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The Structure of μ_4-Oxo-hexa-μ-bromo-tetra[amminecopper(II)]

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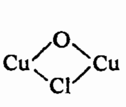
The structure of $Cu_4OBr_6(NH_3)_4$ has been determined by a single-crystal X-ray diffraction study. The compound crystallizes as tetragonal crystals (a = 9.004(10) Å, c = 9.731(13) Å) of space group $P\bar{4}2_1c$ with two molecules per unit cell ($d_{calc.} = 3.44$ g/cm^3; $d_{obs} = 3.35$ g/cm^3). The structure, which is similar to that found for other μ_4-oxo complexes, consists of a central oxide ion coordinated tetrahedrally to four copper(II) ions; the copper(II) ions are bridged in pairs by the six bromide ions and the ammonia molecules complete the trigonal-bipyramidal coordination of the copper(II) ions. The average interatomic distances are: Cu–Cu, 3.12 Å; Cu–O, 1.93 Å; Cu–Br, 2.54 Å; Cu–N, 1.98 Å; the Cu–Br–Cu angle is 76.5°.

Introduction

In several recent papers,[1-4] structures have been reported for polynuclear complexes of copper(II) with the general formula $Cu_4OCl_6L_4$ (where L represents a monodentate ligand). In these complexes a central oxide ion is tetrahedrally cordinated to four copper(II) ions, the copper ions are bridged in pairs by six chloride ions, and the L groups complete the trigonal bipyramidal coordination of the coppers. The dimensions of the central Cu_4O unit (Cu–O, 1.91 Å; Cu–Cu, 3.12 Å; Cu–O–Cu, 109°) for all of the complexes reported are identical to those of the Cu_4O unit in copper(II) oxide. Due to the fact that the chloride ion is considerably larger than the oxide ion, the Cu–Cl–Cu angle in the four-membered ring, I, is closed down to 81°



I

Although corresponding copper complexes with bromide bridges have been reported,[3,5] structures have not been reported for any of these; however, the effect of the increased size of the bromide ion on the central Cu_4O unit and on the bond angle at the bromide would be of considerable interest. The structure of an analogous magnesium complex with bromide bridges has been reported[6] and Mg–Br–Mg angles of about 76° were obtained. We initially attempted a structure determination on $Cu_4OBr_6(TPPO)_4 \cdot 2CH_3NO_2$ (TPPO represents triphenylphosphine oxide); however, problems with disorder prevented refinement of that structur. Crystals of $Cu_4OBr_6(NH_3)_4$ were obtained while attempting to recrystallize bromo{2-phenyl-2-(diethylamino)-ethoxo}copper(II) from nitromethane; in this paper we report the structure of $Cu_4OBr_6(NH_3)_4$.

Experimental Section

Preparation. Bromo{2-phenyl-2-(diethylamino)-ethoxo}copper(II), Cu{O–CH$_2$–CHPh–N(Et)$_2$}Br, was prepared according to the method of Uhlig and Staiger;[7] this compound was then heated in nitromethane and filtered. The filtrate was allowed to stand for several days after which a few well-formed red-brown octahedral-shaped crystals were deposited; the crystals were filtered and then dried in a vacuum dessicator. *Anal.* Calcd. for $Cu_4OBr_6(NH_3)_4$: H, 1.48; N, 6.85; Found: H, 1.64; N, 6.83.

Crystal Data. A well-formed octahedral-shaped crystal with a radius of approx. 0.15 mm was mounted on an apex of the octahedron. Precession photographs indicated a tetragonal unit cell; the absence of *hhl* reflections with $l = 2n+1$ and *h*00 reflections with $h = 2n+1$ uniquely defined the space group as $P\bar{4}2_1c$, No. 114.[8] The crystal was then transferred to a Picker Four-Circle Automated Diffractometer and eight reflections were located and used to obtain cell parameters; the values obtained are $a = 9.004(10)$ Å,[9] $c = 9.731(13)$ Å, and density of 3.44 g/cm^3 for two molecules per unit cell agrees well with the observed density of 3.35(10) g/cm^3 obtained by the flotation method using a mixture of diiodomethane and iodoform.

Intensity Measurements. Intensity measurements were made using the same crystal as used for the space group determination and molybdenum radiation was again used. The intensities were measured with a scintillation counter 21 cm from the crystal the θ–2θ scan technique was used with a take-off angle of 1.6° and a scan rate of 1° min^{-1}. A symmetrical scan of 2°

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[1] J. A. Bertrand and J. A. Kelley, *J. Am. Chem. Soc.*, *88*, 4746 (1966).
[2] J. A. Bertrand, *Inorg. Chem.*, *6*, 495 (1967).
[3] B .T. Kilbourn and J. D. Dunitz, *Inorg. Chim. Acta*, *1*, 209 (1967).
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[5] H. Bock, H. T. Dieck, H. Pyttlik, and M. Schnoller, *Zeit, fur anorg. u. allge. Chemie*, *357*, 54 (1968).
[6] G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, *86*, 4821 (1964).
[7] E. Uhlig and K. Staiger, *Zeit. fur anorg. u. allgem. Chemie*, *346*, 21 (1966).
[8] « International Tables for X-Ray Crystallography », Vol. I. The Kynoch Press, Birmingham, England, 1965.
[9] Numbers in parentheses here and elsewhere in this paper are the estimated standard deviations occurring in the last digits listed.

Table I. Final Positional and Thermal Parameters for $Cu_4OBr_6(NH^3)^4$

Atom	x	y	z	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	0	0	0	0.0059(15)	0.0059(15)	0.0050(13)	0	0	0
Cu	0.0663(6)	0.1596(5)	0.1147(5)	0.0068(7)	0.0036(7)	0.0066(4)	−0.0009(5)	−0.0019(6)	−0.0005(5)
N	0.1343(36)	0.3245(40)	0.2339(35)	0.0029(12)	0.0055(14)	0.0114(23)	−0.0034(13)	−0.0002(5)	−0.0035(14)
Br	0	0	0.3138(5)	0.0144(12)	0.0065(10)	0.0060(5)	−0.0001(11)	0	0
Br′	0.3230(5)	0.1281(5)	0.0031(7)	0.0051(5)	0.0081(6)	0.0102(4)	−0.0008(4)	0.0008(6)	−0.0025(5)

[a] Anisotropic thermal parameters are expressede in the form: $\exp-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}\ell^2+2\beta_{12}hk+2\beta_{13}h\ell+2\beta_{23}k\ell)$.

Table II. Observed and Calculated Structure factors (electrons) for $Cu_4OBr_6(NH_3)_4$

L= 0			
H	K	FO	FC
2	2	96	76
1	3	215	173
2	3	112	93
3	3	135	115
0	4	120	102
1	4	178	153
2	4	138	120
3	4	121	108
4	4	143	130
1	5	65	60
3	5	117	109
4	5	65	60
5	5	101	101
0	6	180	176
1	6	74	70
2	6	123	113
4	6	31	13
5	6	28	30
1	7	52	41
2	7	26	13
3	7	148	152
6	7	57	60
0	8	34	3
1	8	47	46
2	8	34	26
3	8	55	58
4	8	83	87
5	8	28	10
6	8	33	28
8	8	35	22
L= 1			
H	K	FO	FC
1	2	122	111
0	3	56	49
1	3	73	66
2	3	63	56
0	4	28	17
1	4	64	57
2	4	191	166
3	4	107	91
0	5	165	144
1	5	88	77
2	5	38	33
4	5	97	95
0	6	83	82
1	6	51	52
2	6	55	49
3	6	25	9
4	6	56	52
5	6	78	76
0	7	25	21
1	7	85	89
2	7	34	39
3	7	30	21
5	7	78	78
0	8	29	20
1	8	84	86
2	8	51	53
3	8	92	90
4	8	35	32
5	8	31	34
7	8	35	42
L= 2			
H	K	FO	FC
1	1	139	142
0	2	112	122
1	2	203	199
2	2	128	125
0	3	114	116
1	3	89	79
2	3	72	64
3	3	169	157
0	4	156	151
1	4	112	102
2	4	36	27
3	4	71	63
4	4	95	91
0	5	54	45
1	5	66	62
2	5	99	95
3	5	65	62
4	5	59	61
5	5	77	82
0	6	37	27
1	6	91	87
2	6	40	38
3	6	43	40
4	6	82	79
6	6	29	25
0	7	78	77
1	7	51	52
2	7	39	32
3	7	42	35
4	7	38	37
5	7	45	48
6	7	51	51
0	8	38	33
1	8	33	35
2	8	46	49
3	8	43	47
4	8	37	39
6	8	30	24
8	8	46	43
L= 3			
H	K	FO	FC
0	1	68	64
0	2	60	66
1	2	91	94
0	3	143	145
1	3	122	128
2	3	169	168
0	4	45	44
1	4	128	128
2	4	30	23
3	4	41	42
0	5	25	22
1	5	48	48
2	5	82	79
3	5	82	83
4	5	117	119
0	6	66	67
1	6	85	79
2	6	94	95
4	6	57	61
5	6	37	35
0	7	85	85
1	7	79	83
2	7	31	25
3	7	54	51
4	7	33	27
5	7	37	35
6	7	75	81
0	8	41	33
2	8	30	25
3	8	80	85
4	8	33	30
5	8	36	40
6	8	38	43
L= 4			
H	K	FO	FC
0	0	65	56
1	1	129	133
0	2	78	78
1	2	118	125
2	2	58	59
0	3	38	35
1	3	141	149
2	3	33	28
3	3	68	71
0	4	62	47
1	4	29	26
2	4	70	75
3	4	26	19
4	4	39	32
0	5	28	17
2	5	143	149
3	5	33	30
4	5	28	22
5	5	57	60
0	6	56	59
2	6	51	52
3	6	35	35
4	6	59	65
6	6	52	60
0	7	29	32
1	7	29	28
2	7	36	38
4	7	50	50
6	7	26	22
7	7	38	40
0	8	35	40
1	8	28	7
2	8	33	28
3	8	29	23
4	8	27	10
5	8	32	33
6	8	41	46
8	8	39	46
L= 5			
H	K	FO	FC
0	1	139	142
0	2	36	36
1	2	89	93
1	3	91	92
2	3	46	39
2	4	25	24
3	4	85	93
0	5	111	118
1	5	43	42
2	5	39	40
3	5	66	71
4	5	30	27
0	6	44	45
1	6	32	32
2	6	70	79
3	6	91	102
4	6	44	46
5	6	39	42
1	7	56	59
2	7	75	82
3	7	46	44
4	7	41	43
6	7	42	46
1	8	43	47
6	8	30	26
L= 6			
H	K	FO	FC
0	0	128	129
0	1	27	26
1	1	26	25
1	2	101	110
2	2	105	113
0	3	60	66
1	3	117	127
2	3	27	21
3	3	27	18
1	4	38	37
2	4	78	77
4	4	82	83
0	5	39	40
1	5	33	37
2	5	80	87
3	5	40	31
4	5	28	33
5	5	83	86
0	6	69	75
1	6	49	55
3	6	28	20
6	6	37	46
0	7	54	61
2	7	31	34
3	7	35	39
4	7	36	28
6	7	28	32
7	7	34	33
0	8	39	35
2	8	28	21
4	8	37	45
6	8	33	36
L= 7			
H	K	FO	FC
0	1	65	63
0	2	58	61
1	2	47	46
0	3	29	26
1	3	50	48
2	3	49	51
1	4	28	28
2	4	61	65
3	4	34	32
0	5	34	32
2	5	37	35
4	5	66	67
0	6	63	67
1	6	38	43
2	6	28	30
4	6	38	42
5	6	27	19
0	7	31	34
1	7	52	51
3	7	30	28
4	7	28	20
5	7	40	42
3	8	55	58
5	8	26	18
L= 8			
H	K	FO	FC
0	0	114	114
0	1	25	20
1	1	45	40
0	2	66	67
1	2	49	47
2	2	66	70
1	3	33	29
2	3	39	36
3	3	114	116
0	4	102	108
1	4	64	62
2	4	37	29
3	4	44	42
4	4	40	37
1	5	48	43
3	5	26	20
4	5	33	28
1	6	40	39
4	6	37	38
6	6	36	37
1	7	35	30
4	7	25	11
5	7	37	40
6	7	28	27
7	7	34	34
0	8	41	41
1	8	29	19
2	8	32	25
3	8	35	28
4	8	31	21
7	8	27	8
8	8	34	30
L= 9			
H	K	FO	FC
0	1	84	82
0	2	27	5
1	3	26	14
1	4	25	12
2	4	65	63
0	5	31	25
1	5	37	34
2	5	40	36
4	5	50	45
0	6	26	7
1	6	42	40
3	6	34	24
4	6	27	14
5	6	28	17
0	7	31	25
1	7	31	21
2	7	33	25
3	7	26	7
4	7	28	17
5	7	33	30
1	8	31	21
2	8	28	23
3	8	50	51
4	8	27	18
L=10			
H	K	FO	FC
0	0	112	110
1	1	39	35
1	2	41	37
2	2	30	22
0	3	33	30
1	3	44	39
2	3	28	22
3	3	25	15
1	4	42	36
2	4	37	30
3	4	35	25
4	4	40	38
0	5	29	8
2	5	34	9
3	5	37	32
5	5	39	32
0	6	43	37
1	6	31	27
2	6	36	28
4	6	28	17
0	7	30	26
3	7	42	37
4	7	31	7
5	7	32	7
7	7	27	4
0	8	29	1
1	8	29	18
3	8	29	15
4	8	31	21
5	8	30	3
6	8	30	15
7	8	32	5

was taken about the calculated position for each reflection and stationary background counts of 10 seconds were taken at the beginning (bgd1) and at the end (bgd2) of the scan. Calibrated copper attenuators were used in the collection of data; the threshold point was set so that the counting rate would not exceed 10^4 counts/second. The pulse height analyzer was set for approximately a 90% window, centered on the MoKα peak. A total of 483 reflections were collected. Corrected intensities (I) were obtained by subtracting six times the total measured background from the total integrated peak count (CT),

$$I = CT-0.5(t_c/t_b)(bgd1+bgd2)$$

where t_c is the scan time and t_b is the counting time of each background (either bgd1 or bgd2). The corrected intensities were assigned standard deviations according to the formula[10]

$$\sigma(I) = [CT+0.25(t_c/t_b)^2(bgd1+bgd2)+(pI)^2]^{1/2}$$

A total of 340 reflections were accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.30 with $p = 0.02$. The intensities were corrected for Lorentz and polarization effects; since the linear absorption coefficient, μ, was 218 cm^{-1}, it was necessary to correct for absorption. Absorption corrections were obtained by assuming that the crystal was a sphere of radius 0.15 mm.

Structure Analysis. The oxygen, copper, and bromine atoms were located from a three-dimensional Patterson synthesis; the oxygen atoms were placed in the 2a set (site symmetry, $\bar{4}$), the copper atoms were placed in an 8e set, and the bromine atoms were placed in 4c and 8e sets. Three cycles of full-matrix least-squares refinement resulted in a conventional R_1 value $(\Sigma||F_o|-|F_c||/\Sigma|F_o|)$ of 0.15. From an electron density map phased on these atoms, the nitrogen atom was located; after two more cycles of least-squares refinement varying the scale factor, atomic coordinates not defined by symmetry, and individual isotropic temperature factors, and with all of the reflections weighted at unity, the conventional R_1 value dropped to 0.13. At this point, the scattering factor of bromine was corrected for the real and imaginary components of anomalous dispersion; after further refinement with anisotropic temperature factors and a weighting scheme based on counting statistics ($w = 4(I)/\sigma^2(I)$) values of 0.108 and 0.088 were obtained for R_1 and R_2 ($R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$). A final difference Fourier showed some intensity in the regions of the hydrogen atoms but these positions were not included in the refinement; the peaks were in the range of 0.9 to 1.1 electrons in height. Final structure parameters are given in Table I; observed and calculated structure factors are given in Table II.

Computations were carried out on the Burroughs 5500 computer and on the Univac 1108 computer; programs employed included modified versions of Zalkin's FORDAP Fourier summation program, the

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[10] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

Busing-Martin-Levy ORFLS and ARFFE least-squares and function and error programs, and various locally written programs. In structure factor calculations, the scattering factors tabulated by Ibers[11] were employed for all atoms.

Discussion

A perspective drawing of the structure is shown in Figure 1 and selected bond distances and bond angles are given in Table III. As expected, the structure is basically the same as that found for other μ_4-oxo type complexes; a comparison of these structures is given in Table IV.

Table III. Interatomic distances and angles for $Cu_4OBr_6(NH_3)_4$

Atoms	Distance, Å	Atoms	Angle, °
Cu—O	1.915(5)	Cu—O—Cu	108.7(3)
Cu—Cu	3.113(10)		109.9(1)
	3.135(8)	O—Cu—N	179.8(11)
Cu—N	1.98(3)	O—Cu—Br	86.9(2)
Cu—Br	2.485(6)	O—Cu—Br′	87.2(2)
Cu—Br′	2.570(7)		87.5(2)
	2.557(6)	Br—Cu—Br′	118.8(2)
			121.2(2)
		Br′—Cu—Br′	119.3(2)
		N—Cu—Br	92.9(11)
		N—Cu—Br′	93.0(10)
			92.5(11)
		Cu—Br—Cu	77.6(3)
		Cu—Br′—Cu	75.4(3)

Table IV. Comparison of Interatomic distances and angles for $M_4OX_6L_4$ Structures

Complex	Site Symmetry	M—M, Å	M—O, Å	M—L, Å	M—X, Å	M—O—M, °	X—M—X, °	O—M—X, °	M—X—M, °	O—M—L, °
$Cu_4OCl_6(TPPO)_4$	$\bar{4}3$ m	3.11	1.91	1.89	2.38	109.5	119.0	84.4	81.6	180.0
$Cu_4OCl_{10}^{4-}$	23	3.18	1.95	2.17	2.43	109.5	119.1	84.5	81.5	180.0
$Cu_4OCl_{10}^{4-}$	$\bar{4}$	3.14	1.92	2.25	2.41	109.4	119.1	84.6	81.3	177.0
$Cu_4OCl_6(Pyr)_4$	1	3.11	1.90	1.96	2.41	109.5	119.2	84.8	80.2	177.3
$Cu_4OBr_6(NH_3)_4$	$\bar{4}$	3.12	1.92	1.98	2.54	109.3	119.7	87.2	76.5	179.8
$Mg_4OBr_6(Et_2O)_4$	$\bar{4}$	3.20	1.95	2.11	2.60	109.7	119.3	87.5	75.6	179.8

It is interesting that $Cu_4OBr_6(NH_3)_4$ and $Mg_4OBr_6(Et_2O)_4$ crystallize in the same space group and the molecules of both compounds occupy the same sites within the unit cell (sites of $\bar{4}$ symmetry). It is also interesting that the corresponding bond distances and bond angles for the two structures are almost the same in spite of the fact that comparison of the radii of copper and magnesium indicate that magnesium has a radius approximately 0.3 Å larger than that of copper. Another indication that the magnesium radius is greater than that indicated in tables was found in the « cubane-type » compounds, $[M(Acac)(CH_3O)(CH_3OH)]_4$, where crystals with M = Mg, Co, and Ni were found to be isomorphous with almost identical unit cell parameters.

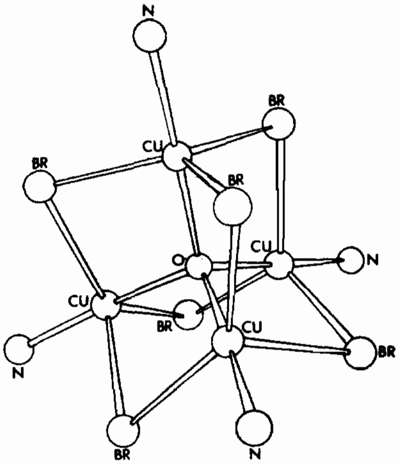

Figure 1. A perspective drawing of the structure of $Cu_4OBr_6(NH_3)_4$

It is also interesting to compare $Cu_4OBr_6(NH_3)_4$ with other μ_4-oxo copper complexes. The central Cu_4O unit in this structure is identical to that found in previous structures with Cu—Cu distances of 3.11(1) and 3.14(1) Å, a Cu—O distance of 1.915(5) Å, and Cu—O—Cu angles of 108.7(3)° and 109.9(1)°. Comparison of molecular site symmetries in the various structures indicates two of higher symmetry ($Cu_4OCl_6(TPPO)_4$ ($\bar{4}3$ m) and the origin $Cu_4OCl_{10}^{4-}$ anion (23)), one of the same symmetry (non-origin $Cu_4OCl_{10}^{4-}$ anion ($\bar{4}$)), and one with lower symmetry ($Cu_4OCl_6(Pyr)_4$) than the present compound. The two of higher symmetry are undistorted, $Cu_4OBr_6(NH_3)_4$ and the non-origin $Cu_4OCl_{10}^{4-}$ anion show similar small distortions of the halide octahedron, and $Cu_4OCl_6(Pyr)_4$ shows significant distortion of the halide octahedron.

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(11) J. A. Ibers in « International Tables for X-ray Crystallography », Vol. 3, The Kynoch Press, Birmingham, England, 1962.