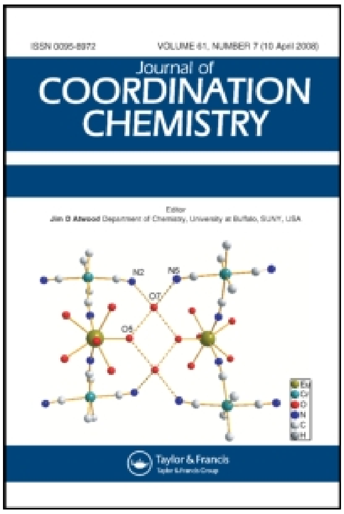

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CRYSTAL STRUCTURE ANALYSES OF TWO CROWN ETHER COMPLEXES OF COPPER(II) NITRATE: $[Cu(NO_3)_2(12\text{-crown-}4)]$ AND $[Cu(OH_2)_2(15\text{-crown-}5)][NO_3]_2$

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Two complexes of copper(II) nitrate, $[Cu(NO_3)_2(12\text{-crown-}4)]$ and $[Cu(OH_2)_2(15\text{-crown-}5)][NO_3]_2$, have been prepared by direct reaction of the hydrated salt with the appropriate crown ether in 3:1 CH_3CN:CH_3OH. The crystal structures of both complexes have been determined. $[Cu(NO_3)_2(12\text{-crown-}4)]$ crystallizes with a directly coordinated crown molecule and two tight ion pairs. Due to the relatively small size of Cu^{2+}, the nitrate anions are monodentate giving Cu^{2+} a coordination number of six and a very distorted octahedral geometry. $[Cu(OH_2)_2(15\text{-crown-}5)][NO_3]_2$ is seven-coordinate with Cu^{2+}/O interactions to the crown ether and two water molecules. The two anions reside in the hydrogen-bonded secondary coordination sphere. There is a fairly wide range of Cu-O(crown ether) distances in both complexes: Cu-O(12-crown-4) = 2.040(4)-2.387(4)Å, Cu-O(15-crown-5) = 2.010(5)-2.343(8)Å.

KEYWORDS: copper(II) nitrate, 12-crown-4, 15-crown-5, complex, X-ray structure

INTRODUCTION

Two 12-crown-4[1,2] and several 15-crown-5[3-15] complexes of first row transition metal(II) complexes have been crystallographically characterized. An interesting feature of these complexes is the variability in the role of the anion in completing the metal's primary coordination sphere. In our work involving the structural characterization of lanthanide[16-20] and Group 2[21] chloride and nitrate polyether complexes, these hard metal ions show a distinct preference for inclusion of NO_3^- in the primary coordination sphere even to the exclusion of the polyether. Chloride anions, on the other hand, compete with solvent or water molecules for inner-sphere sites with the final outcome often determined by steric interactions around the metal.

To further our study of inner- *vs.* outer-sphere anions in crystalline metal/crown ether complexes, we have prepared and structurally characterized $[Cu(NO_3)_2(12\text{-crown-}4)]$ and $[Cu(OH_2)_2(15\text{-crown-}5)][NO_3]_2$. A crystal structure of the latter complex has been published,[3] however we were unable to reproduce the unit cell obtained in that study and decided to carry out our own structural analysis. This

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report details the crystal structures of the two title complexes and compares them to other crystallographically characterized first row transition metal(II) 12-crown-4 and 15-crown-5 complexes.

EXPERIMENTAL

Preparation and Crystallization of Complexes

CH_3CN and CH_3OH were distilled from CaH_2 and stored over 4Å molecular sieves prior to the preparation of a 3:1 CH_3CN:CH_3OH mixed solvent. The crown ethers and the metal salts were used as purchased without further purification.

[Cu(NO$_3$)$_2$(12-crown-4)]

1.20 g 12-crown-4 (6.8 mmol) were added to 15 mL of 3:1 CH_3CH:CH_3OH mixed solvent containing 1.24 g $Cu(NO_3)_2 \cdot 3H_2O$ (5.1 mmol). The mixture was stirred at 60°C for 1.5 h. The supernatant was decanted and cooled to 0°C for 10 h. Slow evaporation at room temperature for several days afforded diffraction quality single crystals.

[Cu(OH$_2$)$_2$(15-crown-5)][NO$_3$]$_2$

1.34 g 15-crown-5 (6.1 mmol) were added to 15 mL of 3:1 CH_3CN:CH_3OH mixed solvent containing 1.29 g $Cu(NO_3)_2 \cdot 3H_2O$ (5.3 mmol). The mixture was stirred at 60°C for 1.5 h during which time the blue color of the copper salt disappeared. The supernatant was decanted and cooled at 0°C for 10 h. Slow evaporation at room temperature afforded the diffraction-quality single crystals after several days.

X-ray Data Collection, Structure Determination and Refinement

[Cu(NO$_3$)$_2$(12-crown-4)]

A blue single crystal of the title complex was mounted in a thin-walled glass capillary flushed with Ar and transferred to the goniometer. The space group was determined to be either the centric $P2_1/m$ or acentric $P2_1$ from the systematic absences. The subsequent solution and successful refinement of the structure was carried out in the acentric space group $P2_1$. A summary of data collection parameters is given in Table 1.

Least-squares refinement with isotropic thermal parameters led to R = 0.071. The hydrogen atoms were placed in calculated positions 0.95Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5Å^2. Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of R = 0.032 and R_w = 0.041. The final values of the positional parameters are given in Table 2.

[Cu(OH$_2$)$_2$(15-crown-5)][NO$_3$]$_2$

A colorless single crystal of the title complex was mounted in a thin-walled glass capillary flushed with Ar and transferred to the goniometer. The space group was

Table 1 Crystal data and summary of intensity data collection and structure refinement.

cmpd.	$[Cu(NO_3)_2(12\text{-crown-}4)]$	$[Cu(OH_2)_2(15\text{-crown-}5)][NO_3]_2$
color/shape	Blue/parallelepiped	Colorless/parallelepiped
for. wt.	363.77	443.85
space group	$P2_1$	$P2_1/c$
temp., °C	20	20
cell constants[a]		
a, Å	7.225(5)	7.375(3)
b, Å	12.594(9)	13.981(4)
c, Å	7.485(5)	8.657(3)
β, deg	102.21(4)	97.35(3)
cell vol., $Å^3$	665.7	885.3
formula units/unit cell	2	2
D_{calc}, g cm^{-3}	1.81	1.66
μ_{calc}, cm^{-1}	17.6	13.6
diffractometer/scan	Enraf-Nonius CAD-4/ω-2θ	Enraf-Nonius CAD-4/ω-2θ
radiation, graphite monochromator	MoKα(λ = 0.71073)	MoKα(λ = 0.71073)
max. crystal dimensions, mm	0.25 × 0.35 × 0.40	0.13 × 0.40 × 0.53
scan width	0.80 + 0.35tanθ	0.80 + 0.35tanθ
standard refl	600;0,10,0;005	600;0,10,0;008
decay of standards	±2%	±2%
refl measured	1314	1770
2θ range, deg	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$
range of h, k, l	+8, +14, ±8	+8, +16, ±10
refl observed $[F_o \geq 5\sigma(F_o)]$[b]	1135	1087
computer programs[c]	SHELX[22]	SHELX
structure solution	SHELXS[23]	SHELXS
no. of parameters varied	189	187
weights	$[\sigma(F_o)^2 + 0.0008F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0032F_o^2]^{-1}$
GOF	0.91	0.80
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.032	0.043
R_w	0.041	0.058
R inverse configuration	0.036,0.050	
largest feature final diff. map	0.3 $e^- Å^{-3}$	0.5 $e^- Å^{-3}$(H(1)[O(6)])

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 refl θ > 20°. [b] Corrections: Lorentz-polarization. [c] Neutral scattering factors and anomalous dispersion corrections from ref. 24.

determined to be the centric $P2_1/c$ from the systematic absences. A summary of data collection parameters is given in Table 1.

Dejehet, *et al.*[3] reported the crystal structure of this complex with a Pc cell of *a* = 14.758(5)Å, *b* = 13.978(4)Å, *c* = 43.914(13)Å, β = 102.19(3)°. This cell contains ten different molecules in the asymmetric unit. Our unit cell could be transformed to nearly that observed by Dejehet *et al.* by doubling our *a* and multiplying our *c* by five. For our crystal however, we found no interleaving reflections that suggested we should do this and thus collected our data in the smaller cell with one half molecule in the asymmetric unit. This did result in the disorder described below; however, we note 15-crown-5 often exhibits this type of disorder in these complexes.[2,4,9,10,12,14]

Solution of this structure revealed that the complex resides on a center of inversion. Since the crown ether cannot support this symmetry, it is disordered. Five unique oxygen positions and ten unique carbon positions were resolved. Thus, there are two orientations of the crown ether related by the center of symmetry. O(1)-O(5) and C(1)-C(10) are all refined at one half occupancy.

Table 2 Final fractional coordinates for [$Cu(NO_3)_2$(12-crown-4)].

Atom	*x/a*	*y/b*	*z/c*	*B*(eqv)[a]
Cu	-0.65178(7)	-0.2500	-0.81619(7)	2.46
O(1)	-0.3397(5)	-0.2839(3)	-0.7603(6)	2.90
O(2)	-0.5453(6)	-0.1787(4)	-0.5713(5)	3.53
O(3)	-0.8505(6)	-0.1030(4)	-0.7836(6)	3.22
O(4)	-0.5485(5)	-0.1231(3)	-0.9549(5)	2.85
O(5)	-0.8364(6)	-0.3389(4)	-0.7266(6)	3.55
O(6)	-0.6117(7)	-0.4544(4)	-0.6607(7)	4.79
O(7)	-0.8995(8)	-0.5004(5)	-0.6630(7)	5.32
O(8)	-0.6733(6)	-0.3353(4)	-1.0359(5)	3.13
O(9)	-0.9436(6)	-0.2587(6)	-1.1397(6)	4.59
O(10)	-0.8404(9)	-0.3804(4)	-1.2963(6)	4.94
N(1)	-0.7823(9)	-0.4335(4)	-0.6820(7)	3.07
N(2)	-0.8248(7)	-0.3234(4)	-1.1628(6)	2.74
C(1)	-0.2459(8)	-0.2498(8)	-0.5787(7)	3.83
C(2)	-0.3936(9)	-0.2384(9)	-0.4651(7)	3.98
C(3)	-0.6904(9)	-0.1427(6)	-0.4787(9)	3.93
C(4)	-0.790(1)	-0.0568(6)	-0.6026(9)	3.88
C(5)	-0.8314(9)	-0.0338(5)	-0.9288(9)	3.62
C(6)	-0.629(1)	-0.0194(5)	-0.945(1)	3.79
C(7)	-0.3455(9)	-0.1203(6)	-0.9312(9)	3.56
C(8)	-0.2727(8)	-0.2313(6)	-0.9055(8)	3.25

[a] $B(eqv) = (8\pi^2/3)[a^2U_{11}(a^*)^2 + b^2U_{22}(b^*)^2 + c^2U_{33}(c^*)^2 + ab(\cos\gamma)U_{12}a^*b^* + ac(\cos\beta)U_{13}a^*c^* + bc(\cos\alpha)U_{23}b^*c^*]$.

The geometrically constrained hydrogen atoms were placed in calculated positions 0.95Å from the bonded carbon atom and allowed to ride on that atom with *B* fixed at 5.5Å^2. The aquo hydrogen atoms were not included in the final refinement. Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.043$ and $R_w = 0.058$. The final values of the positional parameters are given in Table 3.

RESULTS AND DISCUSSION

An ORTEP illustration of [$Cu(NO_3)_2$(12-crown-4)] is presented in Figure 1. The Cu^{2+} ion is coordinated to two monodentate nitrate ions and the four oxygen atoms of the crown ether resulting in a coordination number of six.

The crown ether is severely distorted from its normal coordinated C_4 conformation with planar oxygen atoms. (In the title complex, the oxygen atoms deviate as much as 0.34Å from planarity.) It appears that much of this distortion is a result of the metal ion's preference for octahedral geometry. If Cu^{2+} is considered a very distorted octahedron, O(1) and O(3) are trying to, but cannot quite flex far enough to fill two *trans* coordination sites. The resulting Cu-O(1) and Cu-O(3) distances (2.246(6)Å, and 2.387(4)Å, respectively, Table 4) are thus longer than those observed for Cu-O(2) (2.040(4)Å) and Cu-O(4) (2.125(4)Å). This is exactly the same coordination environment and 12-crown-4 distortion observed in [$CuCl_2$(12-crown-4)].[1]

The Cu-O(5)-N(1) and Cu-O(8)-N(2) angles of 115.4(4)° and 117.4(4)°, respectively, are typical for monodentate nitrate coordination. As expected, the N-O

Table 3 Final fractional coordinates for $[Cu(OH_2)_2(15\text{-crown-}5)][NO_3]_2$.

Atom	*x/a*	*y/b*	*z/c*	*B*(eqv)
Cu	0.5000	0.0000	0.0000	2.95
O(1)	0.4603(8)	0.0638(4)	-0.2096(6)	3.31
O(2)	0.7604(9)	-0.0288(5)	-0.1127(8)	3.10
O(3)	0.6809(9)	-0.1052(5)	0.157(1)	3.43
O(4)	0.406(1)	-0.0079(6)	0.2482(9)	3.49
O(5)	0.2240(9)	0.0731(5)	-0.0139(8)	3.93
O(6)	0.6196(5)	0.1140(2)	0.0843(4)	4.07
O(7)	0.6682(6)	0.2671(3)	-0.1006(4)	6.25
O(8)	0.8377(7)	0.3857(3)	-0.1363(5)	6.63
O(9)	0.9081(6)	0.2892(3)	0.0566(5)	6.84
N(1)	0.8088(6)	0.3134(3)	-0.0602(4)	3.78
C(1)	0.599(2)	0.061(1)	-0.311(2)	3.48
C(2)	0.701(3)	-0.027(1)	-0.279(1)	4.09
C(3)	0.846(2)	-0.117(1)	-0.057(2)	4.72
C(4)	0.861(2)	-0.111(1)	0.116(1)	4.63
C(5)	0.671(2)	-0.101(1)	0.321(1)	3.64
C(6)	0.468(2)	-0.090(1)	0.335(2)	3.78
C(7)	0.213(2)	0.008(1)	0.231(2)	4.83
C(8)	0.170(2)	0.091(1)	0.135(2)	5.52
C(9)	0.231(2)	0.1545(9)	-0.114(1)	4.57
C(10)	0.300(2)	0.119(1)	-0.253(2)	4.26

distances to the coordinated oxygen atoms (O(5), O(8)) are longer (1.29(1)Å, average) than the remaining N-O separations within the nitrate anions (1.225(7)Å, average).

The fact that the NO_3^- anions are monodentate in the title complex is unequivocal but interesting. The Cu-O(5) and Cu-O(8) separations are 1.965(4)Å and 1.943(4)Å, respectively, while the Cu···O(6) and Cu···O(9) distances are nearly 1Å longer at 2.815(5)Å and 2.858(4)Å, respectively. What is interesting is that the corresponding Co^{2+} complex ($[Co(NO_3)_2(12\text{-crown-}4)]^2$) contains one bidentate and one monodentate nitrate anion for a coordination number of seven, despite the fact that the effective ionic radius for six-coordinate Co^{2+} is only 0.015Å larger than that for six-coordinate Cu^{2+}.[25]

The extra donor in the Co^{2+} complex allows the 12-crown-4 molecule to relax to its more normal C_4 conformation, characterized by O-C-C-O torsion angles which are all + gauche (+ 60°) and one C-O-C-C torsion angle between each O-C-C-O unit anti (180°) and one forced toward gauche (88(5)° average). In both the title complex and $[CuCl_2(12\text{-crown-}4)]$, the O-C-C-O torsion angles have the sequence $g^- g^+ g^+ g^-$ and only two of the C-O-C-C torsion angles (one each between consecutive O-C-C-O torsion angles of like sign) are forced toward gauche.

The Co-O(12-crown-4) distances in $[Co(NO_3)_2(12\text{-crown-}4)]$ exhibit a narrower range (2.161(4)-2.210(4)Å) than in either of the Cu^{2+} complexes. Despite the larger size of Co^{2+} and its higher coordination number, the longest M^{2+}-O (crown ether) distances are observed in the Cu^{2+} complexes, a further indication of the distortion of the crown ether. As expected, the $Co\text{-}ONO_2$ separations are longer (2.18(6)Å average) than observed in $[Cu(NO_3)_2(12\text{-crown-}4)]$ (1.95(1)Å).

An ORTEP illustration of $[Cu(OH_2)_2(15\text{-crown-}5)][NO_3]_2$ is presented in Figure 2. The Cu^{2+} ion resides on a crystallographic center of inversion and thus, the crown ether is disordered. There are two orientations of the crown ether, the one

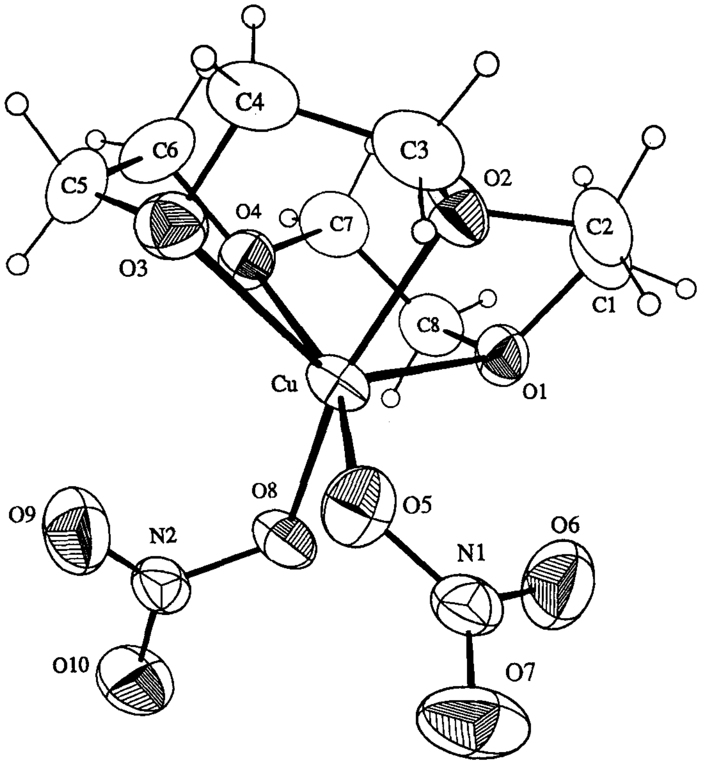

Figure 1 ORTEP illustration of [Cu(NO$_3$)$_2$(12-crown-4)] with 50% probability thermal ellipsoids. The hydrogen atoms have been arbitrarily reduced for clarity.

depicted in Figure 2 and one generated by the center of inversion. To model this disorder, five unique oxygen positions and ten unique carbon positions were located and refined at 50% occupancy. This type of disorder is common for 15-crown-5 in these types of complexes.[2,4,9,10,12,14]

The Cu^{2+} ion is seven-coordinate pentagonal bipyramidal. The apical water molecules reside 1.920(3)Å from the metal ion and are hydrogen-bonded to two nitrate anions *via* O(7) and O(8) (O(6)···O(7) = 2.723(5)Å; O(6)···O(8)a = 2.728(5)Å; O(7)···O(6)···O(8)a = 114.4(2)°). Due to the hydrogen-bonding, the N(1)-O(7) and N(1)-O(8) distances are longer (1.238(2)Å average) than the N(1)-O(9) separation of 1.219(5)Å. The hydrogen-bonding joins the ions into sheets in the *bc* plane.

The pentagonal array of 15-crown-5 oxygen donors around the Cu^{2+} ion is planar to only 0.25Å. The crown conformation is as symmetrical as it can get. The O-C-C-O torsion angles alternate ±g except for O(5)-C(9)-C(10)-O(1) and O(1)-C(1)-C(2)-O(2) which are both g$^-$. The C-O-C-C torsion angles are all anti.

The O(6)···O(7) hydrogen bond eclipses the shortest Cu-O(crown ether) interaction (Cu-O(1) = 2.010(5)Å). This separation seems unusually short and may be an artifact of the disorder. It is the shortest Cu-O(crown ether) bond length in Table 4

Table 4 Comparison of bonding parameters in first row transition metal(II) complexes of 12-crown-4 and 15-crown-5.

		M-O(crown ether)		$M\text{-}OH_2$	$M\text{-}ONO_2$	
Compound	CN	Range, Å	Avg., Å	Avg., Å	Avg., Å	Ref.
$[Cu(NO_3)_2(12C4)]$	6	2.040(4)–2.387(4)	2.2(1)		1.95(1)	a
$[CuCl_2(12C4)]$	6	2.113(3)–2.403(3)	2.2(1)			1
$[Co(NO_3)_2(12C4)]$	7	2.161(4)–2.210(4)	2.19(2)		2.18(6)	2
$[Cu(OH_2)_2(15C5)][NO_3]_2$	7	2.010(5)–2.343(8)	2.2(1)	1.920(3)		a
		2.112(6)–2.365(5)	2.25(8)	1.92(3)		3
$[Cu(CH_3CN)_2(15C5)][Cu_3Cl_8]^b$	7	2.16(2)–2.34(2)	2.24(6)			4
$[CuCl(CH^3CN)(15C5)]_2[Cu_2Cl_6]$	7	2.176(3)–2.360(3)	2.26(6)			4
		2.171(5)–2.349(5)	2.26(6)			5
$[Zn(OH_2)_2(15C5)][NO_3]_2$	7	2.114–2.312	2.22(6)	2.00(1)		6
$[Zn(CH_3CN)_2(15C5)][Zn_2Cl_6]\cdot CH_3CN$	7	2.153(8)–2.235(9)	2.20(3)			7
$[ZnCl(Me_2CO)(15C5)]_2[Zn_2Cl_6]$	7	2.13(2)–2.27(2)	2.20(5)			7
$[ZnCl(OH_2)(15C5)]_2[Zn_2Cl_6]$	7	2.208–2.241	2.19(5)	2.081		8
$[Co(OH_2)_2(15C5)][NO_3]_2{}^b$	7	2.13(1)–2.35(1)	2.22(8)	2.082(5)		2
$[Co(OH_2)_2(15C5)]Cl_2\cdot H_2O^b$	7	2.122(6)–2.243(6)	2.20(6)	2.079(4)		9
$[Co(OH_2)_2(15C5)][CoCl_4]\cdot H_2O$	7	2.166(2)–2.213(2)	2.18(2)	2.076(4)		9
$[Co(OH_2)_2(15C5)][CuCl_4]$	7	2.13(1)–2.23(1)	2.17(4)	2.09(1)		10
$[Co(OHEt)_2(15C5)][CoCl_4]$	7	2.141–2.248	2.18(4)	2.12(1)(OHET)		11
$[Co(CH_3CN)_2(15C5)][CoCl_4]\cdot CH_3CN$	7	2.17(3)–2.25(3)	2.20(3)			12
		2.169(3)–2.205(3)	2.19(1)			13
$[Co(CH_3CN)_2(15C5)][CoCl_3(CH_3CN)]_2\cdot CH_3CN$	7	2.07(2)–2.40(2)	2.2(1)			12
$[Co(CH_3CN)_2(15C5)][Co_2Cl_6]^b$	7	2.176(7)–2.226(8)	2.20(2)			12
$[Co(CH_3CN)_2(15C5)][Cu_2Cl_6]^b$	7	2.10(1)–2.269(8)	2.19(6)			10
$[FeCl_2(15C5)][FeCl_4]^b$	7	2.112–2.192	2.16(3)			14
$[FeBr_2(15C5)]\cdot CH_2Cl_2{}^c$	7	2.175(6)–2.265(6)	2.22(3)			15

[a] This study. [b] The crown ether is disordered. [c] Study done at 163K.

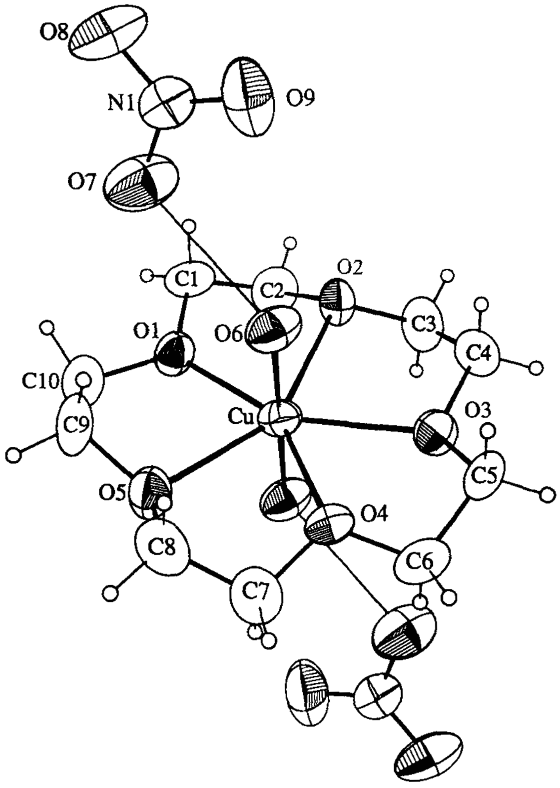

Figure 2 Illustration of the $[Cu(OH_2)_2(15\text{-crown-}5)][NO_3]_2$ formula unit. The aquo hydrogen atoms were not included in the refinement.

and is over 0.1Å shorter than the shortest separation in the Dejehet, *et al.* determination of this same structure.[3]

The comparison of M^{2+}-O bonding parameters in Table 4 for $M^{2+} = Cu^{2+}$, Zn^{2+}, Co^{2+}, and Fe^{2+}, reveals little or no statistical difference in the average M-O(crown ether) distances. All of these average values cluster around 2.2Å with a minimum of 2.16(3)Å and a maximum of 2.26(6)Å. The range in individual M-O separations is 0.393Å (2.010(5)-2.403(2)Å).

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Supplementary Material

Tables of fractional coordinates for hydrogen atoms, thermal parameters, bond distances and angles, least-squares planes results, torsion angles, an ORTEP illustration of the 15-crown-5 disorder, and observed and calculated structure factors or amplitudes (17 pages) are available from RDR upon request.

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