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The Crystal and Molecular Structure of the Mixed-Anion Copper(II) Complex, $LCuClClO_4$, L = 1,1', 4,7,7'-pentamethyldiethylenetriamine, from the Reaction of $LCuClCO_3(ClO_4)CuL$ with Water

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Copper(I) chloride dissolves in methylene chloride containing 1,1',4,7,7'-pentamethylenediethylenetriamine, (L), and an excess of carbon dioxide to give a pale yellow solution which reacts with dioxygen to give a hygroscopic, blue μ-carbonatocopper(II) complex. Reaction of this product with equimolar $AgClO_4$ *in methylene chloride and attempted single crystal growth gives* $LCuClClO_4$*, whose 3-dimensional structure has been determined.*

Introduction

In recent papers [1, 2], we have described the synthesis, structure and properties of the products of quantitative, aprotic oxidations of alkyldiamine copper(I) complexes with dioxygen in the presence of carbon dioxide, *e.g.* eqn. 1.

$$2L_2Cu_2Cl_2 + O_2 + 2CO_2 \xrightarrow[25\ ^{\circ}C]{CH_2Cl_2} 2L_2Cu_2Cl_2CO_3 \qquad (1)$$

The *green* products of reactions 1 are dimeric species containing formal 18-electron metal centers with either symmetrical [1] or asymmetrical [2] bridging carbonate groups and coordinated chloro ligands. They are members of a homologous series of μ-carbonatodicopper(II) complexes which efficiently initiate the oxidative coupling of phenols by dioxygen [1, 2]. This work is being extended to studies of the products of reaction 1 in the presence of tridentate amine ligands such as 1,1', 4,7,7'-pentamethyldiethylenetriamine, pmet, for two reasons:

1) Use of a tridentate ligand might yield *ionic* μ-carbonatodicopper(II) products, *e.g.* $[L_2Cu_2CO_3]X_2$ [3] or $[L_3Cu_3CO_3]X_4$ [4], only three examples of which (with X = nitrate or perchlorate), are presently known.

2) Changes in the coordination environment around the metal centers might drastically alter the efficiency and specificity of catalyzed oxidative coupling reactions of phenols by dioxygen [1, 2].

The product of reaction 1 with L = pmet is the complex $(pmet)_2Cu_2Cl_2CO_3$[†], which differs from the majority [2] of $L_2Cu_2Cl_2CO_3$ complexes with diamine ligands in that it is *blue and extremely hygroscopic.* Like the products with diamine ligands [2], $(pmet)_2Cu_2Cl_2CO_3$ is a non-electrolyte in a range of aprotic solvents and initiates the oxidative coupling of 2,6-dimethylphenol to the corresponding diphenoquinone [1]. To date, attempts to crystallize either $(pmet)_2Cu_2Cl_2CO_3$ or the products of the characteristic [2] reaction 2

$$2AgX(s) + L_2Cu_2Cl_2CO_3 \xrightarrow[25\ ^{\circ}C]{CH_2Cl_2} L_2Cu_2X_2CO_3 + 2AgCl(s) \qquad (2)$$

have been unsuccessful because of the extreme sensitivity of $(pmet)_2Cu_2X_2CO_3$ (X = Cl, ClO_4, BF_4) to water, which results in loss of the carbonate ligands. However, one benefit of this sensitivity to water is a potential method of obtaining amine-copper(II) complexes with two, different coordinated anions. This paper describes the preparation and structure of one such example, $(pmet)CuClClO_4$.

Experimental

The purification of copper(I) chloride, diethyl ether and methylene chloride and the general experi-

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[†] As noted in the text, μ-carbonatocopper(II) complexes with pmet ligands give irreproducible analytical results on attempted isolation as solids. However, their formulation as $pmetCuXCO_3XCupmet$ species seems assured by the measured reaction stoichiometry of eqn. 1 and their similarity in solution to other, characterized [1, 2] μ-carbonatodicopper(II) species. We shall report separately on the structure and more detailed properties of the $pmetCuXCO_3XCupmet$ series.

TABLE I. Atomic Parameters in Fractional Coordinates (×10^4) and Thermal Parameters (×10^2) with e.s.d.s. Temperature factor: $\exp[-2\pi^2(U11(ha^*)^2 + \ldots + 2U12(hka^*b^*) + \ldots]$.

Atom	*X*	*Y*	*Z*	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
Cu	7639(1)	9394(2)	6220(1)	302(9)	367(9)	426(9)	049(10)	−036(9)	−064(10)
N(1)	8829(9)	10910(17)	6585(9)	324(73)	383(82)	543(90)	099(67)	−109(61)	−064(75)
C(2)	8403(14)	12506(22)	6985(11)	656(127)	433(106)	569(111)	028(95)	−070(98)	−259(96)
C(3)	7387(12)	12981(19)	6531(10)	485(101)	310(78)	687(103)	040(88)	−059(92)	069(78)
N(4)	6739(9)	11436(17)	6540(8)	399(76)	455(85)	482(94)	048(67)	−070(65)	−009(71)
C(5)	5940(13)	11534(22)	5835(12)	474(103)	369(112)	659(130)	216(91)	−107(94)	018(102)
C(6)	5527(12)	9773(25)	5701(12)	418(102)	612(139)	771(130)	024(95)	−098(98)	−213(108)
N(7)	6393(10)	8533(17)	5532(8)	524(83)	366(80)	449(83)	−047(73)	−225(73)	−033(65)
C(8)	9513(13)	10111(25)	7221(12)	416(103)	770(159)	767(133)	098(94)	−234(96)	162(108)
C(9)	9424(13)	11415(27)	5827(12)	630(116)	745(150)	557(124)	040(108)	157(103)	016(116)
C(10)	6281(15)	11294(26)	7408(14)	749(141)	700(151)	909(159)	−000(113)	354(127)	−066(121)
C(11)	6054(15)	6742(23)	5721(14)	724(128)	344(112)	1019(166)	−105(102)	−288(119)	125(116)
C(12)	6689(13)	8607(23)	4609(11)	806(134)	630(127)	456(113)	−016(110)	−129(97)	−032(95)
Cl(1)	8617(3)	7147(6)	5857(3)	554(28)	546(32)	837(34)	153(24)	082(26)	−182(28)
Cl(2)	7189(3)	6842(3)	8416(3)	620(30)	647(28)	485(25)	−150(26)	076(23)	−098(23)
O(1)	7556(18)	7913(30)	7770(13)	1709(76)					
O(2)	6409(18)	5972(34)	8027(15)	1835(90)					
O(3)	6783(16)	7550(33)	9102(14)	1763(89)					
O(4)	7922(20)	5365(39)	8500(16)	2359(129)					

Atom	*X*	*Y*	*Z*	*U*
H(2.1)	8934	13523	6915	380
H(2.2)	8270	12298	7639	380
H(3.1)	7030	14000	6855	380
H(3.2)	7540	13366	5896	380
H(5.1)	6278	12030	5291	380
H(5.2)	5366	12402	6054	380
H(6.1)	5142	9359	6271	380
H(6.2)	5023	9779	5199	380
H(8.1)	10125	11015	7373	380
H(8.2)	9872	9012	6955	380
H(8.3)	9138	9804	7775	380
H(9.1)	9756	10274	5530	380
H(9.2)	10009	12277	5949	380
H(9.3)	8923	11952	5357	380
H(11.1)	6675	5873	5572	380
H(11.2)	5435	6387	5338	380
H(11.3)	5892	6681	6362	380
H(12.1)	6001	8268	4240	380
H(12.2)	7241	7754	4474	380
H(12.3)	6855	9887	4489	380
H(10.1)	6838	11192	7878	380
H(10.2)	5808	10149	7443	380
H(10.3)	5783	1233	7588	380

mental procedures for reactions 1, 2 and single crystal growth have been described previously [1, 2]. Pmet was synthesized and purified by literature methods [5].

Synthesis of (pmet)CuClClO$_4$

Methylene chloride, 20 ml containing pmet (0.87 g, 5 mmol) was saturated with dry CO_2. Copper(I) chloride (0.50 g, 5 mmol) was then added under CO_2. The resulting very pale yellow solution was reacted with dry dioxygen and CO_2 for fifteen minutes and then centrifuged to remove traces of excess copper(I) chloride. Dry $AgClO_4$ (Alfa, 1.04 g, 5 mmol) was added to the solution and the mixture was stirred for 12 hr under dry CO_2. Precipitated silver chloride was removed by centrifugation

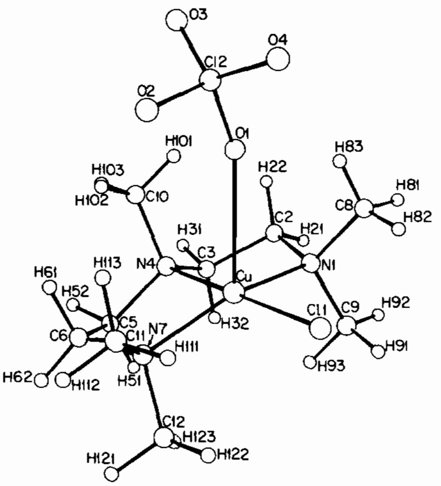

Fig. 1. Molecular structure.

and the solution was then treated with diethyl ether, as described previously [1, 2], in an attempt to grow single crystals of the anticipated μ-carbonatodicopper(II) product. Instead, carbonate-free, blue needle crystals, whose structure is reported here, were obtained together with an amorphous, blue solid which has not been identified (see Discussion).

Crystal Data

$CuCl_2O_4N_3C_9H_{23}$, M = 371.75. Orthorhombic, space group $P2_12_12_1$ with unit cell dimensions: a = 13.123(8), b = 7.730(5), c = 15.646(4) Å, V = 1587 Å^3 with a calculated density of 1.47 g cm^{-3} for $Z = 4$.

Three-dimensional intensity data were collected on a Syntex $P2_1$ automated diffractometer using monochromatized Mo Kα radiation. Of the 1456 unique reflections measured ($2\theta_{max}$ = 48°), 1029 were considered observed ($I \geqslant 3\sigma(I)$).

Elucidation and Refinement of the Structure

A three dimensional Patterson synthesis yielded the position of the copper atom. The remaining non-hydrogen atoms were located in subsequent Fourier syntheses. Hydrogen atom positions were calculated and hydrogen atoms were included in subsequent structure factor calculations, but held invariant during least squares refinement. Anisotropic refinement converged at a residual of 0.066. The space group is polar and at this point the chirality of the structure was examined by inverting all coordinates through ½, ½, ½. Refinement converged at a residual of 0.061 and the correct chirality is defined by the inverted coordinates. The difference Fourier synthesis does indicate some residual electron density in the vicinity of the perchlorate ion but attempts to assign partial oxygen occupancy to these sites did not lead to improvement in agreement of observed and calculated structure factors and the reported structure is considered complete. The final atomic positional parameters are given in Table I. The X-Ray 76 crystallographic computer programs [6] were used throughout structure determination and refinement.

TABLE II. Bond Angles about the Copper Ion.

Cl1–Cu–N1	94.5(4)°
Cl1–Cu–N4	179.4(4)
Cl1–Cu–N7	94.3(4)
Cl1–Cu–O1	85.7(5)
N1–Cu–N4	85.7(5)
N1–Cu–N7	159.5(5)
N1–Cu–O1	91.3(6)
N4–Cu–N7	85.2(5)
N4–Cu–O1	94.8(6)
N7–Cu–O1	107.7(6)

Results

The $(pmet)_2Cu_2X_2CO_3$ complexes are by far the most water-sensitive μ-carbonatodicopper(II) complexes so far encountered in our laboratory [1, 2]. Efforts are continuing to obtain reproducible analytical and molecular weight data for them under rigorously dry experimental conditions*. The blue complex $(pmet)_2Cu_2Cl_2CO_3$ has μ_{eff} (298 K) 1.35 BM (Cu atom)$^{-1}$ and an electronic absorption spectrum with maxima centered at 770 and 290 nm. The corresponding BF_4^- and ClO_4^- complexes from reaction 2 have electronic absorption maxima at 750 and 288 and 758 and 288 nm, respectively. The characteristic [1–3] ir bands for bridging, tridentate carbonate are lost on reaction of any of these complexes with water. The decomposition product $pmetCuClClO_4$ is not a catalyst for the oxidative coupling of 2,6-dimethylphenol [1, 2].

Description of Structure

A labeled drawing of the molecular structure is given in Fig. 1. The copper atom is coordinated by three nitrogen atoms of the ligand, a chloride ion and an oxygen atom of the perchlorate group. The coordination is approximately square pyramidal, with the copper atom displaced 0.168 Å from the plane defined by Cl1, N1, N4 and N7 as the four atoms describing the base of the square pyramid. The apex of the pyramid is occupied by O1 of the perchlorate group. The bond angles involving the copper ion are presented in Table II and the remaining bonding parameters are presented in Fig. 2.

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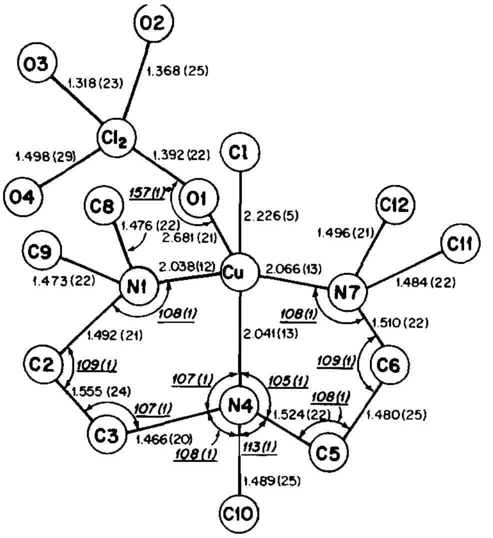
*See footnote † on p. 45.

O1 – Cl_2 – O2	103(1)
O1 – Cl_2 – O3	119(1)
O1 – Cl_2 – O4	107(1)
O2 – Cl_2 – O3	105(1)
O2 – Cl_2 – O4	98(2)
O3 – Cl_2 – O4	120(1)



Cu – N1 – C8	114(1)
Cu – N1 – C9	109(1)
C2 – N1 – C8	107(1)
C2 – N1 – C9	108(1)
C8 – N1 – C9	109(1)
Cu – N4 – C10	114(1)
Cu – N7 – C11	115(1)
Cu – N7 – C12	107(1)
C6 – N7 – C11	109(1)
C6 – N7 – C12	110(1)
C3 – N4 – C5	111(1)

Fig. 2. Bonding parameters.

There are no short intermolecular interactions, the molecules being held together by van der Waals' forces. It is interesting to note that the approximate square-planar coordination geometry about the copper ion in the present structure is similar to that found in the tricopper-carbonate complex reported recently [4]. In this latter structure, each copper is coordinated to three nitrogen atoms of a tridentate amine ligand and an oxygen atom of the μ_3-carbonato ion in the basal plane, with a water molecule occupying the axial site.

Discussion

The water-sensitivity and blue (rather than green) colors of μ-carbonatodicopper(II) complexes which contain anions (*e.g.* acetate, nitrate), potentially capable of increasing the coordination number of copper(II) to greater than 5 has been observed before [2]. Additional ligand donor atoms from particular anions or pmet in analogs of the 18-electron center in $L_2Cu_2Cl_2CO_3$ (L = alkyldiamine) evidently increase the sensitivity of the carbonate moiety to reaction with water. Disproportionation reactions of μ-oxo (*e.g.* eqn. 3, L = N-methyl-2-pyrrolidinone [7]) and μ-carbonatodicopper(II) centers in the presence of water appear to be fairly common, and reaction 4 might account for the production of pmetCuClClO$_4$ in the present system.

$$12LCuCl + 3O_2 + 6H_2O \rightarrow 2L_4Cu_4Cl_6O(OH_2) + 4LCu(OH)_2 \qquad (3)$$

$$H_2O + pmetCuClCO_3ClO_4Cupmet \rightarrow pmetCu(OH)_2 + pmetCuClClO_4 + CO_2 \qquad (4)$$

Although experimentally troublesome in systematic studies of water-sensitive μ-oxo- and μ-carbonatodicopper(II) complexes, reactions such as 4 may be useful for synthesis of mixed anion complexes of copper(II).

Acknowledgements

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