The redox chemistry observed for the diaquo complexes is remarkable both for its extent without change in coordination number and for the fact that so many couples are accessible over a narrow potential range. To put the latter point into perspective, for the diaquo systems the span in potentials from the M(VI)/M(V) to the M(III)/M(II) couples is $\Delta E_{1/2} \sim$ 0.6 V. In acetonitrile, the span in potentials for the Ru(IV)/Ru(III) $Ru(bpy)_2Cl_2^{2+/+}$ couple ($E_{1/2}$ = +1.97 V vs. the SSCE) to the Ru(III)/Ru(II) $Ru(bpy)_2Cl_2^{+/0}$ couple ($E_{1/2}$ = +0.31 V) is $\Delta E_{1/2}$ = 1.66 V. The use of water as solvent and the presence of aquo ligands are both critical features in the observation of the higher oxidation state couples. Water is necessary as a proton source or sink, given the proton demands of the couples. Loss of protons from aquo ligands on oxidation results in the relative stabilization of higher oxidation states. The primary origin of the effect appears to lie in the release of $p\pi$ electron density, which enhances $p\pi(O) \rightarrow d\pi(M)$ overlap and M–O multiple bonding in the higher oxidation state.

Initial observations suggest an extensive chemistry for the higher oxidation states of Ru and Os described here. As an example, Nijs and co-workers have reported that the photooxidation of water is catalyzed on hectorite clays by the presence of *trans*-$(bpy)_2Ru(OH_2)_2^{2+}$.[14] We find that water is oxidized to oxygen by Ce(IV) in the presence of *cis*-$(bpy)_2Ru(OH_2)_2^{2+}$ but, in contrast to the case of solutions containing the dimer $[(bpy)_2(OH_2)RuORu(OH_2)(bpy)_2]^{2+}$,[5] the oxidation of water is *not* catalytic in the presence of the monomer. In addition, the electrolytic oxidation of $Cl^-$ to $Cl_2$ at pH 1 at a carbon-paste electrode is catalyzed in the presence of *cis*-$(bpy)_2Ru(OH_2)_2^{2+}$ and the active form of the catalyst system appears to be *cis*-$(bpy)_2RuO_2^{2+}$.[15]

**Acknowledgment** is made to the National Science Foundation for support of this research under Grant No. CHE-8002433.

**Registry No.** [*cis*-$(bpy)_2Ru(OH_2)_2](ClO_4)_2$, 84988-21-6; *cis*-$(bpy)_2Ru(OH)(OH_2)^{2+}$, 85027-43-6; [*cis*-$(bpy)_2Ru(O)(OH)](ClO_4)_2$, 84988-23-8; *cis*-$(bpy)_2Ru(O)_2^{2+}$, 84988-24-9; *trans*-$(bpy)_2Ru(OH_2)_2^{2+}$, 72174-10-8; *trans*-$(bpy)_2Ru(OH)(OH_2)^{2+}$, 72155-92-1; [*cis*-$(bpy)_2Os(OH_2)_2](ClO_4)_2$, 84988-26-1; *cis*-$(bpy)_2Os(OH)(OH_2)^{2+}$, 84988-27-2; *cis*-$(bpy)_2Os(O)(OH)^{2+}$, 84988-28-3; *cis*-$(bpy)_2Os(O)_2^{2+}$, 84988-29-4; [*trans*-$(bpy)_2Ru(H_2O)(O)](ClO_4)_2$, 85114-20-1; Ru, 7440-18-8; Os, 7440-04-2; $Cl^-$, 16887-00-6.

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## $Ru_5(CO)_{16}(\mu\text{-}PPh_2)(\mu_5\text{-}P)$: A Low-Nuclearity Cluster with a Partially Encapsulated Phosphide

*Sir:*

The ability of transition-metal clusters to encapsulate atoms of the main-group elements within a polyhedral cavity is now well established.[1] Interest in the chemistry of these interstitial clusters has been stimulated by the following observations: (i) The interstitial atom may influence the molecular geometry and electronic structure of the cluster.[2] (ii) There is some evidence[3] that interstitial atoms may have a key role to play in maintaining cluster integrity under the severe conditions necessary for certain catalytic reactions. (iii) Partially exposed, multisite-bound main-group atoms may exhibit unusual chemical reactivity.[4] Much of the recent effort has focused on the carbides,[5] in large part because of the possible involvement of exposed surface carbides in Fischer–Tropsch chemistry. Only a few examples of group 5 element encapsulation in clusters are known.[6,7] Two high-nuclearity anionic rhodium clusters $[Rh_9(CO)_{21}P]^{2-}$ and $[Rh_{10}(CO)_{22}P]^{3-}$, synthesized from monomeric rhodium precursors and triphenylphosphine under extreme conditions, have been characterized.[3,8] In these anions the bare phosphorus atom is truly encapsulated, being located in the center of a capped cubic antiprism or bicapped square antiprism of rhodium atoms. Chemically, these clusters are considerably more stable to degradation under high pressures of CO and hydrogen than high-nuclearity rhodium carbonyl clusters lacking the interstitial atom. To our knowledge the only example of a semiinterstitial phosphide is in the anion $[Co_6(CO)_{14}(\mu\text{-}CO)_2P]^-$, where the phosphorus atom is bonded to all six metal atoms in an open triangulated polyhedron.[9] We describe herein the synthesis and structural characterization of a novel pentanuclear cluster $Ru_5(CO)_{16}(\mu\text{-}PPh_2)(\mu_5\text{-}P)$ (**1**) containing a partially encapsulated bare phosphorus atom. This is the lowest nuclearity cluster phosphide so far characterized[10] and the first ruthenium cluster phosphide. This study demonstrates that the phosphide ligand[11] like the carbide and nitride has the ability to exist in a partially exposed low-coordinate environment. The synthetic route to this cluster phosphide, namely, benzene elimination from a $\mu$-hydrido, $\mu$-diphenylphosphido cluster $Ru_3(CO)_9(H)(PPh_2)$ under moderate conditions may be a useful strategy for the generation of other interstitial or partially encapsulated phosphides.

In the formally unsaturated 46-electron cluster $Ru_3(CO)_9(\mu\text{-}PPh_2)(\mu\text{-}H)$ (**2**) the electron deficiency of one ruthenium atom is partially satisfied by a weak interaction with one P–C(Ph) bond of the phosphido bridge.[12] This interaction suggested that the phosphido bridge might be unusually re-

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(6) A few nitride clusters are known; see: (a) Martinengo, S.; Ciani, G.; Sironi, A.; Heaton, B. T.; Mason, J. *J. Am. Chem. Soc.* **1979**, *101*, 7095. (b) Tachikawa, M.; Stein, J.; Muetterties, E. L.; Teller, R. G.; Beno, M. A.; Gebert, E.; Williams, J. M. *Ibid.* **1980**, *102*, 6648. (c) Fjare, D. E.; Gladfelter, W. L. *Ibid.* **1981**, *103*, 1572.

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(10) Very recently examples of phosphorus atoms linking two dimeric iron carbonyl fragments in a spirocyclic arrangement have been described: Huttner, G.; Gerhard, M.; Bernhard, P.; Von Seyerl, J.; Zsolnai, L. *Chem. Ber.* **1982**, *6*, 2044.

(11) The term "phosphido group" has been used rather generally to describe diorganophosphide (formally $R_2P^-$), organophosphide (formally $RP^{2-}$) and phosphide ($P^{3-}$) ligands. For the purpose of electron counting in cluster chemistry it is more appropriate to consider these ligands as 3-electron ($R_2P$), 4-electron (RP), and 5-electron (P) donors when all of the valence electrons of phosphorus are used for bonding purposes. Since the metal–phosphorus bonds in complexes of these ligands are predominantly covalent, the anionic formalism has little chemical significance.

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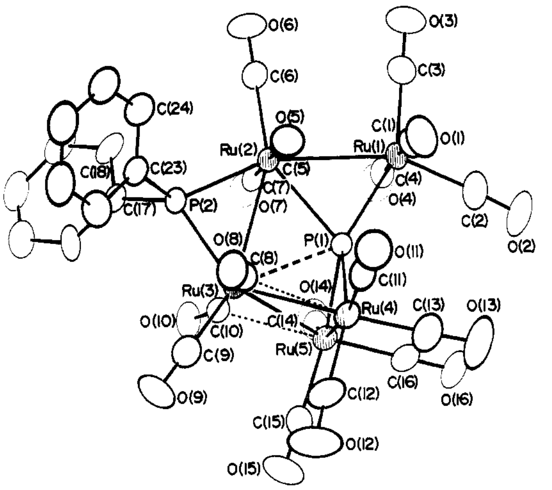

**Figure 1.** Structure of $Ru_5(CO)_{16}(\mu\text{-}PPh_2)(\mu_5\text{-}P)$ showing the atomic numbering. The weakest Ru–phosphide interaction (Ru(3)–P(1)) is shown as a broken, thick line. Semibridging carbonyl group interactions are also illustrated. Molecules of solvent are omitted.

active toward P–C bond cleavage. In heptane (25 mL) at 90 °C for 24 h, under $N_2$, $Ru_3(CO)_9(\mu\text{-}PPh_2)(\mu\text{-}H)$ (0.25 g) is converted into a mixture of products.[13] Chromatography on Florisil (eluant $C_7H_{16}$) separated two major components. The first band (red-brown) contained the phosphinidene complex $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ (40%); the fifth band (orange) afforded on evaporation and recrystallization from hot heptane red crystals (~15%) of a product **1** with $\nu$(CO) bands (in $C_7H_{16}$) 2116 w, 2076 w, 2070 m, 2050 s, 2044 m, 2024 m, 2011 m, 2000 w, 1990 w, and 1978 w cm$^{-1}$ and an AX $^{31}P$ NMR spectrum [$\delta(^{31}P)$ (85% $H_3PO_4$): 232.2 (d), 207.3 (d); $J_{PP}$ = 52 Hz). Subsequent experiments showed that **1** can be obtained in improved yield (~20%) by direct crystallization of the reaction mixture without chromatography when **1** precipitates preferentially.[14] Cluster **1** is air sensitive in solution and decomposes slowly in the solid state over several weeks. The hydride $Ru_3(CO)_{10}(\mu\text{-}PPh_2)(\mu\text{-}H)$, a precursor of the unsaturated species $Ru_3(CO)_9(\mu\text{-}PPh_2)(\mu\text{-}H)$,[12] also yields **1** in 20% yield under similar conditions. Crystals of **1** suitable for X-ray crystallography were obtained from heptane/benzene.[15] A perspective view of the molecule is shown in Figure 1. Although there are no crystallographically imposed symmetry elements, the molecule has overall idealized mirror symmetry with the mirror plane passing through Ru(1), Ru(2), Ru(3), P(1), P(2), and carbonyl groups C(2)–O(2), C(3)–O(3), C(6)–O(6), and C(9)–O(9)[18] and bisecting the Ru(4)–Ru(5) bond. The five metal atoms are joined by only five Ru–Ru bonds in an open array, the only deltahedral fragment being the Ru(3)–Ru(4)–Ru(5) triangle, where the Ru–Ru bond lengths lie within the narrow range 2.818 (1)–2.831 (1) Å. The remaining metal–metal distances are considerably longer (Ru(1)–Ru(2) = 2.921 (1) Å, Ru(2)–Ru(3) = 2.968 (1) Å) with the Ru(2)–Ru(3) edge supported by a $\mu$-$PPh_2$ group. The skeletal stereochemistry of **1** is unprecedented for a pentanuclear cluster. A few examples of open $Ru_5$ structures formally derived from closed $Ru_5$ polyhedra by cleavage of a single Ru–Ru bond are known, but these metal frameworks are fully triangulated.[19]

The phosphide atom P(1) is located "inside" the core of the five metal atoms, but owing to the open nature of the $Ru_5$ structure, this atom can be described as only partially encapsulated.[20] The phosphide does not interact equally strongly with all five metal atoms. Three Ru–P bonds (Ru(1)–P(1) = 2.383 (2) Å; Ru(4)–P(1) = 2.332 (1) Å; Ru(5)–P(1) = 2.327 (2) Å) are relatively short, one (Ru(2)–P(1) = 2.496 (2) Å) is significantly longer, and the interaction with Ru(3) (Ru(3)–P(1) = 2.632 (2) Å) is weak.[21] Thus although P(1) has a coordination number of five, the stereochemistry of this atom cannot be described in terms of a regular polyhedron. In contrast the high-nuclearity rhodium phosphides have the phosphorus atom located in a capped, square antiprismatic cavity[3,8] and in the transition-metal phosphides[24] phosphorus is found in a tricapped-trigonal-prismatic environment.

An electron count indicates that **1** is a closed-shell 80-electron molecule with five Ru–Ru bonds if the phosphide contributes all of its valence electrons to the cluster. It may be significant that carbonyl groups C(8)–O(8) and C(10)–O-

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(13) Thin-layer chromatography showed the presence of nine compounds in the mixture. The colors and solvents used for elution from a Florisil column are as follows: band 1, red-brown, $C_7H_{16}$, ($Ru_4(CO)_{13}(PPh)$); band 2 pale green, $C_7H_{16}$; band 3, cream brown, $C_7H_{16}$; band 4, pale orange, $C_7H_{16}$; band 5, orange, $C_7H_{16}$ ($Ru_5(CO)_{16}(P)(PPh_2)$); band 6, pale orange, $C_7H_{16}/C_6H_6$ 4:1; band 7, purple, $C_7H_6/C_6H_6$ 3:1; band 8, pink, $C_7H_{16}/C_6H_6$ 2:1; band 9 dark red, $C_7H_{16}/C_6H_6$ 2:1. Compounds obtained from bands 1, 5, 7, and 8 were the major products of the reaction. A full description of their identities will be published elsewhere.

(14) Anal. Calcd for $Ru_5(CO)_{16}(P)(PPh_2)$: C, 28.40; H, 0.88; P, 5.43. Found: C, 28.43; H, 0.46; P, 5.25.

(15) Crystal Data: $Ru_5(CO)_{16}(PPh_2)(P)\cdot 2C_6H_6$, space group $P2_1/c$, $a$ = 17.563 (4) Å, $b$ = 14.420 (5) Å, $c$ = 18.604 (5) Å, $\beta$ = 100.20 (2)°, $V$ = 4637 (2) Å$^3$, $\rho_{calcd}$ = 1.899 g·cm$^{-3}$, $\rho_{measd}$ = 1.92 g·cm$^{-3}$, $Z$ = 4, $\mu$(Mo K$\alpha$) = 16.89 cm$^{-1}$. Diffraction data (3.2° ≤ $2\theta$ ≤ 45°) were collected at room temperature with use of graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å) on a Syntex $P2_1$ diffractometer using $\theta$–$2\theta$ scans on a crystal of dimensions 0.14 × 0.15 × 0.19 mm. The scan speed was variable (2.93–29.3° min$^{-1}$) and the scan width from 0.8° below K$\alpha_1$ to 0.8° above K$\alpha_2$. Two standard reflections, $80\bar{4}$ and 604, monitored every 100 measurements declined in intensity by 5% over the course of data collection. Intensities were scaled accordingly. Lorentz and polarization but not absorption ($\mu$(MoK$\alpha$) = 16.89 cm$^{-1}$) corrections were applied to the derivation of structure factor amplitudes. From a total of 6085 measured unique reflections 3756 had $I \geq 3\sigma(I)$ and were used in the solution and refinement of the structure. The five ruthenium atoms were located in a Patterson function and other atoms in subsequent Fourier maps. Isotropic refinement gave an $R$ value ($R = \sum|F_o| - |F_c|/\sum|F_o|$) of 0.070. One cycle of refinement with all non-hydrogen atoms having anisotropic temperature coefficients gave $R$ = 0.039. Convergence was attained with $R$ = 0.032. A weighting scheme of the form $w^{-1} = 1.65 - 0.0097|F_o| + 0.00005|F_o|^2$ afforded $R_w$ ($R_w = [\sum w|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$), the weighted residual, of 0.036. In a final difference map, which was featureless, the maximum electron density was at the level of 0.5 e·Å$^{-3}$. A careful analysis of intra- and intermolecular contacts showed that there were no important interactions between benzene molecules of crystallization and the cluster. Shortest contacts are as follows: C(33)···O(2), 3.352 (19)Å; C(36)···O(7), 3.278 (19) Å. Scattering factors used were taken from ref 16. Corrections for anomalous dispersion were applied to the ruthenium atoms. All calculations, based on the full matrix, were carried out on IBM 4341 systems in the University of Waterloo Computing Centre. Programs used have been described in detail elsewhere.[17]

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(18) Considering the plane defined by Ru(1), Ru(2), and Ru(3) atomic displacements (Å) from this plane are as follows: P(1) (−0.028), P(2) (−0.023), C(2) (−0.011), O(2) (−0.043) C(6) (0.055), O(6) (0.126), C(9) (−0.009), O(9) (−0.023).

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(20) Although the partially encapsulated phosphide has an apparently "open" side (Figure 1), it is by no means certain that an attacking reagent will be able to penetrate the outer sphere of carbonyl groups to react with this phosphorus atom. We are currently examining the possible chemical reactivity of such partially exposed atoms.

(21) The covalent-metallic radius of ruthenium is 1.33 Å.[22] In clusters however a better value for the covalent radius of ruthenium may be half of the average Ru–Ru distance in $Ru_3(CO)_{12}$[23] (1.427 Å). With use of the latter value and the normal covalent radius of phosphorus (1.10 Å), a single covalent Ru(0)–P bond should have a length of ~2.527 Å. Thus all of the Ru–P interactions in **1** can be considered as significant.

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(10) on Ru(3), the atom most weakly bonded to P(1), semibridge to Ru(4) and Ru(5) respectively, the two metals that form the shortest bonds to the phosphide.[25] Such behavior suggests that the phosphide atom may contribute a greater share of its 5-electron donor capacity to Ru(4) and Ru(5).

We have previously noted that in **2**, a 46-electron cluster, there is an activated P-Ph group. The synthesis of **1** from **2** can then be viewed as resulting from the facile loss of phenyl groups from **2** as benzene[26] and subsequent condensation. Since the unsaturated cluster **2** is readily accessible from the 48-electron complex $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$ via thermal, photochemical, or $Me_3NO$ initiation, the strategy of benzene elimination from $\mu$-hydrido, $\mu$-diphenylphosphido complexes may well be generally applicable to the synthesis of cluster-bound phenylphosphides (PPh) or phosphides. We are exploring the wider implications of this suggestion.

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**Registry No.** **1**, 85134-96-9; **2**, 82055-65-0; $C_6H_6$, 71-43-2.

**Supplementary Material Available:** Listings of atomic positions (Table I), anisotropic thermal parameters, (Table II), bond lengths and angles (Table III), and structure factor amplitudes for $Ru_5(CO)_{16}(\mu_5\text{-}P)(\mu\text{-}PPh_2)\cdot 2C_6H_6$ (28 pages). Ordering information is given on any current masthead page.

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(25) The angles Ru(3)–C(8)–O(8) and Ru(3)–C(10)–O(10) are 159.8 (3) and 155.5 (3)°. The Ru(4)–C(8) and Ru(5)–C(10) distances are 2.578 (9) and 2.487 (9) Å.

(26) Benzene has been identified as a product of the thermolysis of **2** by GC. When the thermolysis of **2** is carried out in heptane, samples of **1** crystallized from the reaction mixture contain benzene of crystallization in the lattice.

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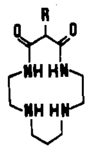
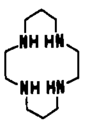
## The Deprotonated Amido vs. the Amino Group in the Stabilization of Coordinated Trivalent Copper and Nickel Cations. An Electrochemical Evaluation

*Sir:*

The tetraaza macrocycle *dioxocyclam* (**1a**) is able to incorporate in aqueous solution the copper(II) ion with simultaneous deprotonation of the two amido groups.[1] The resulting (dioxocyclamato)copper(II) complex in water undergoes chemical or anodic one-electron oxidation which occurs at a moderately positive potential, 0.65 V vs. SCE, to give an authentic Cu(III) species, which persists in water for hours.[2] This is a unique behavior for tetraaza macrocycles in spite of their renowned ability to stabilize unusually high and otherwise unstable oxidation states of the incorporated transition-metal cation.[3] In fact the fully saturated analogue of **1a**, *cyclam* (**2**), which forms water-stable $Ni^{III}$,[4] $Ag^{II}$,[5] and $Ag^{III}$[5] complexes, gives a Cu(III) species only in anhydrous acetonitrile, which persists in solution only in the time scale of the cyclic voltammetry experiment ($E_{1/2}$ for the $Cu^{II}/Cu^{III}$ redox change 0.99 V vs. $Fc^+/Fc$, in MeCN with 0.1 M $Et_4NBF_4$).[6] The stabilizing effect on the trivalent copper exerted by the deprotonated NCO group (amido or peptido) had been previously demonstrated in the broad class of copper polypeptide complexes prepared in Margerum's laboratory.[7] At this stage, it seemed interesting to compare the electrode potential for the $Cu^{II}/Cu^{III}$ redox couple in cyclam and dioxocyclamato complexes, in order to evaluate directly the effect of replacing amine groups by deprotonated amido groups in the stabilization of trivalent copper. However, such a direct comparison was prevented by the fact that the (dioxocyclamato)copper(II) complex is soluble in water but insoluble in most organic solvents such as acetonitrile.



**1a**: R = H
**1b**: R = $CH_2C_6H_5$



**2**

In this connection, we have prepared the macrocycle **1b** (benzyldioxocyclam), in which, in order to increase the solubility of the complex in organic solvents, a lipophilic benzyl group has been inserted in the carbon framework of dioxocyclam, in such a position that cannot alter the donor properties of the ligand. **1b** has been prepared according to Tabushi's procedure[8] by aminolytic condensation of diethyl 3-benzylmalonate and 1,4,8,11-tetraazaundecane in refluxing absolute ethanol (3 days, $5 \times 10^{-2}$ mol dm$^{-3}$). A soluble (benzyldioxocyclamato)copper(II) species can be obtained both in water and in acetonitrile. The complex was prepared in situ in the chosen solvent from equimolecular amounts of $Cu^{2+}$ and **1b** in the presence of base. In aqueous solution the formation of the (benzyldioxocyclamato)copper(II) complex was monitored through pH titration by standard base of **1b** ($H_2L$) in the presence of $Cu^{+2}$ in a 1:1 molar ratio. Complexation occurs with simultaneous release of two protons (from the amido groups) in the pH range 4–5.5. The constant for the equilibrium $Cu^{2+} + H_2L \rightleftharpoons CuL + 2H^+$, calculated from the computer analysis of the titration data[9] (0.25 log unit), is slightly lower than found for *dioxocyclam* (0.44). Aqueous (benzyldioxocyclamato)copper(II) presents an absorption band in the d–d spectrum centered at 20 100 cm$^{-1}$ with an extinction coefficient of 69 dm$^3$ mol$^{-1}$ cm$^{-1}$ (for (dioxocyclamato)copper(II) $\nu$(d–d) = 19 850 cm$^{-1}$, $\epsilon$ = 89 dm$^3$ mol$^{-1}$ cm$^{-1}$). CV studies performed with a carbon-paste electrode in 0.1 M KCl solution indicated that the (benzyldioxocyclamato)copper(II) complex undergoes a one-electron reversible oxidation process (to the $Cu^{III}$ complex) at an $E_{1/2}$ value (0.66 V vs. SCE) very close to that found for the dioxocyclamato analogue under the same conditions (0.65 V vs. SCE).

The (benzyldioxocyclamato)copper(II) complex can be obtained in acetonitrile solution by mixing equimolecular amounts of **1b** and copper(II) acetate. Addition of excess ligand or base (triethylamine) did not alter the intensity and energy of the d–d band, indicating that the macrocyclic com-

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(9) The computer program MINIQUAD (Sabatini, A.; Vacca, A.; Gans, G. *Talanta* **1974**, *21*, 53) was used. log *K* values for stepwise protonation are as follows: for **1b**, log $K_1$ = 9.35 ± 0.02, log $K_2$ = 5.70 ± 0.07; for **1a**, log $K_1$ = 9.52 ± 0.02, log $K_2$ = 5.79 ± 0.05. All the equilibrium data refer to 0.1 M $NaClO_4$ solutions, at 25 °C.

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