**, 783 (1966).
(21) K. Bowman, A. P. Gaughan, and Z. Dori, *J. Am. Chem. Soc.*, **94**, 727 (1972); D. L. McFadden, A. T. McPhail, C. D. Garner, and F. E. Mabbs, *J. Chem. Soc., Dalton Trans.*, 263 (1975).
(22) P. A. Tasker and L. Sklar, *J. Cryst. Mol. Struct.*, **5**, 329 (1975).
(23) B. J. Hathaway, I. M. Procter, A. A. G. Tomlinson, D. S. Brown, J. D. Lee, and B. G. A. Melsom, *Chem. Commun.*, 369 (1967).

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Stereochemistry of Eight-Coordinate Dodecahedral Complexes of the Type MX$_4$Y$_4$. 1. Preparation and Characterization of Some Titanium(IV) and Zirconium(IV) *N*,*N*-Dialkylmonothiocarbamates[1]

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Eight-coordinate titanium(IV) and zirconium(IV) *N*,*N*-dialkylmonothiocarbamate complexes of the type [M(R$_2$mtc)$_4$] (M = Ti, Zr; R = Me, Et, *i*-Pr) have been prepared by reaction of the metal tetrachlorides with alkali metal *N*,*N*,-dialkylmonothiocarbamates in dichloromethane, benzene, or acetonitrile. Low-temperature proton NMR spectra of the [M(Me$_2$mtc)$_4$] complexes exhibit four methyl resonances of approximately equal intensity, consistent with the dodecahedral *mmmm*-C_{2v} stereoisomer that has been found in the solid state for the [M(Et$_2$mtc)$_4$] complexes by X-ray diffraction. This isomer has an all-cis structure with the four sulfur atoms on one side of the coordination group and the four oxygen atoms on the other side. Dipole moments in benzene solution (4.49 ± 0.11 D for [Ti(Et$_2$mtc)$_4$] and 3.61 ± 0.16 D for [Zr(Et$_2$mtc)$_4$]) are also in accord with the highly polar *mmmm*-C_{2v} stereoisomer being the principal species in solution. Variable-temperature NMR spectra of the [M(Me$_2$mtc)$_4$] complexes afford evidence for two distinct kinetic processes: (1) a low-temperature process that involves metal-centered rearrangement and (2) a high-temperature process that involves hindered rotation about the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond in the ligand. Thus, these complexes are of interest as unusual examples of tetrakis chelates that are stereochemically rigid on the NMR time scale. Infrared spectra of the [M(R$_2$mtc)$_4$] complexes are consistent with bidentate attachment of the monothiocarbamate ligands. M–O and M–S stretching frequencies have been identified by comparison of infrared spectra of the complexes and the alkali metal salts.

Introduction

The preparation, properties, and structural chemistry of metal *N*,*N*-dialkyldithiocarbamate complexes have been studied extensively.[2] Less well-known are metal complexes containing the corresponding *N*,*N*-dialkylmonothiocarbamate (R$_2$mtc) ligand **1**. Most of the known monothiocarbamate complexes have been prepared in the last 7 years, and attention has centered primarily on the later transition metals. Complexes of the following metals have been reported: Mn(I),[3,4] Fe(II),[5a,6] Fe(III),[5–7] Co(II),[8a] Co(III),[8b] Rh(I),[9,10]

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