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Structural Characterization of Alkoxo-bridged Copper(II) Complexes with 2-(Alkylthio)ethanol

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Abstract

The crystal structures of three types of alkoxo-bridged copper(II) complexes with 2-(alkylthio)-ethanol were determined by the single crystal X-ray diffraction method. $\{Cu(C_2H_5SCH_2CH_2O)Cl\}_2$ and $\{Cu(C_2H_5SCH_2CH_2O)Br\}_2$ have planar alkoxo-bridged binuclear structures. $\{Cu(i\text{-}C_3H_7SCH_2CH_2O)Cl\}_4$ has a tetranuclear cubane structure in which two binuclear units are strongly bound to each other. $\{Cu(n\text{-}C_3H_7SCH_2CH_2O)Cl\}_4$ is a cubane-like tetranuclear molecule in which two binuclear units are loosely associated. It was confirmed that the relation between the structure and the magnetic and spectral properties observed for alkoxo-bridged copper(II) complexes with 2-(dialkylamino)ethanol is also valid for complexes of 2-(alkylthio)ethanol.

Introduction

A great number of alkoxo-bridged copper(II) complexes with 2-(dialkylamino)ethanol, $[\{Cu(R_2NCH_2CH_2O)X\}_n]$ (abbreviated as Cu(R-no)X), have been prepared and studied extensively for their structures and magnetic properties. Different types of structure have been found in these complexes. There are binuclear (n = 2) [1], tetranuclear (n = 4) [2–4], and polynuclear (n = ∞) [5] molecules. Nishida and Kida classified these complexes into three groups, based on the temperature dependence of magnetic susceptibilities [6]: (1) Complexes whose magnetic behavior can be interpreted in terms of the Bleaney-Bowers equation (type A). These complexes are dialkoxo-bridged binuclear molecules [1], and have a distinct absorption band in the near-UV region ($23–27 \times 10^3$ cm^{-1}). (2) Complexes which obey the Curie-Weiss law, with positive Weiss constants in the 80–300 K range (type B). These complexes are tetranuclear molecules with a cubane Cu_4O_4 core [3]. The magnetic moments of type B complexes are normal at room temperature and the solid-state spectra show no distinct absorption band in the near-UV region. (3) Complexes in which weak antiferromagnetic interaction is operating *i.e.*, showing slightly subnormal magnetic moments or negative Weiss constants (type C). These complexes may show a small peak or shoulder in the near-UV region in the solid-state spectra. Type C complexes are tetranuclear molecules with a cubane-like structure similar to type B complexes [4]. The structural difference between B and C type complexes have been discussed by many workers in relation to magnetic properties [7].

On the other hand, there were no studies on alkoxo-bridged copper(II) complexes with 2-(alkylthio)ethanol, $[\{Cu(RSCH_2CH_2O)X\}_n]$ (abbreviated as Cu(R-so)X) until we reported the synthesis and magnetic and spectral properties of the Cu(R-so)X complexes (where R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, s-C_4H_9, t-C_4H_9; X = Br, Cl) [8]. Similarly to the Cu(R-no)X complexes, the Cu(R-so)X complexes have been classified into three types based on the above criteria, and can be assumed the structure for each of the types. However, their structures have not yet been determined. Thus in this study we have determined the crystal structures of each type of complex by X-ray diffraction, in order to see if the same magnetism-structure relation as found in the Cu(R-no)X complexes is held for the Cu(R-so)X complexes. The complexes chosen were Cu(C_2H_5-so)Cl, Cu(C_2H_5-so)Br (type A), Cu(i-C_3H_7-so)Cl (type B), and Cu(n-C_3H_7-so)Cl (type C). The present results will contribute to the comprehensive elucidation of magnetochemistry of copper(II) complexes.

Experimental

Crystals of Cu(C_2H_5-so)Cl, Cu(C_2H_5-so)Br, Cu(i-C_3H_7-so)Cl, and Cu(n-C_3H_7-so)Cl were prepared by the method previously reported [8]. The diffraction data were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 18.5 ± 0.5 °C. Since the crystals are liable to decompose in the open atmosphere, they were coated with clear varnish. The unit-cell parameters of each crystals were determined by the least-squares refinement based on 25 high-angle reflections. The crystal data are shown in Table I. The intensity data were collected by the 2θ–ω scan technique with a scan rate of 8° min^{-1}. For weak reflections the peak scan

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TABLE I. Crystal Data and Experimental Details.

Type	A	A	B	C
Complex	Cu(C_2H_5-so)Cl	Cu(C_2H_5-so)Br	Cu(i-C_3H_7-so)Cl	Cu(n-C_3H_7-so)Cl
Molecular formula	$Cu_2(C_4H_9OS)_2Cl_2$	$Cu_2(C_4H_9OS)_2Br_2$	$Cu_4(C_5H_{11}OS)_4Cl_4$	$Cu_4(C_5H_{11}OS)_4Cl_4$
Molecular weight	408.3	497.2	872.8	872.8
Crystal system	Triclinic	Triclinic	Tetragonal	Tetragonal
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{4}2_1c$	$I\bar{4}$
a (Å)	7.243(3)	7.320(3)	13.170(4)	14.740(5)
b (Å)	8.459(3)	8.544(3)		
c (Å)	6.068(2)	6.181(2)	9.872(2)	8.028(1)
α (°)	102.68(3)	103.88(2)		
β (°)	99.11(3)	99.61(3)		
γ (°)	88.59(4)	88.15(3)		
D_m (gcm^{-3})	1.90	2.12	1.70	1.66
D_c (gcm^{-3})	1.89	2.23	1.69	1.66
Z	1	1	2	2
μ(Mo Kα) (cm^{-1})	36.2	84.9	29.8	29.8
Crystal size (mm^3)	0.49 x 0.31 x 0.21	0.36 x 0.17 x 0.10	0.40 x 0.28 x 0.05	0.30 x 0.19 x 0.14
$2\theta_{max}$ (°)	62	52	60	56
No. of unique reflections ($F_o > 3\sigma(F_o)$)	2024	1282	1685	1788

was repeated up to four times depending on the intensities. Three standard reflections were monitored every 100 reflections, and their intensities showed good stability. The intensity data were corrected for Lorentz and polarization effects, but not for absorption.

The structures were solved by the heavy-atom method and refined by the block-diagonal least-squares method. In the least-squares refinement, the weighting schemes [9] were $w = (2.4 + |F_o| + 0.022|F_o|^2)^{-1}$ for Cu(C_2H_5-so)Cl, $(5.8 + |F_o| + 0.018|F_o|^2)^{-1}$ for Cu(C_2H_5-so)Br, $(12.3 + |F_o| + 0.007|F_o|^2)^{-1}$ for Cu(i-C_3H_7-so)Cl and $(19.1 + |F_o| + 0.007|F_o|^2)^{-1}$ for Cu(n-C_3H_7-so)Cl. All the hydrogen atoms were located from the difference Fourier maps and were included in the final refinement with the isotropic temperature factors. The final R values were $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.066$, $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.089$ for Cu(C_2H_5-so)Cl, $R_1 = 0.075$, $R_2 = 0.116$ for Cu(C_2H_5-so)Br, $R_1 = 0.053$, $R_2 = 0.082$ for Cu(i-C_3H_7-so)Cl and $R_1 = 0.037$, $R_2 = 0.056$ for Cu(n-C_3H_7-so)Cl. Final difference Fourier syntheses were featureless.

All the calculations were carried out on the FACOM M-200 computer in the Computer Center of Kyushu University, by the use of a local version [10] of the UNICS-III and the ORTEP programs. The final positional and thermal parameters with their estimated standard deviations are given in Table II.* Interatomic distances and bond angles are given in Table III.

Description of the Structures and Discussion

Type A Complex

A perspective drawing of Cu(C_2H_5-so)Cl and the numbering system are illustrated in Fig. 1. The crystals of Cu(C_2H_5-so)Cl and Cu(C_2H_5-so)Br are isomorphous. Both complexes consist of dialkoxo-bridged binuclear units, as expected from the magnetic and spectral properties [8]. The Cu^i-----Cu^{ii} distances and Cu^i–O^i–Cu^{ii} angles (3.034(1) Å,

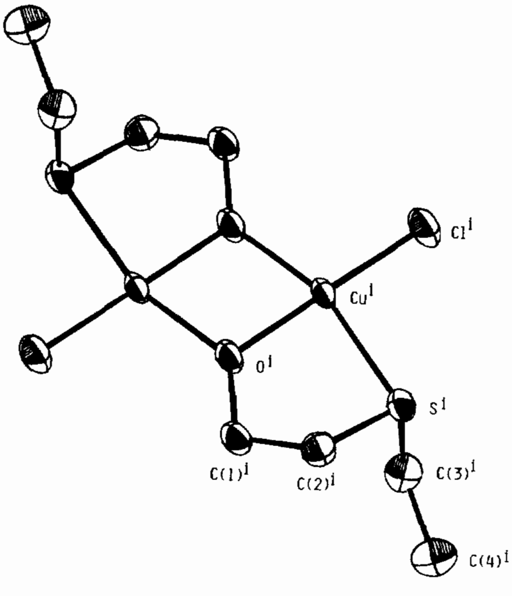

Fig. 1. Molecular structure of Cu(C_2H_5-so)Cl.

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*The anisotropic thermal parameters of the non-hydrogen atoms, and the $F_o - F_c$ tables have been deposited with the Editor-in-Chief.

TABLE II. Fractional Positional Parameters ($\times 10^4$ for non-Hydrogen Atoms; $\times 10^3$ for Hydrogen Atoms) and Thermal Parameters with their e.s.d. s in Parentheses.

Atom	x	y	z	B_{eq} or B (Å^2)
(1) $Cu(C_2H_5\text{-}so)Cl$				
Cu^{i}	9055(1)	162(1)	2097(1)	2.21
Cl^{i}	8055(2)	−1487(2)	4076(2)	3.12
S^{i}	7385(2)	2420(1)	3553(2)	2.54
O^{i}	9558(6)	1342(4)	−121(6)	2.94
C(1)^{i}	8715(7)	2829(5)	−269(8)	2.58
C(2)^{i}	8449(7)	3732(5)	2112(8)	2.64
C(3)^{i}	5064(7)	2085(6)	1866(9)	3.02
C(4)^{i}	3876(8)	3572(8)	2149(12)	3.77
H1(C(1))^{i}	737(8)	261(8)	−136(10)	2.6
H2(C(1))^{i}	959(9)	353(8)	−99(11)	2.6
H1(C(2))^{i}	758(10)	477(9)	201(13)	3.8
H2(C(2))^{i}	980(10)	414(9)	310(12)	3.7
H1(C(3))^{i}	433(10)	115(10)	238(13)	4.3
H2(C(3))^{i}	518(10)	172(9)	7(12)	3.6
H1(C(4))^{i}	255(10)	332(10)	112(13)	4.4
H2(C(4))^{i}	454(11)	453(10)	164(14)	4.4
H3(C(4))^{i}	372(10)	396(10)	393(14)	4.7
(2) $Cu(C_2H_5\text{-}so)Br$				
Br^{i}	7864(2)	−1435(1)	4088(2)	2.35
Cu^{i}	9082(2)	229(1)	2074(2)	1.71
S^{i}	7489(4)	2513(3)	3482(4)	1.92
O^{i}	9654(13)	1378(10)	−83(13)	2.51
C(1)^{i}	8797(17)	2820(13)	−321(19)	2.14
C(2)^{i}	8537(18)	3766(12)	2034(19)	2.20
C(3)^{i}	5187(17)	2129(15)	1833(21)	2.55
C(4)^{i}	3977(18)	3602(19)	2142(25)	3.43
H1(C(1))^{i}	748(19)	255(17)	−142(24)	2.7
H2(C(1))^{i}	968(19)	342(17)	−112(25)	2.8
H1(C(2))^{i}	766(19)	482(18)	193(26)	3.0
H2(C(2))^{i}	982(21)	418(19)	300(28)	3.9
H1(C(3))^{i}	454(21)	116(19)	226(28)	3.9
H2(C(3))^{i}	530(19)	175(17)	13(24)	2.7
H1(C(4))^{i}	258(20)	330(18)	121(26)	3.2
H2(C(4))^{i}	459(20)	459(19)	166(27)	3.5
H3(C(4))^{i}	388(18)	402(16)	390(24)	2.4
(3) $Cu(i\text{-}C_3H_7\text{-}so)Cl$				
Cu^{i}	3987(1)	4336(1)	3888(1)	2.78
Cl^{i}	3673(3)	2705(2)	3514(3)	5.95
S^{i}	3508(2)	4772(2)	1701(2)	3.90
O^{i}	4246(4)	5774(4)	4126(5)	2.81
C(1)^{i}	3663(8)	6469(7)	3323(10)	3.92
C(2)^{i}	3686(8)	6117(9)	1864(10)	4.42
C(3)^{i}	2150(9)	4538(14)	1634(15)	7.29
C(5)^{i}	1703(12)	4887(16)	364(15)	9.15
H1(C(1))^{i}	1601(11)	4846(16)	2851(18)	8.70
H2(C(1))^{i}	397(8)	721(8)	340(10)	4.4
H2(C(1))^{i}	290(7)	651(7)	367(9)	3.1
H1(C(2))^{i}	437(12)	632(11)	144(15)	8.6
H2(C(2))^{i}	308(10)	654(9)	131(13)	6.3
H(C(3))^{i}	198(12)	374(11)	155(17)	9.5
H1(C(4))^{i}	90(12)	469(12)	31(16)	10.4
H2(C(4))^{i}	206(12)	451(12)	−48(15)	9.3

(Continued overleaf)

TABLE II. *(Continued)*

$H3(C(4))^i$	183(13)	564(13)	28(16)	10.5
$H1(C(5))^i$	83(13)	466(12)	281(17)	10.8
$H2(C(5))^i$	170(11)	565(12)	297(15)	9.0
$H3(C(5))^i$	191(13)	447(13)	377(18)	11.5
(4) $Cu(n\text{-}C_3H_7\text{-so})Cl$				
Cu^i	344(1)	945(1)	1620(1)	2.44
Cl^i	1583(1)	1572(1)	2638(2)	3.91
S^i	−542(1)	2252(1)	1718(2)	3.01
O^i	−809(2)	309(2)	1387(5)	2.51
$C(1)^i$	−1510(4)	696(4)	2390(8)	3.19
$C(2)^i$	−1635(4)	1680(4)	1886(9)	3.31
$C(3)^i$	−393(4)	2711(4)	3801(8)	3.34
$C(4)^i$	−921(5)	3602(5)	4018(10)	4.21
$C(5)^i$	−803(8)	3972(6)	5769(12)	6.18
$H1(C(1))^i$	−131(4)	66(4)	370(9)	3.5
$H2(C(1))^i$	−214(5)	33(5)	221(9)	3.9
$H1(C(2))^i$	−204(5)	203(5)	280(10)	4.2
$H2(C(2))^i$	−197(6)	172(6)	69(10)	5.1
$H1(C(3))^i$	32(5)	284(5)	401(9)	3.7
$H2(C(3))^i$	−63(5)	223(5)	471(10)	4.1
$H1(C(4))^i$	−163(6)	347(6)	377(12)	6.0
$H2(C(4))^i$	−67(6)	409(5)	311(12)	5.0
$H1(C(5))^i$	−118(7)	459(6)	591(12)	6.4
$H2(C(5))^i$	−10(8)	410(6)	600(13)	7.7
$H3(C(5))^i$	−107(6)	349(6)	668(14)	6.7

103.9(2)° for $Cu(C_2H_5\text{-so})Cl$ and 3.028(2) Å, 102.9(4)° for $Cu(C_2H_5\text{-so})Br$) fall in the range of those of the dialkoxo-bridged binuclear copper(II) complexes which show strong antiferromagnetic interaction [1, 11, 12]. Each copper atom is coordinated by two alkoxo oxygen atoms, a thioether sulfur atom, and a chlorine or a bromine atom. The coordination geometry around the copper atoms is a distorted square plane. The Cu–O, Cu–X (X = Cl, Br) and Cu–S bond lengths are all in the range of those of reported complexes [13–15].

Type B Complex

A perspective view of a molecule of $Cu(i\text{-}C_3H_7\text{-so})Cl$ is given in Fig. 2. The molecule has a tetranuclear cubane structure, as expected from the magnetic and spectral properties [8]. The unit cell contains two tetranuclear molecules. The symmetry of each molecule is S_4. The four copper(II) ions of the molecule constitute a tetrahedron with Cu-----Cu separations of 3.191(1) (X2) and 3.148(1) Å (X4). The Cu–O bond (1.939(5) Å) in the five-membered chelate ring is of normal length for a equatorial Cu–O bond, whereas the non-chelated Cu–O bond (Cu^i–O^{ii}) is much elongated: 2.343(5) Å. The Cu–O out-of-plane distance (Cu^i–O^{iii}) is 1.989(5) Å. The coordination geometry of each copper atom may be described as a distorted square pyramid with O^i, O^{iii},

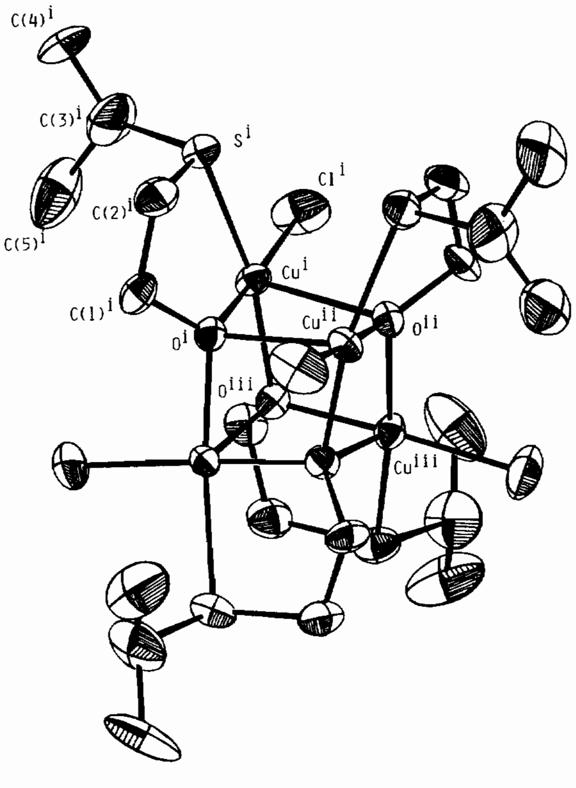

Fig. 2. Molecular structure of $Cu(i\text{-}C_3H_7\text{-so})Cl$.

TABLE III. Interatomic Distances (l/Å) and Bond Angles (φ/°).

Complex	$Cu(C_2H_5\text{-so})Cl$	$Cu(C_2H_5\text{-so})Br$	$Cu(i\text{-}C_3H_7\text{-so})Cl$	$Cu(n\text{-}C_3H_7\text{-so})Cl$
Cu^{i}-----$Cu^{ii\,a}$	3.034(1)	3.028(2)	3.191(1)	2.964(1)
Cu^{i}-----Cu^{iii}			3.148(1)	3.340(1)
$Cu^{i}-O^{i}$	1.924(4)	1.938(10)	1.939(5)	1.951(3)
$Cu^{i}-O^{ii}$	1.927(4)	1.935(8)	2.343(5)	1.979(4)
$Cu^{i}-O^{iii}$			1.989(5)	2.422(4)
$Cu^{i}-S^{i}$	2.319(2)	2.303(3)	2.321(3)	2.329(2)
$Cu^{i}-X^{i\,b}$	2.230(2)	2.381(2)	2.218(3)	2.205(2)
$O^{i}-C(1)^{i}$	1.400(6)	1.393(14)	1.433(11)	1.429(7)
$C(1)^{i}-C(2)^{i}$	1.518(7)	1.525(16)	1.513(14)	1.516(8)
$S^{i}-C(2)^{i}$	1.808(6)	1.810(14)	1.793(12)	1.823(6)
$S^{i}-C(3)^{i}$	1.818(5)	1.813(12)	1.816(13)	1.817(6)
$C(3)^{i}-C(4)^{i}$	1.500(8)	1.508(20)	1.459(22)	1.537(9)
$C(3)^{i}-C(5)^{i}$			1.460(23)	
$C(4)^{i}-C(5)^{i}$				1.517(13)
$Cu^{i}-O^{i}-Cu^{ii}$	103.9(2)	102.9(4)	95.9(2)	97.9(1)
$Cu^{i}-O^{i}-Cu^{iv}$			106.5(2)	99.0(1)
$Cu^{ii}-O^{i}-Cu^{iv}$			92.8(2)	98.2(1)
$O^{i}-Cu^{i}-O^{ii}$	76.1(2)	77.1(4)	82.7(2)	81.0(1)
$O^{i}-Cu^{i}-O^{iii}$			84.9(2)	81.1(1)
$O^{i}-Cu^{i}-S^{i}$	85.8(1)	85.4(3)	85.3(2)	84.9(1)
$O^{i}-Cu^{i}-X^{i}$	168.3(1)	167.7(2)	177.3(2)	163.6(1)
$O^{ii}-Cu^{i}-O^{iii}$			75.0(2)	80.6(1)
$O^{ii}-Cu^{i}-S^{i}$	161.6(1)	161.7(3)	112.2(1)	165.8(1)
$O^{ii}-Cu^{i}-X^{i}$	100.3(1)	99.9(3)	98.1(2)	98.0(1)
$O^{iii}-Cu^{i}-S^{i}$			167.0(2)	95.1(1)
$O^{iii}-Cu^{i}-X^{i}$			97.8(2)	115.0(1)
$S^{i}-Cu^{i}-X^{i}$	96.91(6)	95.9(1)	92.0(1)	96.03(6)
$Cu^{i}-O^{i}-C(1)^{i}$	121.7(3)	122.2(8)	117.5(5)	112.6(3)
$Cu^{ii}-O^{i}-C(1)^{i}$	133.4(3)	132.4(8)	121.1(5)	124.8(3)
$Cu^{iv}-O^{i}-C(1)^{i}$			118.4(5)	119.5(3)
$O^{i}-C(1)^{i}-C(2)^{i}$	108.8(4)	107.1(9)	108.7(8)	108.6(5)
$C(1)^{i}-C(2)^{i}-S^{i}$	110.5(3)	110.9(8)	112.7(7)	110.8(4)
$Cu^{i}-S^{i}-C(2)^{i}$	94.0(2)	94.6(4)	97.2(3)	96.6(2)
$Cu^{i}-S^{i}-C(3)^{i}$	104.3(2)	103.0(4)	105.0(5)	105.8(2)
$C(2)^{i}-S^{i}-C(3)^{i}$	101.9(3)	102.8(6)	107.4(7)	102.2(3)
$S^{i}-C(3)^{i}-C(4)^{i}$	113.0(4)	112.6(8)	112.1(11)	111.2(5)
$S^{i}-C(3)^{i}-C(5)^{i}$			114.3(11)	
$C(4)^{i}-C(3)^{i}-C(5)^{i}$			114.8(14)	
$C(3)^{i}-C(4)^{i}-C(5)^{i}$				110.8(6)

[a] Roman-numeral superscripts refer to the following equivalent positions: (ii) 2 − x, −y, −z for $Cu(C_2H_5\text{-so})Cl$ and $Cu(C_2H_5\text{-so})Br$, (ii) 1 − x, 1 − y, z; (iii) 1 − y, x, 1 − z; (iv) y, 1 − x, 1 − z for $Cu(i\text{-}C_3H_7\text{-so})Cl$, (ii) −x, −y, z; (iii) y, −x, −z; (iv) −y, x, −z for $Cu(n\text{-}C_3H_7\text{-so})Cl$. [b] X denotes Cl or Br atom.

S^{i}, and Cl^{i} in the basal plane and with O^{ii} in the apex. The deviations of the basal atoms from the mean plane are within ±0.1 Å.

Type C Complex

A perspective view of a molecule of $Cu(n\text{-}C_3H_7\text{-so})Cl$ is given in Fig. 3. The unit cell contains two cubane-type molecules. This molecule may be considered as being built up from two binuclear units. The Cu-----Cu distance (Cu^{i}-----Cu^{iii} 3.340(1) Å) between the binuclear units is considerably longer than the Cu-----Cu distance (Cu^{i}-----Cu^{ii} 2.964(2) Å) within the binuclear unit. The coordination geometry of each copper atom is distorted square pyramid with O^{i}, O^{ii}, S^{i}, and Cl^{i} in the basal plane and O^{iii} at the top. Comparison of distances and angles within the Cu_4O_4 core with those observed in type B complex shows that the main structural difference is the Cu–O distances (*e.g.*, $Cu^{i}-O^{iii}$) between the two binuclear units which are associated to form a cubane tetra-

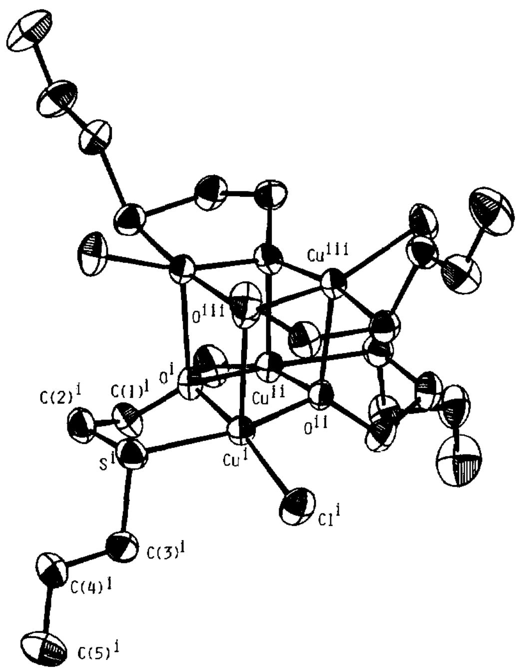

Fig. 3. Molecular structure of Cu(n-C_3H_7-so)Cl.

nuclear molecule. In contrast with type B complex, the interdimer Cu–O distance (Cu^{i}–O^{iii} 2.422(4) Å) is longer than the intradimer Cu–O distances (Cu^{i}–O^{i} 1.951(3) Å and Cu^{i}–O^{ii} 1.979(4) Å). Such a trend was already pointed out in the Cu(R-no)X complexes [7].

In conclusion, it was confirmed that the relation between the structure and the magnetic and spectral properties of the alkoxo-bridged copper(II) complexes with 2-(dialkylamino)ethanol [6, 7] is valid for the present complexes where RS- is substituted for R_2N-group.

References

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