Inorg. Chem. **1982**, *21*, 1881-1886 **1881**

Contribution from the Departments of Chemistry, Purdue University, West Lafayette, Indiana 49707,
and The Polytechnic of North London, Holloway N7 8DB, England

Crystal and Molecular Structures of Bis(4,4′,6,6′-tetramethyl-2,2′-bipyridyl)copper(I) Perchlorate, Bis(4,4′,6,6′-tetramethyl-2,2′-bipyridyl)copper(II) Diperchlorate, and Bis(4,4′,6,6′-tetramethyl-2,2′-bipyridyl)copper(II) Diperchlorate Dihydrate. A Search for Copper(II) and Copper(I) Complexes with a Common Ligand Environment

PHILIP J. BURKE,[1a] KIM HENRICK,*[1b] and DAVID R. McMILLIN*[1a]

Received July 30, 1981

The crystal structures of the title compounds have been determined from diffractometer data and refined with use of the least-squares method. Crystal data for $CuC_{28}H_{32}N_4O_4Cl$ are space group *Pbcn*, $Z = 4$, $a = 16.507$ (3) Å, $b = 13.628$ (2) Å, $c = 12.284$ (2) Å, $V = 2763.4$ Å^3, and $R = 0.093$ for 1593 reflections. The perchlorate anions are uncoordinated, and the copper(I) environment (CuN_4) is pseudotetrahedral with a dihedral angle of 68° between the symmetry-related halves of the molecule. Crystal data for $CuC_{28}H_{32}N_4O_8Cl_2$ are space group $P2_1/c$, $Z = 4$, $a = 17.775$ (2) Å, $b = 12.785$ (3) Å, $c = 14.514$ (2) Å, $\beta = 110.51$ (3)°, $V = 3089.2$ Å^3, and $R = 0.048$ for 2084 reflections. The copper atom is five-coordinate, and the stereochemistry of the complex is distorted trigonal bipyramidal with a perchlorate anion bound at an equatorial position. Crystal data for $CuC_{28}H_{36}N_4O_8Cl_2$ are space group $P2_1/c$, $Z = 8$, $a = 14.594$ (2) Å, $b = 16.192$ (3) Å, $c = 28.934$ (2) Å, $\beta = 103.50$ (4)°, $V = 6648.4$ Å^3, and $R = 0.113$ for 3921 reflections. In this structure the perchlorate anions are uncoordinated and a water molecule is bound at one of the equatorial positions of a distorted trigonal bipyramid about copper. Previous studies of bis(4,4′,6,6′-tetramethyl-2,2′-bipyridyl)copper(II) diperchlorate have been interpreted in terms of a distorted-tetrahedral geometry about copper. An analogous species has been suggested to be the reactive form in an electron-transfer reaction involving ferrocyanide and a corresponding phenanthroline complex of copper(II). The present work suggests that a five-coordinate form is likely to be the dominant species in solution for complexes with these types of ligands.

Introduction

Due to recent structural findings in copper-containing proteins there is increasing interest in copper complexes involving sterically active ligands. In the two "blue-copper" proteins plastocyanin and azurin copper is bound at sites described as distorted tetrahedral.[2,3] In superoxide dismutase four imidazole ligands are disposed in a pseudotetrahedral fashion about copper,[4] although water may also bind as a fifth ligand.[5] Since a tetrahedral coordination geometry is better suited for copper(I), the proteins may regulate the electrode potential by controlling the ligand environment about copper. The kinetics of electron transfer are perhaps also facilitated by restricting the geometry changes that occur with changes in oxidation state.[2,6-10] In principle, small-molecule studies can help establish the significance of the latter effect if ligands that give similar coordination environments for copper(II) and copper(I) can be found.

Complexes of the type $M(bpy)_2{}^{n+}$ (bpy = 2,2′-bipyridine) are constrained to be nonplanar due to steric interactions among hydrogen atoms bound to carbons α to the ring nitrogens.[11] This effect should be enhanced when the hydrogens at the 6- and 6′-positions are replaced with bulkier groups.[12] The ligand tmbp (tmbp = 4,4′,6,6′-tetramethyl-2,2′-bipyridine) is of interest since it reacts with copper(II) to give a light brown solid that analyzes as $Cu(tmbp)_2(ClO_4)_2$ and that has been suggested to involve pseudotetrahedral coordination about copper(II).[13] (The corresponding dihydrate is green and has been considered to involve a different stereochemistry.) In studies of a related phenanthroline complex a pseudotetrahedral form has been suggested to be the reactive species in electron-transfer reactions with ferrocyanide.[10] In order to examine the structural features of copper complexes with this class of ligand, we have solved the crystal structures of $Cu(tmbp)_2ClO_4$, $Cu(tmbp)_2(ClO_4)_2$, and $Cu(tmbp)_2(ClO_4)_2 \cdot 2H_2O$.

A further impetus for this work stems from our interest in the photochemical and photophysical properties of the copper(I) systems.[14,15] In particular, novel quenching of low-lying metal-to-ligand charge-transfer excited states has been observed in donor solvents, and these reactions could be associated with changes in the coordination sphere about the metal center, formally copper(II) in the excited state.[14]

Experimental Section

General Considerations. The ligand tmbp was prepared according to the published procedure.[16] The anhydrous copper(II) complex, $Cu(tmbp)_2(ClO_4)_2$, was prepared according to the reported method.[13] Crystallization of the compound from boiling ethanol solution gave crystals suitable for diffraction studies. Crystals of $Cu(tmbp)_2(ClO_4)_2 \cdot 2H_2O$ were obtained by dissolving $Cu(tmbp)_2(ClO_4)_2$ in aqueous acetonitrile (50%) and allowing the solvent to evaporate slowly. The copper(I) complex, $Cu(tmbp)_2ClO_4$, was prepared by reduction of $Cu(tmbp)_2(ClO_4)_2$ with ascorbate in aqueous acetone solution. Suitable crystals were obtained by slow evaporation of a nitromethane solution of the complex.

Crystallographic Data. Cell parameters for each sample were refined by least-squares analysis of θ values measured for 25 reflections on a Philips PW1100 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). A θ–2θ scan mode was used for

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0020-1669/82/1321-1881$01.25/0

Table I. Summary of Crystal Data and Intensity Collection

	$Cu(tmbp)_2ClO_4$	$Cu(tmbp)_2(ClO_4)_2$	$Cu(tmbp)_2(ClO_4)_2\cdot 2H_2O$
fw	587.3	658.6	694.7
formula	$CuC_{28}H_{32}N_4O_4Cl$	$CuC_{28}H_{32}N_4O_8Cl_2$	$CuC_{28}H_{36}N_4O_8Cl_2$
space group	*Pbcn*	$P2_1/c$	$P2_1/c$
a, Å	16.507 (3)	17.775 (2)	14.594 (2)
b, Å	13.628 (2)	12.785 (3)	16.192 (3)
c, Å	12.284 (2)	14.514 (2)	28.934 (2)
β, deg		110.51 (3)	103.50 (4)
V, Å^3	2763.4	3089.2	6648.4
Z	4	4	8
F(000)	1224	1402	3000
cryst dimens, mm	0.15 × 0.10 × 0.12	0.18 × 0.12 × 0.06	0.15 × 0.13 × 0.09
μ, cm^{-1} (Mo Kα)	8.8	8.4	8.3
final no. of variables	215	371	373
unique data set used, $I > 3[\sigma(I)]$	1593	2084	3921

Table II. Atomic Fractional Cell Coordinates (×10^4) for $Cu(tmbp)_2ClO_4$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu	5000	1290 (2)	2500	C(109)	3383 (9)	−854 (10)	4062 (13)
N(11)	4053 (6)	2024 (7)	1816 (10)	C(110)	4071 (8)	−372 (10)	3745 (13)
N(12)	4047 (6)	476 (8)	3135 (9)	C(111)	4912 (9)	3239 (11)	941 (14)
C(101)	4089 (8)	2857 (9)	1245 (12)	C(112)	1855 (8)	3544 (11)	914 (14)
C(102)	3393 (8)	3356 (10)	887 (14)	C(113)	1867 (10)	−1013 (15)	4166 (18)
C(103)	2620 (8)	3025 (10)	1186 (12)	C(114)	4909 (11)	−764 (12)	4036 (14)
C(104)	2604 (7)	2188 (9)	1822 (11)	Cl	0	1438 (3)	2500
C(105)	3307 (7)	1690 (8)	2139 (11)	O(11)	530 (13)	2031 (3)	3098 (21)
C(106)	3306 (6)	794 (10)	2834 (10)	O(12)	445 (16)	845 (3)	1787 (18)
C(107)	2586 (8)	343 (9)	3115 (12)	O(21)	384 (23)	2031 (3)	1726 (20)
C(108)	2639 (9)	−511 (11)	3747 (12)	O(22)	576 (15)	845 (3)	3016 (31)

data collection, and reflections with 3.0° < θ < 25.0° were examined. Three standard reflections were measured every 2 h during data collection and showed no significant variation in intensities. See Table I for crystal information. For $Cu(tmbp)_2(ClO_4)_2$ and $Cu(tmbp)_2(ClO_4)_2\cdot 2H_2O$ the systematically absent reflections were those uniquely requiring the centrosymmetric space group $P2_1/c$. For $Cu(tmbp)_2ClO_4$ the systematic absences indicated the centrosymmetric space group *Pbcn*. Reflections in one quadrant (±*hkl*) were measured after preliminary screening for $Cu(tmbp)_2(ClO_4)_2\cdot 2H_2O$ (4512 reflections) and $Cu(tmbp)_2(ClO_4)_2$ (2206 reflections); for $Cu(tmbp)_2ClO_4$ 1753 reflections were measured in one octant. No absorption corrections were made. Lorentz and polarization factors were applied, and reflections for which $I < 3[\sigma(I)]$ were rejected. Equivalents were averaged to give 1593, 3921, and 2084 reflections for $Cu(tmbp)_2ClO_4$, $Cu(tmbp)_2(ClO_4)_2\cdot 2H_2O$, and $Cu(tmbp)_2(ClO_4)_2$, respectively.

The structure of $Cu(tmbp)_2(ClO_4)_2\cdot 2H_2O$ was solved by tangent multisolution refinement with the SHELX programs.[17] Due to the pseudosymmetry for this crystal, where the *hkl* reflections with $h + k = 2n + 1$ were weak, the solution required the starting set of phases to be selected with $h + k = 2n + 1$. With use of *E* values >1.55, the fourth *E* map (R_α[18] = 0.029) revealed the positions of 20 of the nonhydrogen atoms with the two molecules per equivalent position related by, approximately, x, y, z and $x - {}^1/_2, y - {}^1/_2, z$. In retrospect one of the possible Patterson solutions for the two Cu atoms was equivalent to the solution obtained by direct methods; however, no recognizable fragments could be found from trial Fourier syntheses on the basis of these two positions. The remaining nonhydrogen atoms were located from successive difference Fourier maps. The four perchlorate groups were all found to be disordered, eight oxygen positions were located around each chlorine atom and were included in the refinement with a common isotropic temperature factor, and each set of four oxygen atoms refined to a population of 0.631 (5) and 0.369 (5). The hydrogen atom positions were not located for this compound. Each of the molecules of noncoordinating H_2O were found to be disordered between two sites and were refined with a common isotropic temperature factor and a common site occupation factor.

The structure of $Cu(tmbp)_2(ClO_4)_2$ was solved by the heavy-atom method and refined by full-matrix least squares. Hydrogen atom positions for $Cu(tmbp)_2(ClO_4)_2$ were evident from difference syntheses but were included in the refinement at geometrically estimated positions with C–H = 1.08 Å assumed. The spectroscopically determined C–H bond distance of 1.08 Å was used to obtain realistic and consistent contact distances. The structure of $Cu(tmbp)_2ClO_4$ was solved by the heavy-atom method with Cu and Cl atoms at special positions. The perchlorate group was found to be disordered across the glide plane, and two positions for each of the independent oxygen atoms were located. For refinement the perchlorate group was treated as two rigid bodies (Cl–O = 1.399 Å and O–Cl–O = 109.4°) with equal populations. Most of the hydrogen atom positions were located; however, these were included in the refinement at geometrically estimated positions. For the final stages of refinement the Cu, Cl, N and O(1), O(2) atoms in $Cu(tmbp)_2(ClO_4)_2\cdot 2H_2O$ were made anisotropic, and for $Cu(tmbp)_2(ClO_4)_2$ all of the nonhydrogen atoms were given anisotropic thermal parameters. In the case of $Cu(tmbp)_2ClO_4$, the Cu, C, N, and Cl atoms were made anisotropic. Positional coordinates for the independent nonhydrogen atoms are given in Tables II–IV. In the final cycle of refinement, *R* for $Cu(tmbp)_2(ClO_4)_2\cdot 2H_2O$ was 0.113 and R' = 0.121, for $Cu(tmbp)_2(ClO_4)_2$, R = 0.048 and R' = 0.041, and for $Cu(tmbp)_2ClO_4$, R = 0.093 and R' = 0.091 [$R' = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$, where $w = (\sigma^2(F_o)^{-1})$]. Neutral-atom scattering factors were used[19] and were corrected for anomalous dispersion effects.[20] A listing of the observed and calculated structure amplitudes for the data used in the refinements is available.[21]

Results and Discussion

The molecular structures of $Cu(tmbp)_2ClO_4$, $Cu(tmbp)_2(ClO_4)_2$, and $Cu(tmbp)_2(ClO_4)_2\cdot 2H_2O$ have been determined crystallographically. Distances and angles pertaining to the coordination group of each structure are given in Tables V and VI. Interatomic bond distances and angles for the tmbp ligands (Tables VII and VIII), selected least-squares planes (Tables IX–XI), molecular dimensions for the perchlorate groups (Table XII), contact distances (Table XIII), calculated positional coordinates for hydrogen atoms (Tables XIV and XV), and thermal parameters (Tables XVI–XVIII) are available as supplementary material.[21]

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(21) See supplementary material paragraph.

Table III. Atomic Fractional Cell Coordinates ($\times 10^4$) for $Cu(tmbp)_2(ClO_4)_2$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu	7192 (1)	3114 (1)	2063 (1)	C(204)	6339 (4)	4926 (6)	−486 (5)
N(11)	8066 (3)	3539 (5)	3283 (4)	C(205)	6481 (4)	4200 (6)	259 (5)
N(12)	7791 (3)	1712 (5)	2343 (4)	C(206)	5855 (4)	3471 (5)	356 (5)
C(101)	8186 (5)	4493 (6)	3702 (6)	C(207)	5100 (4)	3433 (6)	−340 (5)
C(102)	8725 (4)	4627 (6)	4658 (6)	C(208)	4558 (4)	2699 (7)	−245 (6)
C(103)	9158 (4)	3790 (7)	5184 (6)	C(209)	4800 (4)	2050 (6)	569 (6)
C(104)	9015 (4)	2816 (6)	4741 (5)	C(210)	5578 (5)	2129 (6)	1255 (6)
C(105)	8480 (4)	2705 (6)	3797 (5)	C(211)	8692 (4)	4335 (6)	1550 (6)
C(106)	8339 (4)	1690 (6)	3277 (5)	C(212)	6842 (5)	6357 (7)	−1334 (6)
C(107)	8768 (4)	810 (6)	3656 (5)	C(213)	3711 (4)	2619 (8)	−1015 (6)
C(108)	8650 (4)	−115 (6)	3098 (6)	C(214)	5838 (5)	1400 (7)	2137 (6)
C(109)	8118 (4)	−61 (6)	2137 (6)	Cl(1)	5769 (1)	4240 (2)	3015 (2)
C(110)	7700 (4)	865 (6)	1773 (5)	O(11)	6475 (3)	3589 (4)	3203 (4)
C(111)	7731 (5)	5406 (6)	3128 (6)	O(12)	5894 (5)	4905 (8)	3778 (5)
C(112)	9756 (5)	3926 (7)	6229 (6)	O(13)	5099 (5)	3610 (9)	2908 (8)
C(113)	9125 (5)	−1095 (6)	3514 (6)	O(14)	5601 (4)	4752 (6)	2126 (4)
C(114)	7144 (5)	918 (7)	711 (5)	Cl(2)	854 (2)	2507 (2)	3894 (2)
N(21)	7228 (3)	4046 (4)	939 (4)	O(21)	462 (3)	1567 (5)	3966 (5)
N(22)	6109 (3)	2823 (4)	1136 (4)	O(22)	1297 (6)	2829 (5)	4841 (6)
C(201)	7860 (4)	4581 (6)	846 (5)	O(23)	301 (4)	3297 (5)	3392 (5)
C(202)	7739 (4)	5310 (6)	108 (5)	O(24)	1383 (4)	2273 (6)	3380 (6)
C(203)	6969 (4)	5518 (6)	−560 (5)				

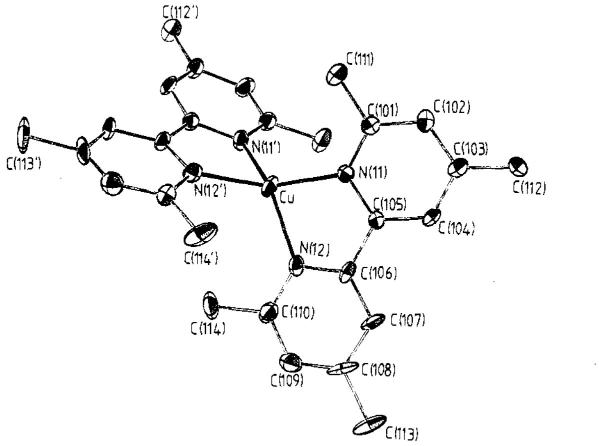

Figure 1. ORTEP drawing of $[Cu(tmbp)_2]^+$. The numbering of the annular carbons increases consecutively about the ligand.

Structure of $Cu(tmbp)_2ClO_4$. The structure consists of discrete $[Cu(tmbp)_2]^+$ cations and uncoordinated perchlorate anions. A view of the centrosymmetric cation, illustrating the atom-numbering scheme, is shown in Figure 1. Each bidentate tmbp ligand coordinates via the pyridine nitrogen atoms to provide a distorted-tetrahedral environment about the copper atom. The extent of distortion is illustrated by the dihedral angle of 68° between the symmetry-related ligands. This value is significantly smaller than that found previously[12] (80.9°) for the related 6,6′-dimethyl-2,2′-bipyridine complex $Cu(dmbp)_2BF_4$.

The Cu–N distances are unequal and, on average, are slightly longer than the corresponding distances within $Cu(dmbp)_2BF_4$.[12] The pyridine rings of each ligand are reasonably planar but are twisted by 5° about the 2,2′-carbon bond. The authors are unaware of any previous structural studies involving the tmbp ligand, but for comparison's sake, it may be noted that the bond angles and distances within tmbp are similar to those reported for dmbp.[12]

Structure of $Cu(tmbp)_2(ClO_4)_2$. The structure consists of uncoordinated perchlorate anions and discrete $[Cu(tmbp)_2ClO_4]^+$ cations in which the copper atom is coordinated by two bidentate tmbp ligands and a perchlorate oxygen atom. A view of the cation, showing the atom-numbering scheme, is given in Figure 2. The stereochemistry of the cation is best described as a distorted trigonal bipyramid with the atoms N(12), N(21), and O(11) occupying the equatorial coordination sites. The three bond angles in the equatorial plane (120.6, 115.6, and 123.8°) are reasonably close to the value of 120° expected for regular trigonal geometry, but the slightly bent N(11)–Cu–N(22) angle of 160.2° indicates some distortion of the molecule toward a square-pyramidal geometry.[22] The structure may be contrasted with that of $Cu(bpy)_2(ClO_4)_2$, which consists[23] of flattened tetrahedral $Cu(bpy)_2^{2+}$ units axially coordinated by perchlorate oxygen atoms at distances of 2.45 and 2.73 Å. The adoption of a similar geometry by $Cu(tmbp)_2(ClO_4)_2$ is presumably prevented by steric interactions between the methyl groups located at the 6,6′-positions.

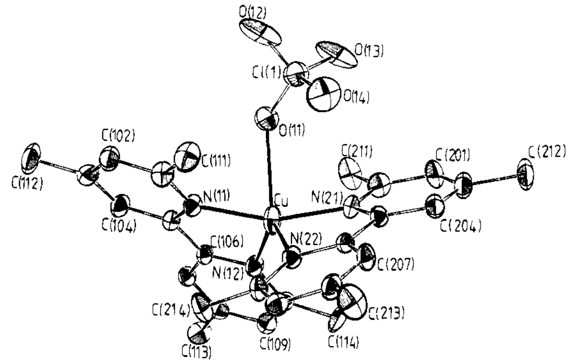

Figure 2. ORTEP drawing of $[Cu(tmbp)_2ClO_4]^+$. The annular carbons are numbered in a consecutive fashion about each ligand.

The Cu–N distances for a given tmbp ligand are not equal, and as noted previously,[12,24] the differences appear to be associated with the degree of twist of the pyridine rings about the 2,2′-carbon bond. Thus, although individual pyridine rings are reasonably planar, the ligands defined by N(11)N(12) and N(21)N(22) are nonplanar with angles of 8 and 10°, respectively, between the pyridine rings. These values are within the range 0.1–11° previously reported for a number of $Cu(bpy)_2^{2+}$ complexes.[25]

The Cu–O distance of 2.491 Å is representative of coordinated perchlorate being slightly less than the range (2.52–2.88 Å) reported for a number of copper(II) complexes with coordinated perchlorate groups.[26] In accord with previous

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Table IV. Atomic Fractional Cell Coordinates (×10^4) for $\mathrm{Cu(tmbp)_2(ClO_4)_2\cdot 2H_2O}$

atom	x	y	z	atom	x	y	z
			Molecule 1				
Cu(1)	−2998 (2)	4757 (1)	3860 (1)	N(22)	−3735 (13)	3751 (8)	3909 (6)
N(11)	−2227 (12)	5766 (10)	3940 (6)	C(201)	−1826 (15)	4060 (12)	3124 (8)
N(12)	−3966 (12)	5559 (9)	3425 (7)	C(202)	−1464 (18)	3362 (16)	2933 (9)
C(101)	−1283 (17)	5860 (14)	4175 (8)	C(203)	−1708 (15)	2572 (13)	3022 (8)
C(102)	−834 (16)	6582 (13)	4271 (8)	C(204)	−2404 (14)	2446 (11)	3267 (7)
C(103)	−1364 (16)	7286 (13)	4125 (8)	C(205)	−2740 (15)	3143 (13)	3469 (8)
C(104)	−2340 (15)	7242 (12)	3889 (7)	C(206)	−3428 (15)	3053 (13)	3754 (8)
C(105)	−2701 (13)	6477 (11)	3812 (7)	C(207)	−3825 (16)	2259 (13)	3796 (8)
C(106)	−3667 (14)	6374 (12)	3524 (7)	C(208)	−4541 (15)	2244 (13)	4048 (8)
C(107)	−4266 (14)	7028 (12)	3368 (7)	C(209)	−4884 (18)	2976 (16)	4240 (9)
C(108)	−5173 (17)	6854 (14)	3088 (8)	C(210)	−4444 (17)	3706 (15)	4137 (9)
C(109)	−5472 (17)	6068 (15)	2957 (9)	C(211)	−1568 (16)	4970 (14)	3033 (9)
C(110)	−4820 (17)	5443 (14)	3130 (9)	C(212)	−1306 (20)	1838 (17)	2764 (10)
C(111)	−751 (21)	5062 (17)	4339 (11)	C(213)	−4931 (19)	1431 (16)	4214 (10)
C(112)	−919 (20)	8201 (17)	4224 (10)	C(214)	−4842 (20)	4503 (17)	4313 (10)
C(113)	−5872 (20)	7593 (17)	2904 (10)	O(1)	−2556 (18)	4575 (11)	4564 (7)
C(114)	−5122 (16)	4530 (13)	2979 (8)	O(1a)	1901 (25)	4519 (19)	4723 (12)
N(21)	−2444 (13)	3902 (9)	3395 (6)	O(1b)	2768 (34)	4411 (27)	4760 (16)
			Molecule 2				
Cu(2)	2050 (2)	−225 (2)	3853 (1)	N(42)	1263 (12)	787 (10)	3909 (6)
N(31)	2811 (12)	−1263 (9)	3893 (6)	C(401)	3184 (16)	537 (14)	3130 (8)
N(32)	1065 (11)	−1025 (9)	3393 (6)	C(402)	3573 (15)	1164 (13)	2900 (8)
C(301)	3761 (17)	−1325 (14)	4111 (8)	C(403)	3344 (16)	1949 (14)	2998 (8)
C(302)	4123 (18)	−2096 (16)	4207 (9)	C(404)	2716 (16)	2081 (14)	3295 (8)
C(303)	3607 (16)	−2794 (13)	4101 (8)	C(405)	2349 (13)	1405 (11)	3489 (6)
C(304)	2700 (16)	−2746 (13)	3838 (8)	C(406)	1575 (13)	1470 (11)	3747 (7)
C(305)	2311 (14)	−1945 (12)	3749 (7)	C(407)	1202 (14)	2241 (11)	3846 (7)
C(306)	1324 (13)	−1798 (11)	3490 (6)	C(408)	483 (15)	2284 (13)	4050 (8)
C(307)	723 (15)	−2457 (12)	3328 (7)	C(409)	168 (16)	1515 (14)	4199 (8)
C(308)	−180 (16)	−2291 (13)	3040 (8)	C(410)	580 (16)	808 (14)	4135 (8)
C(309)	−408 (14)	−1474 (13)	2944 (7)	C(411)	3467 (17)	−389 (14)	3019 (9)
C(310)	252 (15)	−849 (12)	3116 (7)	C(412)	3657 (18)	2700 (15)	2774 (9)
C(311)	4298 (16)	−538 (13)	4271 (8)	C(413)	119 (16)	3117 (14)	4152 (8)
C(312)	4123 (18)	−3656 (15)	4237 (9)	C(414)	297 (18)	−2 (15)	4328 (9)
C(313)	−800 (17)	−3028 (14)	2877 (9)	O(2)	2508 (17)	−181 (11)	4597 (6)
C(314)	−78 (20)	36 (16)	2986 (10)	O(2a)	2286 (32)	4471 (29)	327 (16)
N(41)	2592 (11)	622 (9)	3414 (5)	O(2b)	2657 (32)	5337 (27)	377 (16)
			Perchlorate Groups				
Cl(1)	1695 (9)	4809 (6)	3392 (4)	Cl(3)	3119 (7)	2407 (11)	4986 (4)
O(11)	894 (37)	4319 (36)	3213 (21)	O(31)	3516 (22)	2503 (20)	5427 (22)
O(12)	1905 (41)	5002 (32)	3883 (24)	O(32)	2139 (39)	2204 (29)	4984 (19)
O(13)	1420 (43)	5548 (43)	3247 (25)	O(33)	3463 (24)	3029 (27)	4840 (24)
O(14)	2537 (39)	4335 (34)	3357 (19)	O(34)	3380 (27)	1842 (32)	4637 (21)
O(15)	1775 (27)	5338 (40)	2964 (19)	O(35)	3649 (23)	3282 (27)	5206 (26)
O(16)	1440 (22)	4001 (21)	3147 (18)	O(36)	3014 (24)	2613 (30)	4403 (24)
O(17)	2446 (29)	5374 (28)	3291 (22)	O(37)	2165 (25)	2709 (25)	4997 (28)
O(18)	2353 (30)	4427 (23)	3803 (23)	O(38)	3362 (26)	1581 (23)	5368 (29)
Cl(2)	6786 (10)	−229 (7)	3371 (4)	Cl(4)	8088 (7)	2419 (6)	4993 (3)
O(21)	6261 (19)	−758 (19)	3541 (22)	O(41)	8637 (20)	2277 (23)	5408 (21)
O(22)	7137 (20)	−552 (24)	2999 (21)	O(42)	7243 (27)	1869 (23)	4955 (17)
O(23)	7497 (25)	178 (23)	3691 (24)	O(43)	8361 (21)	2398 (24)	4569 (28)
O(24)	6207 (22)	426 (26)	3156 (25)	O(44)	7546 (28)	3106 (23)	4994 (20)
O(25)	7217 (25)	305 (24)	3156 (21)	O(45)	7208 (31)	2552 (23)	4973 (22)
O(26)	5864 (24)	306 (21)	3199 (26)	O(46)	8274 (29)	3105 (23)	4677 (24)
O(27)	6590 (31)	−1019 (22)	3134 (20)	O(47)	8120 (24)	1927 (23)	4546 (22)
O(28)	6566 (30)	−85 (24)	3818 (26)	O(48)	8770 (28)	1801 (24)	5246 (26)

Table V. Molecular Dimensions in the Coordination Group for $\mathrm{Cu(tmbp)_2ClO_4}$

(a) Distances (Å)

Cu-N(11)	2.037 (10)	Cu-N(12)	2.076 (10)

(b) Angles (Deg)

N(11)-Cu-N(12)	80.6 (4)	N(12)-Cu-N(11)′	133.5 (4)
N(11)-Cu-N(11)′	121.2 (4)	N(12)-Cu-N(12)′	115.4 (4)
[N(11)-Cu-N(12)′	133.5 (4)]	[N(11)′-Cu-N(12)′	80.6 (4)]

(c) Polyhedral Edge Lengths (Å)

N(11)···N(12)	2.66	N(12)···N(11)′	3.78
N(11)···N(11)′	3.55		

observations the Cl–O(11) distance is significantly larger than those of the remaining Cl–O bonds in the coordinated perchlorate group.[27]

Structure of $\mathrm{Cu(tmbp)_2(ClO_4)_2\cdot 2H_2O}$. The structure consists of discrete $[\mathrm{Cu(tmbp)_2OH_2}]^{2+}$ cations together with two uncoordinated perchlorate anions and an uncoordinated water molecule, the copper being five-coordinate. Due to pseudosymmetry in the crystal two forms of the cation are present (molecules 1 and 2). A view of molecule 1, showing the atom-numbering scheme, is given in Figure 3.

The stereochemistry of molecule 1 may best be described as a distorted trigonal bipyramid. The reasonably linear N(11)–Cu(1)–N(22) angle of 170° is consistent with this geometry, but distortion toward square-pyramidal geometry is evidenced by the fairly large deviations from 120° of the N(12)–Cu(1)–N(21) and N(12)–Cu(1)–O(1) bond angles,

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[27] Butcher, R. J.; O'Connor, C. J.; Sinn, E. *Inorg. Chem.* **1981**, *20*, 537.

Table VI. Molecular Dimensions in the Coordination Groups of $Cu(tmbp)_2(ClO_4)_2$ and $Cu(tmbp)_2(ClO_4)_2 \cdot 2H_2O$

		$[Cu(tmbp)_2H_2O]^{2+}$			
$[Cu(tmbp)_2ClO_4]^+$		molecule 1		molecule 2	
		(a) Distances (Å)			
Cu-N(11)	1.979 (5)	Cu(1)-N(11)	1.968 (16)	Cu(2)-N(31)	2.003 (16)
Cu-N(12)	2.052 (6)	Cu(1)-N(12)	2.106 (16)	Cu(2)-N(32)	2.150 (15)
Cu-N(21)	2.040 (6)	Cu(1)-N(21)	2.211 (18)	Cu(2)-N(41)	2.142 (17)
Cu-N(22)	1.959 (5)	Cu(1)-N(22)	1.974 (16)	Cu(2)-N(42)	2.029 (17)
Cu-O(11)	2.491 (6)	Cu(1)-O(1)	2.004 (19)	Cu(2)-O(2)	2.100 (18)
		(b) Angles (Deg)			
N(11)-Cu-N(12)	82.6 (2)	N(11)-Cu(1)-N(12)	81 (1)	N(31)-Cu(2)-N(32)	79 (1)
N(11)-Cu-N(21)	108.7 (2)	N(11)-Cu(1)-N(21)	108 (1)	N(31)-Cu(2)-N(41)	107 (1)
N(11)-Cu-N(22)	160.2 (3)	N(11)-Cu(1)-N(22)	170 (1)	N(31)-Cu(2)-N(42)	172 (1)
N(11)-Cu-O(11)	76.3 (2)	N(11)-Cu(1)-O(1)	88 (1)	N(31)-Cu(2)-O(2)	86 (1)
N(12)-Cu-N(21)	120.6 (3)	N(12)-Cu(1)-N(21)	108 (1)	N(32)-Cu(2)-N(41)	108 (1)
N(12)-Cu-N(22)	106.7 (2)	N(12)-Cu(1)-N(22)	106 (1)	N(32)-Cu(2)-N(42)	103 (1)
N(12)-Cu-O(11)	115.6 (2)	N(12)-Cu(1)-O(1)	135 (1)	N(32)-Cu(2)-O(2)	131 (1)
N(21)-Cu-N(22)	82.0 (2)	N(21)-Cu(1)-N(22)	79 (1)	N(41)-Cu(2)-N(42)	80 (1)
N(21)-Cu-O(11)	123.8 (2)	N(21)-Cu(1)-O(1)	117 (1)	N(41)-Cu(2)-O(2)	121 (1)
N(22)-Cu-O(11)	84.0 (2)	N(22)-Cu(1)-O(1)	82 (1)	N(42)-Cu(2)-O(2)	87 (1)
		(c) Polyhedral Edge Lengths (Å)			
N(11)···N(12)	2.66	N(31)···N(32)	2.65	N(11)···N(12)	2.65
N(11)···N(21)	3.27	N(31)···N(41)	3.38	N(11)···N(21)	3.34
N(11)···O(1)	2.79	N(31)···O(2)	2.76	N(11)···O(11)	2.80
N(22)···N(12)	3.22	N(42)···N(32)	3.23	N(22)···N(12)	3.27
N(22)···N(21)	2.62	N(42)···N(41)	2.67	N(22)···N(21)	2.68
N(22)···O(1)	3.00	N(42)···O(2)	2.61	N(22)···O(11)	2.83
O(1)···N(12)	3.85	O(2)···N(32)	3.80	O(11)···N(12)	3.87
N(12)···N(21)	3.55	N(32)···N(41)	3.50	N(12)···N(21)	3.47
N(21)···O(1)	4.00	N(41)···O(2)	3.59	N(21)···O(11)	3.69

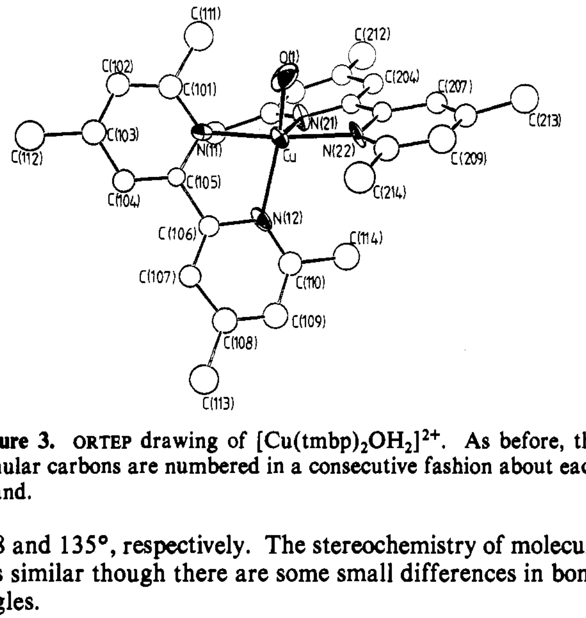

Figure 3. ORTEP drawing of $[Cu(tmbp)_2OH_2]^{2+}$. As before, the annular carbons are numbered in a consecutive fashion about each ligand.

108 and 135°, respectively. The stereochemistry of molecule 2 is similar though there are some small differences in bond angles.

As found previously, the tmbp ligands are nonplanar and are twisted about the 2,2′-carbon bond by 8 and 5° (ligands defined by N(11)N(12) and N(21)N(22), respectively) and by 7 and 10° (ligands defined by N(31)N(32) and N(41)N(42), respectively). In contrast to the case for the previous structure, there is a correlation in the opposite sense between the Cu–N distances for each ligand and the degree of twist about the 2,2′-carbon bond.

An interesting feature of this structure is the presence of coordinated water. The diaquo cation $[Cu(bpy)_2(H_2O)_2]^{2+}$ is said to exist in aqueous solution[28] and is believed to have a cis configuration.[29] However, to our knowledge only one bis(2,2′-bipyridyl)copper(II) complex has been found to contain a coordinated water molecule in the crystal.[25]

Conclusions

Bis(bipyridine) complexes with bulky substituents in the 6- and 6′-positions have appeared to offer some promise for giving pseudotetrahedral complexes of both copper(I) and copper(II). And in fact, on the basis of visible and IR spectra as well as conductometric measurements in nitrobenzene, a pseudotetrahedral structure has been considered likely for the copper complex in $Cu(tmbp)_2(ClO_4)_2$.[13] As we have shown, however, this is not the case in the solid state, where the coordination geometry is in fact based on a trigonal bipyramid with a coordinated perchlorate anion. The perchlorate ligand is replaced by water in crystals of $Cu(tmbp)_2(ClO_4)_2 \cdot 2H_2O$. These results, together with the well-established fact that perchlorate is weakly ligating, suggest that a coordination number of greater than 4 is apt to persist in solution as well.

In studies of a related phenanthroline complex having methyl groups in the 2- and 9-positions, Sykes and co-workers have observed limiting kinetics in the reduction of the copper(II) complex by $Fe(CN)_6^{4-}$. These results have been interpreted in terms of transition between a five-coordinate and a pseudotetrahedral form of the copper(II) complex prior to electron transfer.[10] If our results are of any relevance to the phenanthroline systems, it seems unlikely that significant amounts of a pseudotetrahedral form of the complex will exist at equilibrium in aqueous solution.

Finally, we wish to comment on the connection this structural work may have with the photochemistry of copper(I) systems. We have found that $Cu(dmp)_2^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) is emissive in dichloromethane but that the emission is apparently quenched by adding potential Lewis bases like methanol and acetone.[14] Similar results are found for $Cu(tmbp)_2^+$.[30] We have suggested that the action of these donors could conceivably be associated with coordination to copper, which is formally copper(II) in the

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metal-to-ligand charge-transfer excited state. The present work supports the idea that the coordination number of copper may tend to increase in the excited state.

Acknowledgment. This work was supported in part by Grant No. GM22764 from the National Institutes of Health.

Registry No. $Cu(tmbp)_2ClO_4$, 15633-36-0; $Cu(tmbp)_2(ClO_4)_2$, 80800-41-5; $Cu(tmbp)_2(ClO_4)_2{\cdot}2H_2O$, 80844-90-2.

Supplementary Material Available: Interatomic bond distances and angles for the tmbp ligands (Tables VII and VIII), selected least-squares planes (Tables IX–XI), molecular dimensions for the perchlorate groups (Table XII), contact distances (Table XIII), hydrogen atom coordinates (Tables XIV and XV), thermal parameters (Tables XVI–XVIII), and observed and calculated structure amplitudes for $Cu(tmbp)_2ClO_4$, $Cu(tmbp)_2(ClO_4)_2$, and $Cu(tmbp)_2(ClO_4)_2{\cdot}2H_2O$ (59 pages). Ordering information is given on any current masthead page.

Contribution from the Institute of Chemistry,
University of Dortmund, D-4600 Dortmund 50, West Germany

Preparation and Crystal Structure of Dirhenium Pentaphosphide, Re_2P_5, a Diamagnetic Semiconducting Polyphosphide with Rhomboidal Re_4 Clusters

REINHOLD RÜHL and WOLFGANG JEITSCHKO*

Received August 4, 1981

The new compound Re_2P_5 was prepared by reaction of the elemental components in a tin flux. It crystallizes with triclinic symmetry, space group $P\bar{1}$, and the lattice constants $a = 8.229$ (2) Å, $b = 8.336$ (5), $c = 7.329$ (2) Å, $\alpha = 112.28$ (2)°, $\beta = 87.11$ (2)°, $\gamma = 110.18$ (2)°, and $Z = 4$. The crystal structure was determined from 4675 single-crystal diffractometer data and refined to a conventional R value of 0.038 and 129 variable parameters. It can be rationalized completely by classical two-electron Re–Re, Re–P, and P–P bonds in agreement with the diamagnetism and the semiconductivity of the compound. Formal oxidation numbers are +3 and +4 for the Re atoms and 0, −1, −2, and −3 for the P atoms. The Re atoms are situated in P octahedra which are distorted by Re–Re bonds (between 2.85 and 2.96 Å) across common edges thus forming rhomboidal Re_4 clusters. The P atoms are all tetrahedrally coordinated by P and Re atoms. In stressing ionicity they may be considered as forming homonuclear polyanions of P pairs and four-membered zigzag chains. One kind of P atoms is surrounded only by four Re atoms, while others form a branched infinite P chain. Chemical bonding in Re_2P_5 and closely related Re_6P_{13} is briefly discussed to rationalize their different physical properties.

Introduction

The first and systematic study of the rhenium–phosphorus system was carried out by Haraldsen,[1] who—using Biltz's[2] tensimetric technique of thermal decomposition under vacuum—found the four compositions $ReP_{0.56}$, $ReP_{1.18}$, $ReP_{2.06}$, and $ReP_{2.98}$ in equilibrium with vaporous phosphorus. In aiming for simple atomic ratios, he assigned to them the tentative formulas Re_2P, ReP, ReP_2, and ReP_3. The crystal structures of the two metal-rich compounds were determined by Rundqvist,[3,4] who established their ideal compositions as Re_2P and Re_3P_4. A compound "Re_3P_7" was mentioned by Hulliger[5] and found its way into review articles[6,7] but later was shown[4] to be identical with Re_3P_4. More recently we have prepared and characterized ReP_4[8] and Re_6P_{13}[9,10] which—as judged from similarities in X-ray powder patterns—seem to correspond to the two compounds with high P content prepared by Haraldsen. The latter compound was reported independently also by others.[11] The new compound Re_2P_5 described in the present paper has many similarities with Re_6P_{13} including the Re_4 clusters.

Preparation and Properties

The direct synthesis of transition-metal phosphides and especially polyphosphides is difficult. At relatively low temperatures (e.g. 800 K), the reaction is usually very slow because of the inertness of the components, and at higher temperatures polyphosphides tend to decompose into lower phosphides and phosphorus vapor. With the tin flux technique—which was already used by Jolibois[12] to grow crystals of NiP_2 and NiP_3—these difficulties can be overcome as long as the desired transition-metal polyphosphides are thermodynamically more stable than the mixture of the corresponding transition-metal stannides and tin phosphides. Tin is especially useful as a solvent because of its low melting point and because the tin-rich matrix can be dissolved with hydrochloric acid, which usually does not attack the crystals of the transition-metal phosphides. Recent examples for the use of a tin flux to grow transition-metal phosphides are the growth of CuP_2,[13] PtP_2,[14] RuP_2 and IrP_2,[15] and RhP_3.[16] In our laboratory this technique was used extensively to prepare new phosphides and polyphosphides such as $LaFe_4P_{12}$[17] and $ThFe_4P_{12}$,[18] $EuCo_2P_2$,[19] $EuNi_2P_2$,[20] $La_6Ni_6P_{17}$,[21] $Er_2Ni_{12}P_7$,[22] FeP_4,[23] RuP_4 and OsP_4,[24] three modifications of MnP_4,[24-26] as well as Re_6P_{13}[10] and ReP_4.[8]

Starting materials for the preparation of Re_2P_5 were powders of rhenium (Ventron, 99.997), red phosphorus, and tin (both from Merck,

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