Synthesis and Crystal Structure of a Novel Copper(I) Crown Complex: A Spectrochemical Metal Ion Probe for Alkali Metal and Alkaline Earth Metal Cations

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The chemistry of crown ethers and related inclusion compounds has been of growing interest in the past two decades.[1] The interactions within transition metal−crown ether−alkali or alkaline earth metal systems have received increasing attention.[2] Although there have been numerous reports on the metal-to-ligand charge transfer (MLCT) excited state chemistry of copper(I) diimines, pioneered by McMillin and co-workers,[3] there has been no report on the study of this class of compounds as metal ion probes. In this communication, we report the synthesis, crystal structure, and the cation-binding properties of a novel copper(I) complex, $[Cu(PPh_3)_2(L_1)]BF_4$ (**1**) [L_1 = *N*-(2-pyridinylmethylene)-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclodecin-16-ylamine], consisting of a copper(I) center coordinated to a diimine ligand in conjugation with a benzo-15-crown-5 moiety. Its photophysical and electrochemical properties have also been compared with those of the uncrowned model complex $[Cu(PPh_3)_2(L_2)]BF_4$ (**2**) [L_2 = *N*-(2-pyridinylmethylene)phenylamine].

An orange prismatic crystal of **1** was used for the crystal structure determination.[4] The crystal structure of the cation of **1** with its atomic numbering is depicted in Figure 1. The Cu(I) center adopts a distorted tetrahedral geometry with the N(1)−Cu−N(2) angle, 80.0(4)°, much smaller than that expected for a tetrahedral molecule. This probably arises as a result of the steric demand of the bidentate diimine ligand. The average bond distances of Cu−P (2.2655(40) Å) and Cu−N (2.112(10) Å) are found to be typical when compared with those of similar $[Cu^I(PPh_3)_2(N\text{-}N)]^+$ complexes.[5] It is interesting to note that the least-squares planes of the pyridyl ring and the phenyl ring of the benzocrown unit exhibit a dihedral angle of *ca.* 21.7°, which would result in some loss of π-conjugation.

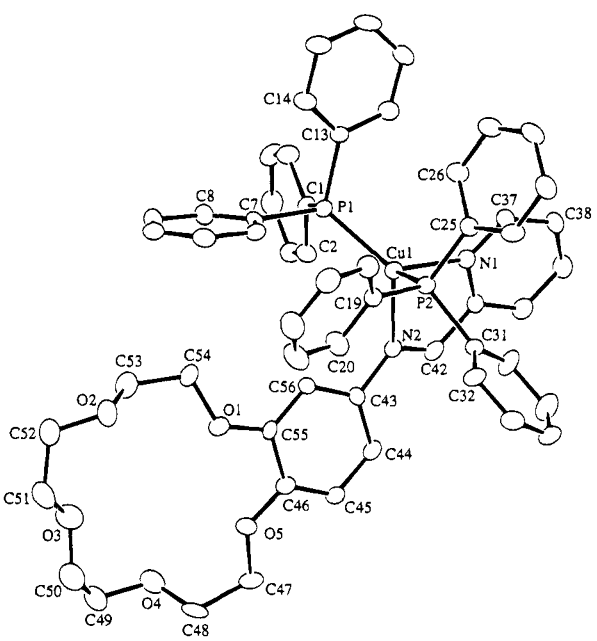

Figure 1. Perspective view of the cation of **1** with its atomic numbering, showing thermal ellipsoids at the 25% probability level. Selected bond distances (Å) and angles (deg): Cu−N(1) 2.106(10), Cu−N(2) 2.118(9), Cu−P(1) 2.263(4), Cu−P(2) 2.268(4); P(1)−Cu−P(2) 125.4(1), P(1)−Cu−N(1) 111.8(3), P(1)−Cu−N(2) 115.0(3), P(2)−Cu−N(1) 105.7(3), P(2)−Cu−N(2) 109.4(3), N(1)−Cu−N(2) 80.0(4).

Both complexes **1** and **2** show low-energy absorption bands at *ca.* 350−400 nm in MeOH, tentatively assigned as a d(Cu) → π*(L) MLCT/π(L) → π*(L) IL admixture, given the low-energy ππ* absorption of the free ligand L (for example, for L_1 in MeOH, λ_{abs} = 350 nm). The higher energy of the low-energy absorption band of **1** (374 nm in MeOH) relative to that of **2** (395 nm in MeOH) is in line with the presence of the electron-donating polyether ring in **1**, which destabilizes the π* orbital of L_1. In methanol, the MLCT/IL absorption band of **1** exhibits a significant blue shift upon addition of alkali or alkaline earth metal ions (Figure 2). These shifts were ascribed to the binding of the cations to the polyether cavity, as similar shifts were absent for the uncrowned complex **2**. Upon addition of an excess of 15-crown-5 to a methanolic solution of **1** and M^+ or M^{2+}, a complete reversible shift of the absorption band back to the original position is observed, representing a confirmatory piece of evidence for the interaction of **1** with the guest cations. A similar shift of absorption band to the blue upon addition of cations is also observed in a related Ru(II) system.[6] Sodium ion gives the largest stability constant among the investigated ions with log *K* = 2.25, obtained from a plot[7] of $[A_0/(A_0 - A)]$ versus $\{1/[Na^+]\}$ in MeOH (0.08 M $^nBu_4NBF_4$). The almost

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(1) See for example: (a) Weber, E.; Toner, J. L.; Goldberg, I.; Vogtle, F.; Laidler, D. A.; Stoddart, J. F.; Bartsch, R. A.; Liotta, C. L. *Crown Ethers and Analogs*; Wiley: New York, 1989. (b) Cooper, S. R. *Crown Compounds Toward Future Applications*; VCH: Weinheim, Germany, 1992. (c) Dietrich, B.; Viout, P.; Lehn, J. M. *Macrocyclic Chemistry Aspects of Organic and Inorganic Supramolecular Chemistry*; VCH: Weinheim, Germany, 1993.

(2) See for example: (a) Yoon, D. I.; Berg-Brennan, C. A.; Lu, H.; Hupp, J. T. *Inorg. Chem.* **1992**, *31*, 3192. (b) Beer, P. D. *Adv. Inorg. Chem.* **1992**, *39*, 79 and references therein.

(3) (a) Buckner, M. T.; McMillin, D. R. *J. Chem. Soc., Chem. Commun.* **1978**, 759. (b) Buckner, M. T.; Matthews, T. G.; Lytle, F. E.; McMillin, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 5846. (c) Rader, R. A.; McMillin, D. R.; Buckner, M. T.; Matthews, T. G.; Casadonte, D. J.; Lengel, R. K.; Whittaker, S. B.; Darmon, L. M.; Lytle, F. E. *J. Am. Chem. Soc.* **1981**, *103*, 5906. (d) McMillin, D. R.; Kirchhoff, J. R.; Goodwin, K. V. *Coord. Chem. Rev.* **1985**, *64*, 83 and references therein. (e) Palmer, C. E. A.; McMillin, D. R. *Inorg. Chem.* **1987**, *26*, 3837.

(4) Crystal data: $CuP_2O_5N_2C_{56}H_{54}{}^+BF_4{}^-\cdot CH_2Cl_2$; orange prism, dimensions 0.10 × 0.15 × 0.15 mm), fw = 1132.28, monoclinic, $P2_1/n$, a = 15.166(3) Å, b = 16.771(3) Å, c = 22.339(3) Å, β = 107.01(1)°, V = 5433.3(1.0) Å^3, Z = 4, D_c = 1.384 g cm^{-3}, T = 298 K. Convergence for 637 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.008F_o^2)^2]$ for 3478 reflections with $I \geq 3\sigma(I)$ was reached at R = 0.080 and R_w = 0.079.

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(6) Beer, P. D.; Kocian, O.; Mortimer, R. J.; Ridgway, C. *J. Chem. Soc., Dalton Trans.* **1993**, 2629.

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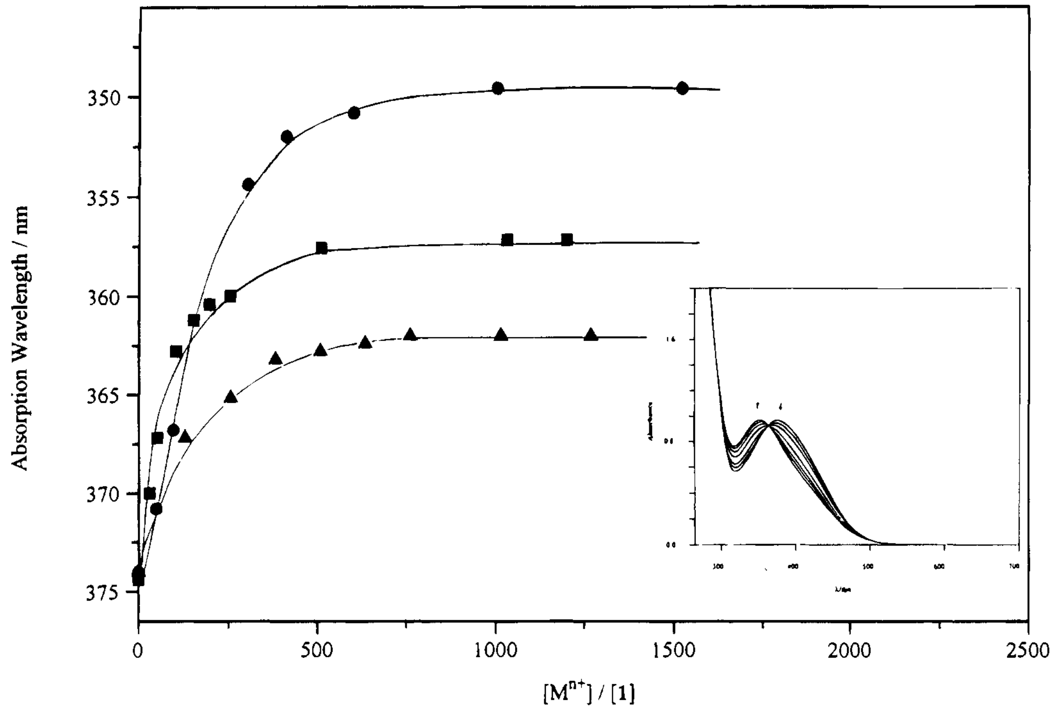

Figure 2. Wavelength of the MLCT/IL absorption band of **1** vs the [M^{n+}]/[**1**] ratio for M^{n+} = Na$^+$ (■), Ba^{2+} (●), K$^+$ (▲). The insert shows the electronic absorption spectrum of **1** in anhydrous methanol (106.0 μM) upon addition of 0, 5, 10, 21, 32, 44, 64 mM Ba(ClO$_4$)$_2$.

perfect linearity of the fit (R = 0.998) is supportive of a stoichiometry of 1:1. This is in accordance with the well-known preference of benzo-15-crown-5 for the sodium ion with its appropriate cavity size.[8] With Ba^{2+}, a log K = 1.72 and a stoichiometry of 1:1 were obtained. In the case of K$^+$, no satisfactory fit with [$A_0/(A_0 - A)$] versus {1/[K$^+$]} (based on the stoichiometry of a 1:1 model) was found. The plots are consistent with the formation of two complexes of stoichiometries 1:2 (K$^+$:**1**) and 1:1. This is further supported by the absence of a well-defined isosbestic point in the uv–visible absorption spectral traces. A similar 1:2 sandwich binding model has been commonly observed in other K$^+$–(benzo-15-crown-5) systems.[9]

Both **1** and **2** show dual luminescence with a high-energy intraligand emission and a lower energy MLCT orange-red luminescence upon irradiation of light with λ > 350 nm (**1**, 639 nm in MeOH; **2**, 675 nm in MeOH). Surprisingly, unlike most Cu(I) diimine complexes, which have been found to be nonemissive in donor solvents such as MeOH owing to solvent-induced quenching via exciplex formation,[3d,10] both **1** and **2** are emissive in MeOH. It is likely that in **1** and **2**, the steric bulk of L$_1$, L$_2$, and triphenylphosphine protects the metal center from attack by the solvent molecules.[3d] Upon addition of alkali and alkaline earth metal ions, the emission intensity is enhanced. However, attempts to utilize these data for quantitative work were unsuccessful as a result of the masking effect of the more intense higher energy phosphine intraligand emission.

Cyclic voltammetric studies of both **1** and **2** in CH$_2$Cl$_2$ (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) show an irreversible metal-centered oxidation wave (**1**, +1.27 V, **2**, +1.34 V vs SCE) and a quasi-reversible ligand-centered reduction couple (**1**, −1.28 V, **2**, −1.26 V vs SCE). The more negative value of the ligand-based reduction potential of **1** indicates the reduced ease of L$_1$ reduction compared to that of L$_2$, which is in accordance with the higher π^* orbital energy of L$_1$. The ligand-based reduction couple showed only a small shift in potential (*ca.* 0.05 V) upon the addition of an excess of sodium ions. However, due to the quasi-reversible nature of the reduction, investigation in the ion binding properties of **1** by cyclic voltammetry was not practicable under the influence of other factors such as those of kinetic origin.

The present work demonstrates the ability of a diimine ligand conjugated with a crown ether to act as a bridging unit between a soft transition metal center and a hard group I/IIA metal ion. The cation binding ability of **1** could serve as a model for the design and development of efficient alkali/alkaline earth metal ion probes. Extension of work in this area involving other transition metal centers is in progress.

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Supporting Information Available: Text giving details of the synthesis and characterization of L$_1$, **1**, and **2** and the structure solution and tables giving photophysical and electrochemical data for **1** and **2**, crystal data, atomic coordinates, isotropic thermal parameters, anisotropic displacement parameters, and selected bond distances and angles (18 pages). Ordering information is given on any current masthead page.

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