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Silver(I) Assisted Metal Exchange Reaction. A Generalized Synthesis of Tris-Chelated Copper(II) Complexes of Neutral N,N-Donors

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Introduction

This report describes a general synthetic route for the syntheses of monomeric hexacoordinated tris-chelated complexes of Cu(II). The syntheses have been achieved following the silver(I) assisted metal exchange reaction strategy,[1−6] which recently has been developed by us and successfully used for the controlled syntheses of transition-metal complexes of desired compositions. Using three neutral N,N-donors, viz., *N-p*-tolylpyridine-2-aldimine (L^1, ptsb), 2,2′-bipyridine (L^2, bpy) and 1,10-phenanthroline (L^3, phen), it has been possible to isolate two complete series of tris(chelates) of general formulas $[CuL^1{}_nL^2{}_{3-n}](ClO_4)_2$ and $[CuL^2{}_nL^3{}_{3-n}](ClO_4)_2$ ($n = 0-3$) in the pure crystalline state. It may be noted here that monomeric tris(chelates) of Cu(II) involving N,N-donors are uncommon[7,8] due to pronounced Jahn−Teller distortions, and a mixed-ligand complex of the above type does not exist at all. The three-dimensional structures of a mixed-ligand complex, $[CuL^1{}_2L^2](ClO_4)_2$, and a tris(chelate), $[CuL^2{}_3](ClO_4)_2$, have been solved by X-ray diffraction.

Results and Discussion

A. Syntheses. The examples of tris-chelated cupric complexes of neutral N,N-donors are limited. The examples[9−11] are $[Cu(en)_3]^{2+}$ (en = ethylenediamine), $[Cu(bpy)_3]^{2+}$, and $[Cu(phen)_3]^{2+}$. Mixed-ligand tris(chelates) of Cu(II) are, however, not known. The silver(I) assisted transmetalation synthetic route to synthesize such complexes is described herein. Three bidentate ligands (L^1-L^3) were chosen for this purpose. All of them are known to form stable[12−14] compounds of silver(I). The syntheses of the complexes are elaborated by Schemes, 1 and 2.

Scheme 1

$$CuCl_2{\cdot}2H_2O + L \xrightarrow[L = L^1-L^3]{CH_3CN} CuLCl_2$$

Scheme 2

$$CuL'Cl_2 + 2AgL''_2{}^{+} \xrightarrow[\substack{L' = L^1-L^3 \\ L'' = L^1-L^3}]{} [CuL'_nL''_{3-n}]^{2+} + 2L'' + 2AgCl$$
$$n = 0-3$$

Scheme 1 illustrates the syntheses of the dichloro compounds $CuLCl_2$ by the direct reaction of equimolar quantities of $CuCl_2{\cdot}2H_2O$ and L in good yields (80−85%). These are found to be suitable starting compounds for syntheses of the tris-chelated species. Scheme 2 describes a general synthetic methodology for syntheses of the tris(chelates) of Cu(II). By the selection of an appropriate combination of reactants, the mixed-ligand complexes of desired compositions can be prepared very easily. For example, the reaction of CuL^1Cl_2 and 2 mol of $[AgL^2{}_2]^+$ produces $[CuL^1L^2{}_2]^{2+}$, whereas a similar reaction starting from CuL^2Cl_2 and $[AgL^1{}_2]^+$ (1:2 molar proportion) yields $[CuL^2L^1{}_2]^{2+}$. The syntheses of pure tris(chelates) $[CuL_3]^{2+}$ can be achieved by the direct reaction of $CuLCl_2$ and the silver compound of the same ligand. All of the tris complexes described above are obtained in the crystalline state as their perchlorate salts in high yields (ca. 75%).

By contrast, the reaction of $Cu(NO_3)_2{\cdot}3H_2O$ and free L in ethanol produces bis(chelates), $CuL_2{}^{2+}$. The differences in the compositions of the products from these two different routes may be viewed as follows. In the reaction of solvated cupric ion and free L, the stepwise substitution of solvents by L starts with the two most labile trans sites (Jahn−Teller effect) whereas, in the silver-assisted route, initial attack of the silver reagent presumably occurs at the two chlorides which are in relative cis positions in $CuLCl_2$. The most important outcome of the above synthetic methodology is the isolation of a series of mixed tris(chelates) of predetermined compositions by the controlled insertion of ligands to the metal ion, which have in the past not been known.

These complexes are paramagnetic, and the magnetic moments (μ_{eff} values) fall in the range 1.75−1.85 μ_B. Their IR spectral patterns are typical for complexes of these ligands.

In the synthesis of mixed-ligand complexes, the formation of a mixture of species of different compositions due to scrambling of ligands cannot be ruled out. However, analysis of the spectral data as well as voltammetric responses of the bulk materials (Table 1, Figure 1) indicated that the product obtained from each of the above reactions is pure. All of the

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Table 1. Characterization Data for the Complexes

complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})[a]	$E_{1/2}$, V (ΔE_p, mV)[b] for Cu(II) ↔ Cu(I)
$[Cu(ptsb)_3](ClO_4)_2$	677 (94), 320 (24 600), 300 (24 300)	0.29 (180)
$[Cu(bpy)_3](ClO_4)_2$	680 (106), 295 (38 400)	0.04 (160)
$[Cu(phen)_3](ClO_4)_2$	675 (105), 290 (36 250)	0.03 (170)
$[Cu(bpy)(ptsb)_2](ClO_4)_2$	655 (91), 330 sh (20 380), 310 sh (33 840), 300 (35 770)	0.19 (220)
$[Cu(ptsb)(bpy)_2](ClO_4)_2$	680 (105), 305 sh (26 800), 295 (32 800)	0.06 (180)
$[Cu(phen)(bpy)_2](ClO_4)_2$	680 (70), 295 (27 750)	0.03 (210)
$[Cu(bpy)(phen)_2](ClO_4)_2$	685 (86), 290 (25 780)	0.15 (210)
$[Cu(ptsb)Cl_2]$[c]	725, 325	0.28 (200)
$[Cu(bpy)Cl_2]$[c]	650, 370	0.11 (170)
$[Cu(phen)Cl_2]$[c]	680, 380	0.12 (180)

[a] Data obtained from absorption spectra: solvent, CH_3CN. [b] Data obtained from cyclic voltammetric experiments: solvent, CH_3CN (0.1 M TBAP); $v = 50$ mV s^{-1}. [c] The dihalo complexes are only sparingly soluble in common organic solvents. Quantitative spectra could not be recorded.

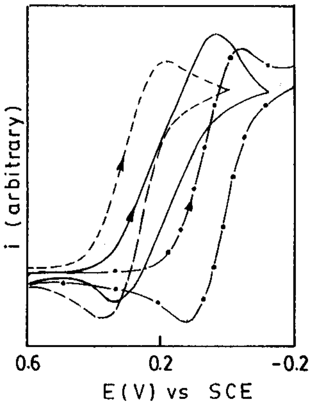

Figure 1. Cyclic voltammograms of (a) $[Cu(ptsb)_3]^{2+}$ (— — —), (b) $[Cu(bpy)(ptsb)_2]^{2+}$ (—), and (c) $[Cu(bpy)_3]^{2+}$ (—•—•) in CH_3CN (0.1M TBAP).

tris(chelates) showed almost similar spectral features (Table 1) with varied absorption maxima and intensities. The lowest energy transition, in the range 680−650 nm, is weak and broad and is assigned to a d−d transition. In the case of dihalo complexes these transitions occur in the range 725−650 nm. Neither the spectra nor the voltammetric responses of the tris(chelates) showed any sign of the presence of a mixture of compounds. In the series $[Cu(ptsb)_n(bpy)_{3-n}]^{2+}$ ($n = 0-3$), the $E_{1/2}$ occurs at 0.29 V for $[Cu(ptsb)_3]^{2+}$ and decreases with the substitution of each ptsb by a bpy ligand. Thus, the $E_{1/2}$ values (Table 1) of the mixed-ligand complexes $[Cu(ptsb)_2(bpy)]^{2+}$ and $[Cu(ptsb)(bpy)_2]^{2+}$ lie between those of $[Cu(ptsb)_3]^{2+}$ and $[Cu(bpy)_3]^{2+}$. Each of the dihalo complexes also showed one quasi-reversible redox process. The value of $E_{1/2}$ for $Cu(ptsb)Cl_2$ appears at 0.28 V, which is about 160 mV more anodic than those for $Cu(bpy)Cl_2$ and $Cu(phen)Cl_2$. Final characterization of the complexes was made by the analysis of single-crystal X-ray data of two representative complexes which are elaborated below.

B. Structure. A survey of the literature indicates that X-ray structural investigations on tris-chelated Cu(II)−N_6 complexes involving neutral ligands are solely confined[9−11] to the complexes of three identical N,N-donors. Structurally characterized mixed-ligand tris-chelated cupric complexes of neutral ligands are, however, unknown. Consequently, there has been interest in the structures of the mixed-ligand compounds. In almost all cases the compounds appear to be crystalline but were not suitable for X-ray study. Fortunately, after several trials, X-ray-quality crystals of $[CuL^1{}_2L^2](ClO_4)_2$ could be isolated. Crystals of this compound were found to be very weak scatterers, and the structure determination was not routine (Experimental Section). Details of the diffraction experiment are provided as Supporting Information. For the purpose of this report we use this structural analysis only to establish identity and gross features of the system. The six-coordinate copper center in the dicationic complex has distorted octahedral geometry (Figure 2), in which the distortions are of two distinct origins. First, there is the Jahn−Teller elongation of the two Cu−ligand bonds in relative trans positions. In this case, the two elongated bonds are to the nitrogen atoms attached to the *p*-tolyl groups of the ptsb ligands. The second main distortion of the coordination shell around the copper atom is the contraction of three of the N−M−N angles from the ideal octahedral values, imposed by the three chelate ligands. The chelate angle for the bpy ligand, N(1)−Cu(1)−N(2), is 80.6(3)°, while the values for the two ptsb ligands are slightly smaller: N(3)−Cu(1)−N(4), 76.7(4)°; N(5)−Cu(1)−N(6), 75.2(4)°. The cation approximates to overall C_2 symmetry. The 2-fold axis bisects the N(1)−Cu(1)−N(2) angle, as well as the angle N(3)−Cu(1)−N(5).

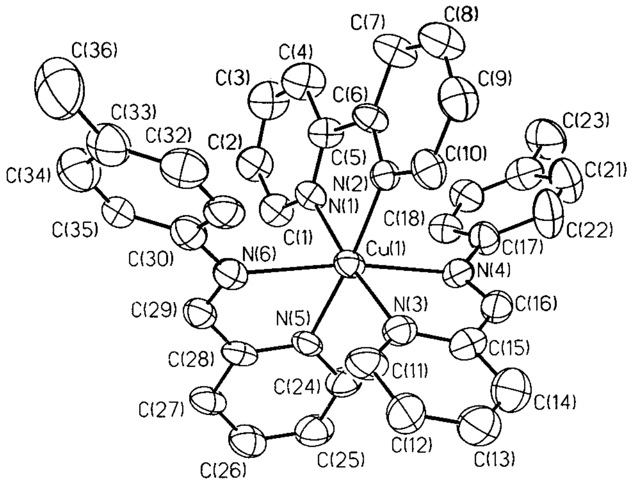

Figure 2. Thermal ellipsoid plot of the cationic complex $[Cu(bpy)(ptsb)_2]^{2+}$. Atoms are represented by their 40% probability ellipsoids.

The structural analysis of $[Cu(bpy)_3](ClO_4)_2$ revealed that the coordination geometry of the complex about the copper(II) is also distorted octahedral (Figure 3). The types of distortions are similar to those observed for $[Cu(bpy)(ptsb)_2](ClO_4)_2$. There are four similar Cu−N(py) bonds in the mixed-ligand compound on the equatorial plane, with a mean length of 2.023(9) Å, which is statistically equivalent to the four equal Cu−N(py) bonds in $[Cu(bpy)_3]^{2+}$, mean 2.031(3) Å. The remaining two Cu−N(imine) bonds are of very similar lengths: Cu−N(4) and Cu−N(6), 2.395(10) and 2.444(10) Å, respectively. By contrast, the elongated bonds in $[Cu(bpy)_3]^{2+}$ are quite different: Cu−N(4), 2.453(3) Å, and Cu−N(5), 2.237(3) Å. It may be mentioned here that the structural analysis of $[Cu(en)_3](ClO_4)_2$ showed that it is essentially nondistorted at room temperature with strong dynamic Jahn−Teller effects operative; on the other hand, the complex $[Cu(phen)_3](ClO_4)_2$ exhibits[11] a static Jahn−Teller distortion with two long bonds of similar length.

Experimental Section

Materials. Cupric salts, $CuCl_2{\cdot}2H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$, were obtained from S. D. Fine Chem. Ltd. The ligands and their silver

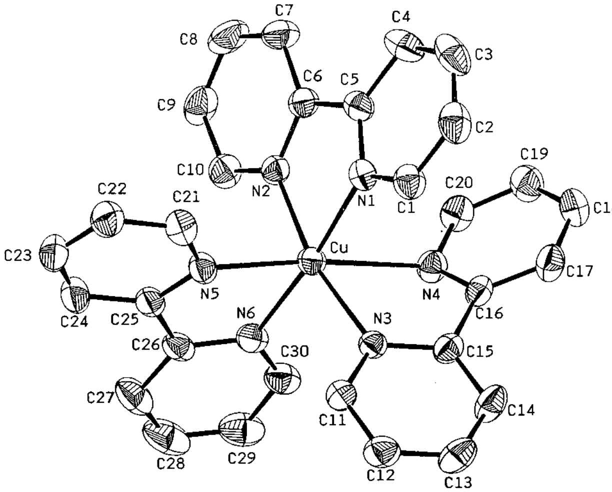

Figure 3. Thermal ellipsoid plot of the cationic complex $[Cu(bpy)_3]^{2+}$. Atoms are represented by their 40% probability ellipsoids.

complexes, $[AgL_2]X\cdot nH_2O$ (X = ClO_4, NO_3), were prepared as previously described.[12-14] All other chemicals and organic solvents used in synthesis were of reagent grade commercial materials. For electrochemical and spectral data, spectro grade CH_3CN was used. Commercial tetraethylammonium bromide was converted to tetrabutylammonium perchlorate (TBAP) as described before.[15]

Measurements. IR spectra were recorded as KBr disks (4000−300 cm^{-1}) using a Perkin-Elmer IR-783 spectrophotometer. The magnetic susceptibilities of the samples were measured on a PAR 155 vibrating sample magnetometer fitted with a Walker Scientific L 75 FBAL magnet. Microanalyses (C, H, N) were done by using a Perkin-Elmer 240C elemental analyzer. Electrochemical measurements were done using the PAR model 370-4 electrochemistry system as described before.[16] The potentials reported here are referenced to the SCE.

Preparation of Complexes. *CAUTION*! Perchlorate salts of metal complexes are explosive. Although no detonation tendencies have been observed, caution is advised and handling of only small quantities is recommended.

Dichloro(*N*-*p*-tolylpyridine-2-aldimine)copper(II), $CuCl_2$(ptsb). $CuCl_2\cdot 2H_2O$ (0.100 g, 0.60 mmol) in 30 mL of acetonitrile was mixed with L^1 (0.117 g, 0.60 mmol), and the mixture was stirred vigorously at room temperature for 1 h. The brown crystalline product was isolated by filtration, washed with ether, and finally dried in vacuo. Yield: 84%. Anal. Calcd for $CuC_{13}H_{12}N_2Cl_2$: C, 47.20; H, 3.63; N, 8.47. Found: C, 46.80; H, 3.64; N, 8.23. μ_{eff} (298 K): 1.76 μ_B. ν_{max}, cm^{-1} (KBr): $\nu_{C=N,C=C}$ 1600, 1590; ν_{Cu-Cl} 360.

The other two dichloro compounds were synthesized similarly by using appropriate ligands.

$CuCl_2$(bpy). Color: light green. Yield: 80%. Anal. Calcd for $CuC_{10}H_8N_2Cl_2$: C, 41.30; H, 2.75; N, 9.63. Found: C, 41.59; H, 2.65; N, 9.65. μ_{eff} (298 K): 1.79 μ_B. ν_{max}, cm^{-1} (KBr): $\nu_{C=N,C=C}$ 1610, 1590; ν_{Cu-Cl} 355.

$CuCl_2$(phen): Color: light green. Yield: 82%. Anal. Calcd for $CuC_{12}H_8N_2Cl_2$: C, 43.31; H, 2.41; N, 8.42. Found: C, 43.35; H, 2.50; N, 8.48. μ_{eff} (298 K): 1.75 μ_B. ν_{max}, cm^{-1} (KBr): $\nu_{C=N,C=C}$ 1605, 1590; ν_{Cu-Cl} 355.

The tris-chelated complexes were prepared by using a general procedure. A representative example is described below.

Tris(*N*-*p*-tolylpyridine-2-aldimine)copper(II) Perchlorate, $[Cu(ptsb)_3](ClO_4)_2$. A mixture of $CuCl_2$(ptsb) (0.331 g, 1 mmol) and $[Ag(ptsb)_2](ClO_4)$ (0.119 g, 2 mmol) in 30 mL of methanol was heated to reflux for 1 h. The resulting brown solution was cooled and filtered through quantitative filter paper to remove insoluble AgCl. The filtrate was then concentrated to 10 mL and left overnight at room temperature. The dark green crystals that were deposited were filtered off and washed with ether (3 × 5 mL). Yield: 76%. Anal. Calcd for $CuC_{39}H_{36}N_6O_8Cl_2$: C, 55.02; H, 4.23; N, 9.87. Found: C, 54.84; H, 4.35; N, 9.59. μ_{eff} (298 K): 1.87 μ_B. ν_{max}, cm^{-1} (KBr): $\nu_{C=N,C=C}$ 1625, 1590; ν_{ClO_4} 1100, 625.

Table 2. Crystal Data for $[Cu(bpy)(ptsb)_2](ClO_4)_2$ and $[Cu(bpy)_3](ClO_4)_2$

	$[Cu(bpy)(ptsb)_2]$-$(ClO_4)_2$	$[Cu(bpy)_3]$-$(ClO_4)_2$
formula	$CuC_{36}H_{32}N_6Cl_2O_8$	$CuC_{30}H_{25}N_6Cl_2O_{8.5}$
fw	811.12	739.00
space group	*I*2/*a*	$P\bar{1}$
a, Å	26.127(3)	7.927(3)
b, Å	10.6965(7)	11.0236(14)
c, Å	27.074(4)	18.4768(22)
α (deg)	90	79.648(10)
β (deg)	103.90(1)	89.793(17)
γ (deg)	90	82.110(17)
V, $Å^3$	7344.7(14)	1572.9(7)
Z	8	2
T, °C	23 ± 2	25
λ, Å	0.7107	0.7107
ρ_{calcd}, g cm^{-3}	1.467	1.560
transm factors, max, min	0.918, 0.836	0.939, 1.000
R	0.088[a]	0.036[a]
wR2	0.226[b]	
R_w		0.035[c]
GOF	1.05	1.80
largest difference peak and trough, e/$Å^3$	0.67, −0.63	0.30, −0.24

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

$[Cu(bpy)_3](ClO_4)_2$. Color: blue. Yield: 80%. Anal. Calcd for $CuC_{30}H_{24}N_6O_8Cl_2$: C, 49.28; H, 3.28; N, 11.50. Found: C, 49.08; H, 3.29; N, 11.47. μ_{eff} (298 K): 1.84 μ_B. ν_{max}, cm^{-1} (KBr): $\nu_{C=N,C=C}$ 1605, 1595; ν_{ClO_4} 1100, 630.

$[Cu(phen)_3](ClO_4)_2$. Color: blue. Yield: 75%. Anal. Calcd for $CuC_{36}H_{24}N_6O_8Cl_2$: C, 58.46; H, 3.25; N, 11.37. Found: C, 58.35; H, 3.15; N, 11.28. μ_{eff} (298 K): 1.79 μ_B. ν_{max}, cm^{-1} (KBr): $\nu_{C=N,C=C}$ 1610, 1590; ν_{ClO_4} 1100, 625.

Mixed-ligand complexes were also prepared similarly by using appropriate reactants at a room temperature (298 K). For example, for the synthesis of $[Cu(bpy)(ptsb)_2](ClO_4)_2$, $CuCl_2$(bpy) was reacted with 2 mol of $[Ag(ptsb)_2](ClO_4)$, and for the synthesis of $[Cu(ptsb)(bpy)_2](ClO_4)_2$, $CuCl_2$(ptsb) was reacted with hydrated $[Ag(bpy)_2](NO_3)$ and aqueous $NaClO_4$ was added for crystallization. The yields and selected characterization data are as follows.

$[Cu(bpy)(ptsb)_2](ClO_4)_2$. Color: green. Yield: 82%. Anal. Calcd for $CuC_{36}H_{32}N_6O_8Cl_2$: C, 53.30; H, 3.94; N, 10.36. Found: C, 52.96; H, 4.02; N, 10.48. μ_{eff} (298 K): 1.84 μ_B. ν_{max}, cm^{-1} (KBr): $\nu_{C=N,C=C}$ 1625, 1600; ν_{ClO_4} 1100, 625.

$[Cu(ptsb)(bpy)_2](ClO_4)_2$. Color: green. Yield: 72%. Anal. Calcd for $CuC_{33}H_{28}N_6O_8Cl_2$: C, 51.39; H, 3.63; N, 10.90. Found: C, 50.72; H, 3.69; N, 11.20. μ_{eff} (298 K): 1.77 μ_B. ν_{max}, cm^{-1} (KBr): $\nu_{C=N,C=C}$ 1630, 1600; ν_{ClO_4} 1100, 630.

$[Cu(phen)(bpy)_2](ClO_4)_2$. Color: blue. Yield: 84%. Anal. Calcd for $CuC_{32}H_{24}N_6O_8Cl_2$: C, 50.89; H, 3.18; N, 11.13. Found: C, 50.68; H, 3.27; N, 11.01. μ_{eff} (298 K): 1.78 μ_B. ν_{max}, cm^{-1} (KBr): $\nu_{C=N,C=C}$ 1620, 1600; ν_{ClO_4} 1100, 625.

$[Cu(bpy)(phen)_2](ClO_4)_2$. Color: blue. Yield: 80%. Anal. Calcd for $CuC_{34}H_{24}N_6O_8Cl_2$: C, 52.40; H, 3.08; N, 10.78. Found: C, 52.87; H, 3.35; N, 10.62. μ_{eff} (298 K): 1.84 μ_B. ν_{max}, cm^{-1} (KBr): $\nu_{C=N,C=C}$ 1620, 1600; ν_{ClO_4} 1100, 630.

X-ray Structure Determination. Single crystals of $[Cu(ptsb)_2(bpy)](ClO_4)_2$ and $[Cu(bpy)_3](ClO_4)_2$ were obtained directly from the respective reaction mixtures. The crystal data are summarized in Table 2. Tables containing full listings of atom positions, anisotropic thermal parameters, bond lengths, and bond angles are available as Supporting Information.

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[Cu(bpy)(ptsb)$_2$](ClO$_4$)$_2$. Diffraction data were collected at room temperature on a Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Crystals of this compound were found to be very weak scatterers, and the structure determination was not routine. Details of the diffraction experiment are provided as Supporting Information. In brief, intensity data were gathered slowly, in keeping with the weakness of the diffraction pattern. The data were gathered in two shells, and for the upper shell a scan time of up to 3 min/reflection was used. Absorption corrections were applied, based on measurements of 13 ψ-scans, four of which were of scattering vectors in general positions, that is, with the Eulerian angle χ not approximately 90°, so as to achieve a more complete coverage of the absorption surface of the crystal. The structure was solved by the automated Patterson interpretation routine incorporated in the package SHELXTL-PLUS[17,18] followed by difference direct methods and peak-list optimization. Hydrogen atoms were placed at calculated positions, except for the methyl hydrogen atoms, which were located in a local slant Fourier calculation. All of the hydrogen atoms were treated as riders. In the final, convergent refinement, 462 variable parameters were fitted to 4420 data and 396 restraints, giving an observation-to-parameter ratio of 10.4. All reflections with non-negative intensities were used in the refinement, and the structural model was refined to F_o^2. The weighting scheme was adjusted in such a way as to attain, as far as possible, a constant distribution of weighted deviates as a function of the magnitude of F_o.

Although it was clear at the outset of the structure determination that this was not going to be a routine case, it was hoped to be able to extract as much valid structural information as possible through the use of careful data collection and absorption correction techniques, and above all by using a statistically sound refinement method, as incorporated in the program SHELXL-93.[18] The final least-squares residuals *R* and R2 (Table 2) are rather high in comparison with those that would be derived from a routine structure determination. No unusual effects in the usual first indicators of problems, namely, the anisotropic displacement parameters of the non-hydrogen atoms and the final difference electron density, were observed. Nevertheless, for the purposes of this report this structure determination was used mainly to establish gross features of the system, and no attempts have been made to draw conclusions based on fine details.

[Cu(bpy)$_3$](ClO$_4$)$_2$. Intensity data were collected at room temperature on an Enraf-Nonius diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). The dimensions of the crystal were $0.20 \times 0.30 \times 0.50$ mm^3. A total of 4117 unique reflections were measured, of which 3267 with $I > 2\sigma(I)$ were used in structure solution refinement. The structure was solved by the heavy-atom method and refined by least squares. The final least-squares cycle, calculated with 456 parameters, gave $R = 0.036$ and $R_w = 0.035$. The goodness of fit is 1.80. The final difference Fourier map showed no unusual feature with residuals in the range -0.240 to $+0.300$ e Å^{-3}.

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Supporting Information Available: Tables of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for [Cu(bpy)(ptsb)$_2$](ClO$_4$)$_2$ and [Cu(bpy)$_3$](ClO$_4$)$_2$ and experimental details and a table of hydrogen atom coordinates for [Cu(bpy)(ptsb)$_2$](ClO$_4$)$_2$ (17 pages). Ordering information is given on any current masthead page.

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(17) Data reduction and initial structure solution were carried out on the VAX cluster with the commercial package SHELXTL-PLUS Release 4.21/V: 1990, Siemens Analytical X-ray Instruments, Inc., Madison, WI. Least-squares refinements were done by the program SHELXL-93.[18]

(18) Sheldrick, G. M. SHELXL-93: Fortran-77 program for the refinement of crystal structure from diffraction data. University of Göttingen, 1993.