

spectrum of **4** at 1500 G. There are four copper hyperfine lines resolved on this signal with an average spacing of 75 G, as well. The only significant difference among the spectra of compounds **2-4** is the resolution of a very weak transition at 3640 G ($H(Z)_2$ signal⁵⁶) in compound **3**. Since the frozen-solution spectrum of compound **2** is similar to its powder spectrum, it appears that the open structure present in the solid state persists as well in solution. The spectral parameters of **4** ($g_{\parallel} > 2.1$) indicate that the copper(II) ions are distorted toward square-pyramidal geometry⁵⁹ rather than toward the trigonal-bipyramidal geometry observed in the crystal structure. This may indicate that the strained geometry observed in the solid state (twisting of the phenol ring relative to the Cu_2O_2 plane) may be relaxed in the frozen acetonitrile/toluene/methanol solution and that the Cu(II) centers may be in environments that resemble square-pyramidal geometries.

The frozen-solution spectrum of complex **5** (supplementary material) is very similar to the spectra of complexes **2-4**, but much broader. The g_{\parallel} signal is very broad, trailing into the $\Delta M_S = 2$ region and essentially obscuring this signal. The overall shape of the spectrum indicates that the Cu(II) centers also may be in square-pyramidal environments. It is important to note, however, that the method used to determine g values in this study is not very accurate,^{56,57} so an exact ground-state configuration for these complexes in solution is not obtainable at the present time.

Conclusions

New open type dinuclear polyimidazole copper(II) complexes (**2** and **3**) have been synthesized and used to prepare two doubly bridged dinuclear Cu(II) complexes (**4** and **5**). Complexes **3** and

4 have been characterized by X-ray crystallography and shown to have copper centers with square-pyramidal and distorted trigonal-bipyramidal geometries, respectively. Magnetic susceptibility data presented for complexes **2** and **5** (supplementary material) demonstrate that the Cu(II) ions are essentially uncoupled magnetically. The exchange interaction is much stronger in compound **4** and is antiferromagnetic. Both the electronic spectral and frozen-solution (acetonitrile/toluene/methanol) EPR spectral data of compounds **2** and **3** are consistent with the open type structure observed in the crystal structure of **3**. The electronic spectral data for complexes **4** and **5** in acetonitrile solution are consistent with the closed structures observed by X-ray crystallography. In frozen acetonitrile/toluene/methanol solution, however, the EPR spectra of complexes **4** and **5** are more consistent with dinuclear Cu(II) complexes having square-pyramidal geometries, in contrast with their solid-state structures. It appears then that the constraining nature of the Hbimp ligand is influenced by the physical state of the samples.

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Supplementary Material Available: Tables of crystallographic data, non-hydrogen positional parameters and general anisotropic displacement parameters, non-hydrogen bond distances and angles, hydrogen positional and thermal parameters, and hydrogen bond distances and angles for **3** and **4**, a perspective view (PLUTO) of the disordered $[Cu_2bimp(\mu-N_3)]^{2+}$ cation, electronic absorption spectra of the complexes, tables of magnetic data for **2**, **4**, and **5**, a plot of μ_{eff} vs T data for **5**, a frozen-solution EPR spectrum of **5**, and powder EPR spectra of **2-5** (40 pages); listings of structure factors for **3** and **4** (32 pages). Ordering information is given on any current masthead page.

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Synthesis of 3- and 4-Coordinate Coinage Metal $[ML_3][X]$, $[MXL_3]$, and $[ML_4][X]$ Complexes: Crystal Structures of $[Cu\{P(p-C_6H_4OMe)\}_3][ClO_4]$ and $[Cu\{Sb(p-C_6H_4F)\}_3][BF_4]$

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Forty-nine complexes of the type $[M\{Z(Ph)_m(p-C_6H_4Y)_{3-m}\}][X]$ ($M = Cu, Ag; X = BF_4, ClO_4; Z = P, As, Sb; Y = Cl, F, Me, OMe; n = 3, 4; m = 0-2$) have been prepared and characterized with the intent of demonstrating electronic control of their stereochemistry. With electron-withdrawing substituents ($Y = Cl, F$), primarily $n = 3$ complexes are formed. IR spectra are, however, characteristic of coordinated anions, indicating the existence of 4-coordinate complexes. In a few instances, where $M = Cu, Z = Sb$, and $Y = F$, $n = 4$ complexes are isolated. For electron-donating substituents ($Y = Me, OMe$), both $n = 3$ and $n = 4$ complexes are obtained, with $n = 3$ preferred for Cu and $n = 4$ dominating for Ag. Coordination of the anions is generally not anticipated for the $n = 3$ complexes, based on the IR spectra. One Ag complex with $n = 2$ was isolated. Crystals of $[Cu\{P(p-C_6H_4OMe)\}_3][ClO_4]$ are in the rhombohedral space group $R\bar{3}$, with $a = 19.423$ (7) Å, $c = 27.616$ (18) Å, and $Z = 6$ at $T = -120$ °C. The structural refinement converged to $R = 0.098$. The structure consists of isolated $[CuL_3]^+$ cations and $[ClO_4]^-$ anions. The Cu atom is 3-coordinate, with the Cu atom lying only 0.23 Å out of the plane of the three phosphorus atoms. The $[Cu\{Sb(p-C_6H_4F)\}_3][BF_4]$ salt is trigonal, space group $P31c$, with $a = 13.489$ (1) Å, $c = 23.327$ (3) Å, and $Z = 2$ at 22 °C. The structure refined to $R = 0.052$. The 4-coordinate Cu atom is located at a site of C_3 symmetry, with three Sb atoms at 2.556 (1) Å and one at 2.547 (1) Å.

Introduction

In previous papers^{1,2} we have attempted to define more precisely the steric limits by group VB ligands, of 2-, 3-, and 4-coordinate univalent coinage metal cations. While it was apparent that the

ZPh_3 ligands normally form $[ML_4][X]$ ($X = ClO_4, BF_4$) complexes, the complex $\{Cu(FBF_3)(PPh_3)_3\}^3$ and the salts $[M-(PPh_3)_2][BF_4]$ ($M = Ag, Au^5$) have previously been isolated. Thus, the isolation of complexes containing less than four neutral

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Table I. Physical Properties of $[\text{CuL}_n][\text{X}]$ Complexes ($n = 3, 4$) Containing Electron-Rich Tertiary Phosphine, Arsine, or Stibine Ligands

complex	conductivity/S ^a	anion peaks ^b /cm ⁻¹	anion symmetry
$[\text{Cu}\{\text{As}(p\text{-C}_6\text{H}_4\text{Me})_3\}_4][\text{BF}_4]$	25.8	1050	T_d
$[\text{Cu}\{\text{As}(p\text{-C}_6\text{H}_4\text{Me})_3\}_4][\text{ClO}_4]$	22.3	1090, 620	T_d
$[\text{Cu}\{\text{As}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_4][\text{BF}_4]$	27.2	1030	T_d
$[\text{Cu}\{\text{Sb}(p\text{-C}_6\text{H}_4\text{Me})_3\}_4][\text{BF}_4]$	25.2	1060	T_d
$[\text{Cu}\{\text{Sb}(p\text{-C}_6\text{H}_4\text{Me})_3\}_4][\text{ClO}_4]$	24.8	1095, 620	T_d
$[\text{Cu}\{\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3\}_3][\text{BF}_4]$	21.7	1050	T_d
$[\text{Cu}\{\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3\}_3][\text{ClO}_4]$	19.4	1095	T_d
$[\text{Cu}\{\text{PPh}(p\text{-C}_6\text{H}_4\text{Me})_2\}_3][\text{BF}_4]$	26.2	1050	T_d
$[\text{Cu}\{\text{PPh}(p\text{-C}_6\text{H}_4\text{Me})_2\}_3][\text{ClO}_4]$	26.9	1100	T_d
$[\text{Cu}(\text{FBF}_3)\{\text{PPh}_2(p\text{-C}_6\text{H}_4\text{Me})\}_3]$	23.0	1095, 1050	C_{3v}
$[\text{Cu}(\text{OCIO}_3)\{\text{PPh}_2(p\text{-C}_6\text{H}_4\text{Me})\}_3]$	31.5	1095, 1050	C_{3v}
$[\text{Cu}\{\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_3][\text{BF}_4]$	24.6	1052	T_d
$[\text{Cu}\{\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_3][\text{ClO}_4]$	21.7	1070, 625	T_d
$[\text{Cu}\{\text{PPh}(p\text{-C}_6\text{H}_4\text{OMe})_2\}_3][\text{BF}_4]$	24.3	1050	T_d
$[\text{Cu}\{\text{PPh}(p\text{-C}_6\text{H}_4\text{OMe})_2\}_3][\text{ClO}_4]$	21.7	1100, 620	T_d
$[\text{Cu}\{\text{As}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_3][\text{ClO}_4]$	22.5	1100	T_d

^a Determined on mM nitrobenzene solutions. ^b Nujol mulls.

Table II. Physical Properties of $[\text{AgL}_n][\text{X}]$ Complexes ($n = 2-4$) Containing Electron-Rich Tertiary Phosphine, Arsine, or Stibine Ligands

complex	conductivity/S ^a	anion peaks ^b /cm ⁻¹	anion symmetry
$[\text{Ag}(\text{OCIO}_3)\{\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_2]$	28.8	1130, 1050	C_{3v}
$[\text{Ag}\{\text{PPh}_2(p\text{-C}_6\text{H}_4\text{Me})_3\}_3][\text{ClO}_4]$	21.3	1120	T_d
$[\text{Ag}\{\text{PPh}(p\text{-C}_6\text{H}_4\text{Me})_2\}_3][\text{ClO}_4]$	23.0	1090	T_d
$[\text{Ag}\{\text{As}(p\text{-C}_6\text{H}_4\text{Me})_3\}_3][\text{ClO}_4]$	26.2	1090, 636	T_d
$[\text{Ag}\{\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3\}_4][\text{ClO}_4]$	24.0	1050	T_d
$[\text{Ag}\{\text{PPh}_2(p\text{-C}_6\text{H}_4\text{Me})_4\}_4][\text{ClO}_4]$	38.0	1120	T_d
$[\text{Ag}\{\text{PPh}_2(p\text{-C}_6\text{H}_4\text{OMe})_4\}_4][\text{ClO}_4]$	25.6	1090	T_d
$[\text{Ag}\{\text{PPh}_2(p\text{-C}_6\text{H}_4\text{OMe})_4\}_4][\text{BF}_4]$	26.3	1052	T_d
$[\text{Ag}\{\text{PPh}(p\text{-C}_6\text{H}_4\text{OMe})_2\}_4][\text{BF}_4]$	21.3	1055	T_d
$[\text{Ag}\{\text{PPh}(p\text{-C}_6\text{H}_4\text{OMe})_2\}_4][\text{ClO}_4]$	20.2	1095, 625	T_d
$[\text{Ag}\{\text{As}(p\text{-C}_6\text{H}_4\text{Me})_3\}_4][\text{BF}_4]$	26.8	1050	T_d
$[\text{Ag}\{\text{As}(p\text{-C}_6\text{H}_4\text{Me})_3\}_4][\text{ClO}_4]$	25.8	1095, 620	T_d
$[\text{Ag}\{\text{As}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_4][\text{BF}_4]$	27.0	1030	T_d
$[\text{Ag}\{\text{As}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_4][\text{ClO}_4]$	29.0	1100	T_d
$[\text{Ag}\{\text{Sb}(p\text{-C}_6\text{H}_4\text{Me})_3\}_4][\text{BF}_4]$	26.0	1060	T_d
$[\text{Ag}\{\text{Sb}(p\text{-C}_6\text{H}_4\text{Me})_3\}_4][\text{ClO}_4]$	25.1	1095, 625	T_d

^a Determined in mM nitrobenzene solutions. ^b Nujol mull spectra.

ligands, coupled with the absence of any $[\text{M}(\text{PPh}_2\text{R})_4]^+$ ($\text{R} = \text{cycloalkyl}$) cations,² implies that the steric dividing line between $[\text{ML}_3]^+$ complexes and $[\text{ML}_4]^+$ complexes lies close to PPh_3 .

Nevertheless, the steric properties of the neutral ligands are not the sole determinants of cation stoichiometry with these metals. The electronic properties of the ligands can also determine cation stoichiometry. This is well illustrated by the stoichiometries of the copper(I) perchlorate complexes formed by pyridine, 2-methylpyridine, and 4-methylpyridine. The second ligand forms a $[\text{CuL}_3][\text{X}]$ complex,^{6a} presumably for steric reasons, but the first and last ligands, which have similar steric requirements, form $[\text{Cu}(\text{py})_4]^+$ and $[\text{Cu}(4\text{-Mepy})_3]^+$ cations, respectively.^{6b}

It was decided to modify the electronic properties of the ZPh_3 ligands by synthesizing ligands of the type $\text{Z}(p\text{-C}_6\text{H}_4\text{Y})_3$ where Y is a substituent that either donates electrons (giving electron-rich ligands) or withdraws electrons to give ligands with a lower electron density on Z than was present in the triphenyl species. The first type employed typically contains methyl or methoxy substituents, and the second, chloro or fluoro substituents. With the tertiary phosphine ligands, still finer control of their electronic properties could be achieved by synthesizing $\text{PPh}_m(p\text{-C}_6\text{H}_4\text{Y})_{3-m}$ ligands ($m = 1, 2$). In this paper, we thus report the synthesis and characterization of a wide range of $[\text{M}(\text{ZR}_2\text{R}')_n][\text{X}]$ complexes, with $\text{M} = \text{Cu}$ or Ag ; $\text{Z} = \text{P}, \text{As},$ or Sb ; $\text{R}, \text{R}' = \text{para}$ -substituted phenyl group; $n = 3, 4$; and $\text{X} = \text{ClO}_4$ or BF_4 . Silver(I) complexes containing only two neutral ligands were isolated at low ligand:silver ratios in the preparative reactions. Silver(I) complexes of this stoichiometry are quite common. There are two

types of these complexes. Linear $[\text{AgL}_2]^+$ cations are known,⁷ and we have previously investigated the interactions between nonlinear $[\text{AgL}_2]^+$ ions and the anions. These interactions lead to the anion being deformed from pure T_d symmetry before true anion coordination has been achieved.⁷ It might be expected that there is greater interaction between the anion and silver when the latter is coordinated to two electron-poor ligands. The electron-rich trimesitylphosphine ligand forms a linear complex.⁷ In addition, the structures of $[\text{Cu}\{\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3\}_3][\text{ClO}_4]$ and $[\text{Cu}\{\text{Sb}(p\text{-C}_6\text{H}_4\text{F})_3\}_4][\text{BF}_4]$ are reported.

Discussion

A total of sixteen copper(I) complexes, five of $\text{Cu}[\text{ZR}_2\text{R}'_4][\text{X}]$ and eleven of $\text{Cu}[\text{ZR}_2\text{R}'_3][\text{X}]$ stoichiometry, have been prepared with electron-rich ligands (Table I). Ligands based on As and Sb formed predominantly $n = 4$ complexes, while the phosphine ligands formed exclusively $n = 3$ complexes. Of the $n = 3$ systems, only two had properties characteristic of anion coordination. In contrast, with silver(I), one $\text{Ag}[\text{ZR}_3][\text{X}]$, three $\text{Ag}[\text{ZR}_2\text{R}'_3][\text{X}]$, and twelve $\text{Ag}[\text{ZR}_2\text{R}'_4][\text{X}]$ complexes were obtained (Table II). The preference of As and Sb ligands to form $n = 4$ systems is again apparent, but now the phosphine ligands also show that tendency.

With the electron-poor ligands, only two of the eighteen complexes prepared (Table III) had $n = 4$ (both with Sb ligands). Of the fourteen complexes with $n = 3$, and the two with $n = 2$, all have physical characteristics compatible with anion coordination.

The electron-rich ligands ZAR_3 are more powerful reducing agents than their unsubstituted analogues. Tri-*p*-anisylstibine

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Table III. Physical Properties of [CuL_n][X] and [AgL_n][X] Complexes (n = 2–4) Containing Electron-Poor Phosphine, Arsine, or Stibine Ligands

complex	conductivity/S ^a	anion bands/cm ⁻¹ ^b	anion symmetry
[Cu(FBF ₃)(P(<i>p</i> -C ₆ H ₄ F) ₃) ₃]	26.6	1050, 960*	C _{3v}
[Cu(OClO ₃)(P(<i>p</i> -C ₆ H ₄ F) ₃) ₃]	23.5	1040	C _{3v}
[Cu(FBF ₃)(P(<i>p</i> -C ₆ H ₄ Cl) ₃) ₃]	13.6	1060	c
[Cu(OClO ₃)(P(<i>p</i> -C ₆ H ₄ Cl) ₃) ₃]	21.5	1100	c
[Cu(FBF ₃)(As(<i>p</i> -C ₆ H ₄ F) ₃) ₃]	27.8	1120, 1030	C _{3v}
[Cu(OClO ₃)(As(<i>p</i> -C ₆ H ₄ F) ₃) ₃]	27.0	1120, 1035, 625	C _{3v}
[Cu(Sb(<i>p</i> -C ₆ H ₄ F) ₃) ₄][BF ₄]	25.2	1060	T _d
[Cu(Sb(<i>p</i> -C ₆ H ₄ F) ₃) ₄][ClO ₄]	22.0	1120, 625	T _d
[Ag(FBF ₃)(P(<i>p</i> -C ₆ H ₄ F) ₃) ₂]	26.6	1090, 1050	C _{3v}
[Ag(OClO ₃)(P(<i>p</i> -C ₆ H ₄ F) ₃) ₂]	22.0	1100, 1060	C _{3v}
[Ag(FBF ₃)(P(<i>p</i> -C ₆ H ₄ F) ₃) ₃]	22.0	1090, 1050	C _{3v}
[Ag(OClO ₃)(P(<i>p</i> -C ₆ H ₄ F) ₃) ₃]	26.6	1100, 1060, 618	C _{3v}
[Ag(FBF ₃)(P(<i>p</i> -C ₆ H ₄ Cl) ₃) ₃]	26.6	1050	e
[Ag(OClO ₃)(P(<i>p</i> -C ₆ H ₄ Cl) ₃) ₃]	24.0	1100, 625	e
[Ag(FBF ₃)(As(<i>p</i> -C ₆ H ₄ F) ₃) ₃]	31.8	1070, 1000	C _{3v}
[Ag(OClO ₃)(As(<i>p</i> -C ₆ H ₄ F) ₃) ₃]	29.4	1110, 1050, 625	C _{3v}
[Ag(FBF ₃)(Sb(<i>p</i> -C ₆ H ₄ F) ₃) ₃]	34.5	1050	d
[Ag(OClO ₃)(Sb(<i>p</i> -C ₆ H ₄ F) ₃) ₃]	38.0	1100, 1040, 615	C _{3v}

^a Determined on mM nitrobenzene solutions. ^b Nujol mulls. ^c No assignment possible because of neutral ligand absorptions. ^d Very broad peak centered on 1050 cm⁻¹, no assignment possible. *Shoulder on broad 1050-cm⁻¹ band.

reduced both copper(II) tetrafluoroborate and silver(I) perchlorate or tetrafluoroborate to the metals. The corresponding tertiary phosphine similarly reduced ethanolic solutions of AgBF₄. Complexes of the substituted ligands are much more soluble than those of the triphenyl ligands and this also hinders their isolation.

Electron-Rich Ligands. The ZR₃ (Z = As, Sb) ligands in this class predominantly form [ML₄][X] complexes, thus demonstrating that the steric limits for forming complexes of this stoichiometry have not been changed by substitution of the ligands' skeletons. Two of these ligands formed [ML₃][ClO₄] compounds (M = Cu, L = As(*p*-C₆H₄OMe)₃; M = Ag, L = As(*p*-C₆H₄Me)₃).

With the tertiary phosphines in this series, copper(I) complexes usually exhibited [CuL₃][X] stoichiometry. The physical properties of these complexes suggest that there is little or no interaction between the metal and anion. However, on the basis of the IR spectra, it seems possible that some interaction exists between the anionic and cationic species in the [Cu{PPh(*p*-C₆H₄Me)₂}[X] (X = ClO₄, BF₄) complexes. However, the splittings observed in the IR spectra may be due to effects of lower site symmetry and slight electrostatic distortion of the anion from pure T_d symmetry. A major difference is to be noted between the type of copper and silver complexes formed in this series. Silver most frequently forms [AgL₄][X] type complexes. In a few instances, notably with PPh₂(*p*-C₆H₄Me), PPh(*p*-C₆H₄Me)₂, and As(*p*-C₆H₄Me)₃, [AgL₃][ClO₄] complexes are formed.

The lesser number of [AgL₃][X] complexes arises from the greater spatial extent of the 5sp³ orbital on silver. The greater volume occupied by this orbital allows it to accommodate the lone pair from a fourth tertiary phosphine ligand.

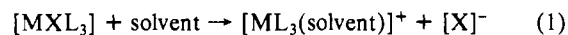
It is believed that the reason 3-coordinate cations are formed is because the electron-donating properties of the parasubstituent are transmitted to the group VB atom and inhibit its ability to act as a π acceptor from the metal. This in turn increases the electron density on the metal and renders it incapable of accepting the lone pair from a fourth Group VB ligand. The fact that there is very little π bonding between copper and tri-*p*-anisylphosphine can be seen from the Cu–P bond, which is merely 2% shorter than the calculated σ-bond value of 2.35 Å.⁸

A 3-coordinate copper(I) cation is formed by tri-*p*-anisylarsine, the most electron-rich tertiary arsine investigated. It would seem, therefore, that the greater spatial extent of the arsenic 5sp³ hybrid orbitals would usually allow the arsenic to accept π electrons from the metals and thereby permit the formation of [ML₄]⁺ cations, despite the greater electron density on arsenic when it is bonded to three electron-donating aryl groups. The even larger antimony atom in ligands of this type invariably forms [ML₄][X] complexes.

Electron-Poor Ligands. The behavior of ligands containing electron-withdrawing aryl groups is the converse of that seen for electron-rich ligands. These accept π electrons from the metals so efficiently that the metals in turn form [ML₄][X] complexes, [MXL₃] acido complexes, or less commonly, [ML₃][X] complexes. Acidosilver(I) complexes are more common than those of copper. This implies that the electron density is even lower on the larger silver(I) ion than on the copper(I) and is demonstrated by silver forming acido complexes with an electron-poor tertiary stibine. That the smaller copper(I) ion forms [Cu(SbAr₃)₄][X] complexes clearly demonstrates that this effect has electronic rather than steric origins. Indeed, unlike our earlier work using mixed aryl/alkyl tertiary phosphines, the stoichiometries of the copper complexes isolated were invariant with the metal:ligand ratio employed in its preparation. However, two ligands form silver(I) complexes of both [AgL₃][ClO₄] and [AgL₄][ClO₄] (L = PPh₂(*p*-C₆H₄Me) and As(*p*-C₆H₄Me)₃) stoichiometry. The isolation of the [AgL₃]⁺ species is unusual since ligands of greater electron-donating power where the tolyl group(s) has(have) been replaced by anisyl group(s) form [AgL₄]⁺ complexes. It seems likely that both the [AgL₃][ClO₄] complexes are isolated because of their anomalously low solubilities.

X-ray crystallography (vide infra) of [Cu{Sb(*p*-C₆H₄F)₃}]₄[BF₄] shows the metal–ligand bond to be very short. There have been no previous measurements of copper(I)–antimony bond lengths. If the σ-bond radius of sp²-hybridized carbon is taken to be 0.70 Å, then the σ-bond radius of sp³-hybridized antimony is 1.42 Å (the C–Sb bond length is 2.12 Å). Hence, by the assignment of the radius of 1.44 Å to tetrahedrally coordinated copper,^{4a} the expected copper–antimony single bond length is 2.86 Å. The observed bond length is 2.556 Å, some 11% shorter, which indicates a considerable degree of d_π–d_π bonding, particularly as four π-acid ligands are coordinated to copper.

The physical properties of these complexes are generally in accordance with their assigned structures, but some anomalies exist. Many of the conductivities of the acido complexes in nitrobenzene are representative of 1:1 electrolytes rather than covalent compounds. This is ascribed to solvation and ionization in this solvent.



Some of the [ML₄][X] complexes, which must contain free anions, have infrared spectra implying anion coordination. An example is the perchlorate salt of the [Cu{Sb(*p*-C₆H₄F)₃}]₄⁺ cation. These anomalies are probably due to site symmetry.

Structure Descriptions. The structures of both salts consist of isolated [Cu(ZAR₃)_n]⁺ cations (n = 3, 4) and X⁻ counterions. The copper ion for the [Cu{P(*p*-C₆H₄OMe)₃}]₃[ClO₄] salt is 3-coor-

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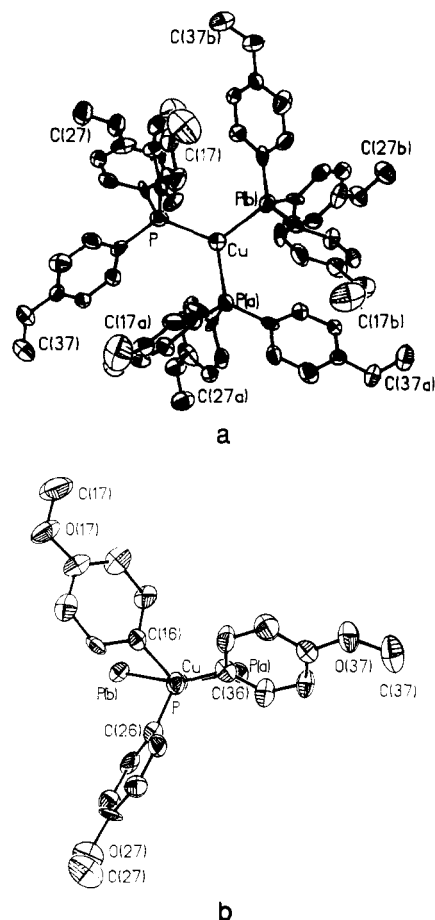


Figure 1. (a) Illustration of the $[\text{Cu}\{\text{P}(\text{p}\text{-C}_6\text{H}_4\text{OMe})_3\}_3]^+$ cation as viewed parallel to the C_3 axis (crystallographic c axis). (b) Illustration of the $[\text{Cu}\{\text{P}(\text{p}\text{-C}_6\text{H}_4\text{OMe})_3\}_3]^+$ cation as viewed parallel to the Cu-P bond. For clarity, only the R groups on one phosphine ligand are included.

dinate, while for the $[\text{Cu}\{\text{Sb}(\text{p}\text{-C}_6\text{H}_4\text{F})_3\}_4][\text{BF}_4]$ salt, 4-coordination is attained by the copper ion. Both cations have C_3 symmetry, as seen in Figures 1a and 2a. In the $[\text{Cu}\{\text{P}(\text{p}\text{-C}_6\text{H}_4\text{OMe})_3\}_3]^+$ complex, the CuP_3 moiety is nearly planar, with the Cu^+ ion lying 0.23 Å out of the plane of the three P atoms. As can be seen in Figure 1b, one of the $\text{p}\text{-C}_6\text{H}_4\text{OMe}$ groups of each PAR_3 ligand occupies a site in the CuP_3 plane, with the other two $\text{p}\text{-C}_6\text{H}_4\text{OMe}$ groups lying on either side of this plane. This arrangement effectively blocks the access of the ClO_4^- counterion to the Cu^+ ion, ensuring the retention of its 3-coordination. The planes of the aryl groups of the individual PAR_3 ligands are twisted away from an idealized propeller conformation, as seen in Figure 1b. The Cu-P distance is 2.302 (3) Å, while the P-Cu-P bond angle is 119.1 (1)°.

For the $\text{Sb}(\text{p}\text{-C}_6\text{H}_4\text{F})_3$ cation, two crystallographically independent ligands coordinate to the copper ion. Sb(2) lies on the 3-fold axis, and thus the aryl groups are required to assume a propeller-like configuration (Figure 2a). The phenyl groups in the other ligand (Figure 2b) are twisted away from a propeller conformation, in a manner not too different from that in the $\text{p}\text{-C}_6\text{H}_4\text{OMe}$ complex. The tetrahedral coordination about the Cu atom shows compression along the 3-fold axis, with the Cu-Sb(2) distance (2.547 Å) shorter than the Cu-Sb(1) distance (2.556 Å) by 0.009 Å, while the Sb(2)-Cu-Sb(1) angle (114.0°) is opened up beyond the idealized tetrahedral angle, and the Sb(1)-Cu-Sb(1) angles are compressed to 104.7°. This indicates the existence of some degree of steric flexibility about the copper(I) ion even in these 4-coordinate complexes and implies that the $[\text{CuL}_3]^+$ cations do not have their stoichiometry determined by steric factors.

Summary

It has been demonstrated in this series of three papers^{1,2} that $\text{ZR}_2\text{R}'$ ligands ($Z = \text{P, As, or Sb}$; $\text{R, R}' = \text{Ph, C}_6\text{H}_4\text{Y, or cy}$

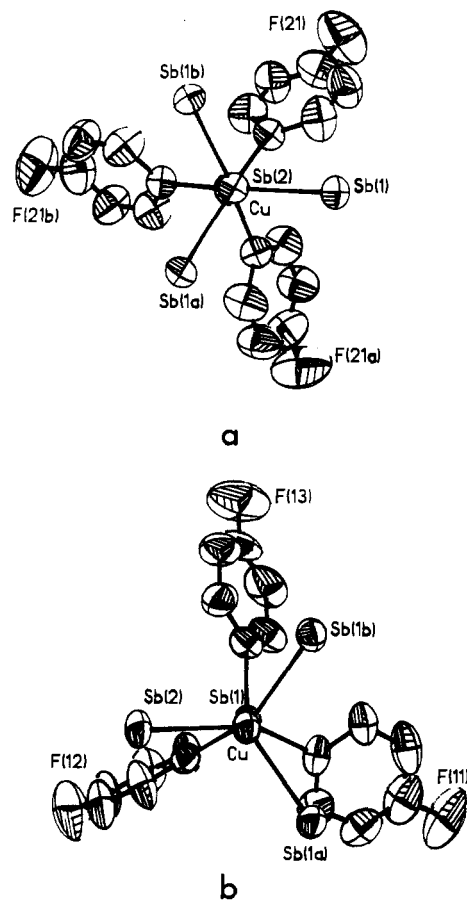


Figure 2. Illustration of the $[\text{Cu}\{\text{Sb}(\text{p}\text{-C}_6\text{H}_4\text{F})_3\}_4]^+$ cation (a) as viewed parallel to the C_3 axis (Cu-Sb(2) bond) and (b) as viewed parallel to the Cu-Sb(1) bond. For clarity, only the R groups on one phosphine ligand are included.

cloalkyl) form a series of $\text{M}(\text{ZR}_2\text{R}')_n\text{X}$ complexes with Cu(I), Ag(I), and Au(I) in which $n = 2, 3,$ or 4. The dependence of the value of n upon the size and electron-donor properties of Z, as well as the bulk of the R and R' groups has been explored. Despite the folklore concerning the noncoordinating ability of the $\text{X} = \text{ClO}_4$ and BF_4 anions, crystal structure analyses have shown that $\text{M}\cdots\text{X}$ interactions are significant in the $n = 2$ and $n = 3$ complexes, leading to substantial distortion of the hypothetical idealized linear ($n = 2$) or trigonal-planar ($n = 3$) coordination geometry for the metal(I) coordination sphere.

The bulkier cycloalkyl R groups favor the formation of $n = 2$ and $n = 3$ complexes. Factors which favor the $n = 4$ complexes include (a) large M(I) ions, (b) large Z atoms, (c) smaller R groups, and (d) electron-donating R groups.

Experimental Section

The tertiary phosphine ligands were synthesized as previously described.^{1,2} $\text{P}(\text{p}\text{-C}_6\text{H}_4\text{Cl})_3$ was purchased from Aldrich, and $\text{P}(\text{p}\text{-C}_6\text{H}_4\text{F})_3$ was obtained from Professor Sir Geoffrey Wilkinson, FRS. The tertiary arsines were prepared in the same manner as the PAR_3 compounds¹ but by employing AsCl_3 in place of PCl_3 . The arsenic trichloride was used without purification. The tertiary stibines were also prepared in analogous fashion to the PR_3 compounds but by using SbCl_3 in place of PCl_3 . Antimony trichloride was dried by treating it with SOCl_2 at reflux temperature. The solid was filtered off and stored in a vacuum desiccator for several days over KOH pellets, which removed any HCl, SO_2 , and SO_2Cl_2 adhering to the dry SbCl_3 . Slight reduction to elemental antimony was observed during the drying operation, but the element gave no deleterious side effects in the subsequent reactions of the dried compound.

Copper and silver complexes were prepared from the appropriate hydrated copper(II) or silver(I) salts, respectively, by allowing them to react with a minimum of 3.5 equiv of ligands in refluxing ethanolic solution. The methods of isolation and purification of these compounds have been described earlier.

Carbon and hydrogen microanalyses were carried out by Mr. M. F. Newman of the North East London Polytechnic Analytical Service.

Table IV. Melting Points and Analytical Data for Complexes Prepared

compd	mp/°C	found anal.			required anal.		
		% C	% H	% Z	% C	% H	% Z
[Cu{P(<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [BF ₄]	230–33	71.27	5.87		71.15	5.97	
[Cu{P(<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [ClO ₄]	210–24	70.69	6.11		70.38	5.90	8.63
[Cu{P(<i>p</i> -C ₆ H ₄ OMe) ₃ }] ₃ [BF ₄]	224–26	62.66	5.11		62.66	5.25	
[Cu{P(<i>p</i> -C ₆ H ₄ OMe) ₃ }] ₃ [ClO ₄]	205–09	61.99	5.10	7.30	62.02	5.20	7.61
[Cu{PPh(<i>p</i> -C ₆ H ₄ Me) ₂ }] ₃ [BF ₄]	202–03	70.30	5.26	9.12	70.55	5.26	8.98
[Cu{PPh(<i>p</i> -C ₆ H ₄ Me) ₂ }] ₃ [ClO ₄]	137–40	69.41	5.79	9.06	69.69	5.56	8.98
[Cu(BF ₄)] ₃ {PPh ₂ (<i>p</i> -C ₆ H ₄ Me) ₃ }	201–02	69.60	5.55		69.89	5.25	
[Cu(ClO ₄)] ₃ {PPh ₂ (<i>p</i> -C ₆ H ₄ Me) ₃ }	158–60	69.16	5.50	9.52	68.81	5.47	9.33
[Cu{PPh(<i>p</i> -C ₆ H ₄ OMe) ₂ }] ₃ [BF ₄]	130–40	64.65	5.29		64.49	5.14	
[Cu{PPh(<i>p</i> -C ₆ H ₄ OMe) ₂ }] ₃ [ClO ₄]	160–76	64.06	5.13	8.06	63.77	5.08	8.22
[Cu(BF ₄)] ₃ {P(<i>p</i> -C ₆ H ₄ F) ₃ }	256–58	59.27	3.30		59.00	3.33	
[Cu(ClO ₄)] ₃ {P(<i>p</i> -C ₆ H ₄ F) ₃ }	206–08	58.83	3.31		58.33	3.26	
[Cu(BF ₄)] ₃ {P(<i>p</i> -C ₆ H ₄ Cl) ₃ }	278–84	52.26	2.99		52.00	2.90	
[Cu(ClO ₄)] ₃ {P(<i>p</i> -C ₆ H ₄ Cl) ₃ }	197–98	51.64	2.44	7.48	51.48	2.88	7.36
[Cu(BF ₄)] ₃ {As(<i>p</i> -C ₆ H ₄ F) ₃ }	217–18	52.37	3.31		52.69	2.95	
[Cu(ClO ₄)] ₃ {As(<i>p</i> -C ₆ H ₄ F) ₃ }	215–17	52.17	2.81	18.26	52.15	2.91	18.07
[Cu{As(<i>p</i> -C ₆ H ₄ OMe) ₃ }] ₃ [ClO ₄]	159–60	56.29	5.16		55.97	4.69	
[Cu{As(<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [BF ₄]	185–86	64.79	5.87		65.36	5.44	
[Cu{As(<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [ClO ₄]	210–11	64.39	5.59	19.03	64.80	5.44	19.15
[Cu{Sb(<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [BF ₄]	232–39	58.55	4.86		58.28	4.89	
[Cu{Sb(<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [ClO ₄]	208–09	57.96	4.84	27.80	57.86	4.85	27.93
[Cu{Sb(<i>p</i> -C ₆ H ₄ F) ₃ }] ₃ [BF ₄]	160–61	49.09	2.88		48.60	2.72	
[Cu{Sb(<i>p</i> -C ₆ H ₄ F) ₃ }] ₃ [ClO ₄]	164–67	47.97	2.62	27.40	48.28	2.70	27.19
[Ag(ClO ₄)] ₃ {P(<i>p</i> -C ₆ H ₄ OMe) ₃ }	82–96	54.72	4.42	6.97	55.31	4.64	6.79
[Ag(BF ₄)] ₃ {P(<i>p</i> -C ₆ H ₄ F) ₃ }	210–11	52.50	3.60		52.27	3.17	
[Ag(ClO ₄)] ₃ {P(<i>p</i> -C ₆ H ₄ F) ₃ }	230–32	51.54	2.88		51.48	2.88	
[Ag(BF ₄)] ₃ {P(<i>p</i> -C ₆ H ₄ F) ₃ }	264–65	57.13	3.27	7.90	56.72	3.17	8.12
[Ag(ClO ₄)] ₃ {P(<i>p</i> -C ₆ H ₄ F) ₃ }	240–41	56.57	3.32	7.87	56.10	3.13	8.03
[Ag(BF ₄)] ₃ {P(<i>p</i> -C ₆ H ₄ Cl) ₃ }	250–78	50.27	2.87		50.22	2.80	
[Ag(ClO ₄)] ₃ {P(<i>p</i> -C ₆ H ₄ Cl) ₃ }	228–29	50.00	2.80	7.26	49.73	2.78	7.12
[Ag{PPh ₂ (<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [ClO ₄]	178–83	65.57	4.86	9.37	66.06	4.96	8.96
[Ag{PPh(<i>p</i> -C ₆ H ₄ Me) ₂ }] ₃ [ClO ₄]	117–20	66.52	5.53	8.74	66.82	5.32	8.62
[Ag{P(<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [ClO ₄]	224–25	69.61	5.20		70.81	5.94	
[Ag{PPh ₂ (<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [ClO ₄]	166–80	68.57	5.48	10.04	69.54	5.22	9.43
[Ag{PPh ₂ (<i>p</i> -C ₆ H ₄ OMe) ₃ }] ₃ [BF ₄]	155–58	66.72	5.06		66.93	5.03	
[Ag{PPh ₂ (<i>p</i> -C ₆ H ₄ OMe) ₃ }] ₃ [ClO ₄]	158–59	66.97	4.90	8.78	66.31	4.87	9.00
[Ag{PPh(<i>p</i> -C ₆ H ₄ OMe) ₂ }] ₃ [BF ₄]	89–93	64.18	5.19		64.75	5.16	
[Ag{PPh(<i>p</i> -C ₆ H ₄ OMe) ₂ }] ₃ [ClO ₄]	90–96	64.24	5.21		64.20	5.10	
[Ag{As(<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [ClO ₄]	230–31	60.39	5.09	17.85	60.42	5.07	17.90
[Ag(BF ₄)] ₃ {As(<i>p</i> -C ₆ H ₄ F) ₃ }	233–34	50.81	2.93		50.85	2.84	
[Ag(ClO ₄)] ₃ {As(<i>p</i> -C ₆ H ₄ F) ₃ }	200–04	50.76	2.97	17.50	50.35	2.81	17.45
[Ag{As(<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [BF ₄]	238–39	63.12	5.22		63.52	5.33	
[Ag{As(<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [ClO ₄]	228–29	62.75	5.35	18.99	63.02	5.28	18.71
[Ag{As(<i>p</i> -C ₆ H ₄ OMe) ₃ }] ₃ [BF ₄]	184–85	56.67	5.09		56.68	4.75	
[Ag{As(<i>p</i> -C ₆ H ₄ OMe) ₃ }] ₃ [ClO ₄]	175–76	56.31	4.88		56.28	4.72	
[Ag(BF ₄)] ₃ {Sb(<i>p</i> -C ₆ H ₄ F) ₃ }	198–99	45.48	2.78		45.81	2.56	
[Ag(ClO ₄)] ₃ {Sb(<i>p</i> -C ₆ H ₄ F) ₃ }	192–94	45.50	2.65	25.45	45.40	2.54	25.57
[Ag{Sb(<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [BF ₄]	230–32	57.03	5.00		56.83	4.76	
[Ag{Sb(<i>p</i> -C ₆ H ₄ Me) ₃ }] ₃ [ClO ₄]	204–06	56.50	4.87	27.45	56.43	4.73	27.23

Phosphorus and arsenic microanalyses were carried out by Analytische Laboratorien, Elbach, Gummersbach, German Federal Republic. Conductivity measurements were made on millimolar nitrobenzene solutions, thermostated at 25 °C, by using a Wayne Kerr Universal Bridge B221 instrument. The cell constant was determined by using aqueous potassium chloride solutions of known concentration. AR nitrobenzene was further purified by drying it over CaCl₂ and redistilling; the fraction distilling in the range 209–211 °C/760 mm was collected and used immediately. Melting points were determined in an electrothermal melting point apparatus and are uncorrected. Infrared spectra were obtained in Nujol or hexachlorobuta-1,3-diene mulls between potassium bromide plates by using either a Perkin-Elmer 377 or 781 spectrophotometer, the latter in conjunction with a Perkin-Elmer 3600 data station.

The crystal structure of the colorless, hexagonal parallelepipedal trigonal crystals of [Cu{P(*p*-C₆H₄OMe)₃}]₃[ClO₄] was determined by using diffraction data collected at –120 °C on a Nicolet R3m/E diffractometer system at Montana State University utilizing Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$).⁹ The crystal utilized for data collection exhibited very broad but symmetric diffraction peaks. This large mosaic spread may be in part the cause of the high *R* value obtained upon refinement. No absorption corrections were performed. The diffraction data showed $\bar{3}$ Laue group symmetry, and systematic absences led to the choice of *R* $\bar{3}$

Table V. Bond Lengths (Å) and Angles (deg)

atoms	distance	atoms	angle
[Cu{P(<i>p</i> -C ₆ H ₄ OMe) ₃ }] ₃ [ClO ₄]			
Cu–P	2.302 (3)	P–Cu–P(A)	119.1 (1)
P–C(16)	1.822 (12)	Cu–P–C(16)	105.2 (4)
P–C(26)	1.781 (10)	Cu–P–C(26)	116.3 (4)
P–C(36)	1.822 (15)	C(16)–P–C(26)	104.3 (5)
		Cu–P–C(36)	122.2 (3)
		C(16)–P–C(36)	103.0 (6)
		C(26)–P–C(36)	103.8 (6)
[Cu{Sb(<i>p</i> -C ₆ H ₄ F) ₃ }] ₃ [BF ₄]			
Cu–Sb(1)	2.556 (1)	Sb(1)–Cu–Sb(2)	114.0 (1)
Cu–Sb(2)	2.547 (1)	Sb(1)–Cu–Sb(1A)	104.7 (1)
Sb(1)–C(16)	2.126 (14)	Cu–Sb(1)–C(16)	115.3 (3)
Sb(1)–C(26)	2.112 (17)	Cu–Sb(1)–C(26)	120.7 (3)
Sb(1)–C(36)	2.127 (12)	Cu–Sb(1)–C(36)	116.0 (4)
Sb(2)–C(46)	2.103 (13)	Cu–Sb(1)–C(46)	119.4 (3)
		C(16)–Sb(1)–C(26)	101.3 (6)
		C(16)–Sb(1)–C(36)	101.0 (6)
		C(26)–Sb(1)–C(36)	99.4 (5)
		C(46)–Sb(2)–C(46A)	98.0 (4)

(9) Campana, C. F.; Shepherd, D. F.; Litchman, W. M. *Inorg. Chem.* **1981**, *20*, 4039.

or *R* $\bar{3}$. Although the intensity statistics indicated the lack of a center of inversion, satisfactory structure solution and refinement was obtained in

Table VI. Crystallographic Data

	[Cu{P(<i>p</i> -C ₆ H ₄ OMe) ₃ }] ₃ [ClO ₄]	[Cu{Sb(<i>p</i> -C ₆ H ₄ F) ₃ }] ₄ [BF ₄]
chem formula	C ₆₃ H ₆₃ ClCuO ₁₃ P ₃	C ₇₂ H ₄₈ BCuF ₁₆ Sb ₄
fw	1220.2	1771.1
space group	<i>R</i> 3̄	<i>P</i> 31 <i>c</i>
<i>a</i> , Å	19.423 (7)	13.489 (1)
<i>c</i> , Å	27.616 (18)	23.327 (3)
<i>V</i> , Å ³	9022.4	3675.8
<i>Z</i>	6	2
<i>T</i> , °C	-120	22
<i>λ</i> , Å	0.71069	0.71069
<i>ρ</i> _{calcd} , g cm ⁻³	1.35	1.61
<i>μ</i> , cm ⁻¹	5.3	18.4
<i>R</i> (<i>F</i> _o)	0.098	0.052
<i>R</i> _w (<i>F</i> _o)	0.086	0.053

Table VII. Atomic Coordinates (×10⁴) and isotropic thermal parameters (Å² × 10³) for Cu{P(*p*-C₆H₄OMe)₃}₃[ClO₄]

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
Cu	6667	3333	-351 (1)	39 (1)
P	6158 (2)	1985 (2)	-269 (1)	38 (2)
C(11)	5698 (7)	2064 (6)	669 (5)	46 (6)
C(12)	5203 (7)	1902 (6)	1062 (4)	54 (7)
C(13)	4415 (9)	1376 (8)	1012 (5)	50 (8)
C(14)	4130 (7)	979 (7)	573 (5)	47 (7)
C(15)	4631 (7)	1146 (6)	178 (4)	37 (6)
C(16)	5439 (7)	1683 (6)	222 (4)	33 (7)
O(17)	3864 (5)	1177 (5)	1365 (3)	69 (6)
C(17)	4123 (9)	1506 (9)	1834 (4)	91 (11)
C(21)	5398 (6)	597 (7)	-830 (4)	41 (6)
C(22)	4932 (6)	123 (7)	-1208 (4)	39 (6)
C(23)	4660 (7)	455 (8)	-1553 (4)	51 (7)
C(24)	4879 (7)	1254 (7)	-1521 (4)	49 (7)
C(25)	5344 (6)	1705 (6)	-1139 (4)	41 (6)
C(26)	5599 (6)	1386 (6)	-768 (4)	32 (6)
O(27)	4191 (5)	41 (5)	-1931 (3)	59 (5)
C(27)	3921 (8)	-780 (7)	-1964 (5)	73 (9)
C(31)	7472 (6)	1774 (6)	-329 (4)	46 (6)
C(32)	7957 (6)	1468 (6)	-206 (4)	41 (6)
C(33)	7725 (6)	926 (6)	159 (4)	33 (6)
C(34)	7023 (6)	677 (7)	402 (4)	54 (7)
C(35)	6552 (6)	1000 (6)	273 (4)	48 (6)
C(36)	6775 (6)	1564 (6)	-91 (4)	39 (6)
O(37)	8174 (4)	591 (4)	321 (3)	54 (5)
C(37)	8969 (7)	921 (8)	149 (5)	78 (9)
Cl	0	0	1145 (3)	59 (3)
O(1)	0	0	1689 (8)	76 (14)
O(11)	0	0	598 (11)	81 (16)
O(2)	308 (33)	793 (11)	1067 (26)	136 (20)
O(12)	-667 (43)	-663 (30)	1346 (28)	51 (27)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U*_{*ij*} tensor.

*R*3̄, as outlined below, except for a disorder of the perchlorate anion. The choice of the *R*3̄ space group would have required the presence of two independent cations, which did not seem justified since no disorder or anomalous thermal motion was evident. The structure was solved via the direct methods program SOLV in the SHELXTL structure solution package.¹⁰ This yielded heavy-atom (Cu, P) positions, and lighter atoms were located on subsequent difference syntheses. A summary of crystal data and refinement results are given in Table VI. Final positional parameters are given in Table VII, and pertinent bond distances and angles are reported in Table V. A full summary of data collection and refinement parameters are included in the supplementary material, as well as a complete listing of bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions.

(10) Sheldrick, G. *SHELXTL, Version 4.1*; Nicolet Analytical Instruments: Madison, WI, 1984.

Table VIII. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for Cu{P(*p*-C₆H₄OMe)₃}₃[ClO₄]

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Sb(1)	5776 (1)	1337 (1)	-445 (1)	52 (1)
C(11)	7278 (14)	1043 (14)	-1337 (7)	82 (8)
C(12)	7709 (16)	1090 (16)	-1886 (9)	97 (10)
C(13)	7281 (23)	1311 (19)	-2342 (8)	122 (14)
C(14)	6408 (23)	1531 (17)	-2289 (7)	115 (13)
C(15)	5916 (17)	1495 (15)	-1761 (7)	86 (9)
C(16)	6388 (13)	1269 (11)	-1275 (5)	62 (6)
C(21)	5367 (14)	-1075 (13)	-250 (6)	80 (8)
C(22)	5324 (17)	-2008 (13)	39 (8)	91 (10)
C(23)	5859 (20)	-1786 (17)	557 (7)	97 (12)
C(24)	6411 (21)	-755 (19)	786 (7)	111 (14)
C(25)	6399 (18)	142 (15)	483 (6)	92 (11)
C(26)	5877 (11)	5 (12)	-23 (6)	58 (6)
C(31)	3452 (14)	-293 (12)	-1023 (8)	84 (8)
C(32)	2294 (16)	-791 (18)	-1102 (10)	122 (11)
C(33)	1641 (13)	-595 (17)	-732 (11)	118 (11)
C(34)	2146 (13)	203 (16)	-330 (9)	102 (9)
C(35)	3331 (15)	750 (15)	-230 (8)	89 (10)
C(36)	3981 (10)	498 (11)	-595 (6)	62 (6)
Sb(2)	6667	3333	1092 (1)	57 (1)
C(41)	4277 (17)	1277 (16)	1367 (7)	101 (11)
C(42)	3283 (19)	629 (19)	1647 (10)	124 (12)
C(43)	3099 (19)	1119 (24)	2126 (9)	123 (15)
C(44)	3861 (19)	2211 (19)	2319 (9)	111 (11)
C(45)	4867 (18)	2830 (18)	2014 (7)	100 (11)
C(46)	5109 (12)	2389 (12)	1534 (5)	63 (7)
F(11)	7719 (15)	1379 (14)	-2868 (5)	178 (11)
F(12)	5836 (16)	-2662 (13)	842 (6)	171 (13)
F(13)	5241 (11)	-1089 (15)	-808 (10)	198 (11)
F(1)	6342 (19)	2277 (15)	3296 (7)	192 (13)
F(2)	6667	3333	4079 (10)	127 (7)
B	6667	3333	3472 (15)	82 (9)
F(21)	2066 (13)	481 (17)	2408 (7)	197 (11)
Cu	6667	3333	0	48 (1)

The crystal structure of the colorless, hexagonal parallelepipedal trigonal crystals of [Cu{Sb(*p*-C₆H₄F)₃}]₄[BF₄] was determined by using diffraction data collected at room temperature on a Nicolet R3m/E diffractometer system at Washington State University utilizing Mo *K*α radiation (*λ* = 0.71069 Å).⁹ The diffraction symmetry and systematic absences led to the choice of *P*3̄1*c* (centrosymmetric) or *P*31*c* (acentric). With *Z* = 2, the site symmetry constraints expected for the Cu atom indicated the latter as the correct choice. The structure solution was thus obtained in *P*31*c* via the direct-methods program SOLV in the SHELXTL structure solution package.¹⁰ This yielded heavy-atom (Cu, Sb) positions, and lighter atoms were located on subsequent difference syntheses. A summary of crystal data and refinement results are given in Table VI. Final positional parameters are given in Table VIII, and pertinent bond distances and angles are reported in Table V. A full summary of data collection and refinement parameters are included in the supplementary material, as well as a complete listing of bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions.

The structure refinement for both complexes was straightforward. No disorder was resolved, except for the ClO₄⁻ anion in the former salt.

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Supplementary Material Available: Tables of crystal data collection parameters, hydrogen atom positions, thermal parameters, and complete bond distances and angles and two stereographic illustrations (14 pages); a table of *F*_o/*F*_c (11 pages). Ordering information is given on any current masthead page.