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Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
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Chang-Lin Chuang[a]; Kitae Lim[a]; James W. Canary[a]
[a] Department of Chemistry, New York University, New York, NY

To cite this Article Chuang, Chang-Lin , Lim, Kitae and Canary, James W.(1995) 'The influence of phenyl substituents on the redox potentials of sterically hindered tripodal ligand/copper complexes', Supramolecular Chemistry, 5: 1, 39 — 43
To link to this Article: DOI: 10.1080/10610279508029886
URL: http://dx.doi.org/10.1080/10610279508029886

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SUPRAMOLECULAR CHEMISTRY, Vol. 5, pp. 39–43
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The influence of phenyl substituents on the redox potentials of sterically hindered tripodal ligand/copper complexes

CHANG-LIN CHUANG, KITAE LIM and JAMES W. CANARY*

Department of Chemistry, New York University, Washington Square, New York, NY 10003

(Received June 6, 1994)

The structural characterization of Cu(I) and Cu(II) complexes of *tris(6-phenyl-2-pyridylmethyl)amine* (tppa), a derivative of the known tris(2-pyridylmethyl)amine (tpa), was recently reported. The phenyl substituents in [Cu(tppa)AN]$(ClO_4)_2$ stabilize the Cu(I) state by 300–480 mV relative to [Cu(tpa)AN]$(ClO_4)_2$. Reported here is the synthesis of the compounds bis(2-pyridylmethyl)-6-phenyl-2-pyridylmethylamine (Phtpa) and bis(6-phenyl-2-pyridylmethyl)-2-pyridylmethylamine (Ph_2tpa) and the synthesis and cyclic voltammetry studies of their Cu(II) perchlorate complexes. The mechanism by which the phenyl groups increase the redox potential was found to be solvent-dependent: in AN, the increase in potential is primarily due to reduced local dielectric; in IBN, DMF, and DMA, the steric interaction between coordinated solvent and the phenyl substituents becomes important. The redox behavior of these complexes is consistent with anticipated modes of binding of solvent molecules in the inner sphere of the Cu(II) complexes.

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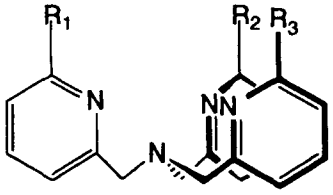
INTRODUCTION

Recently, host-guest complexes have been reported in which metal cations play an integral role in the recognition of organic substrates.[1-8] Several receptors,[9-12] vesicles,[13] and other supramolecular structures that can be activated or deactivated by means of redox changes have also been reported.[14] We recently described a tripodal ligand/copper complex that binds a solvent (guest) molecule in an electrophilic coordination site in its oxidized state.[15] In its reduced state, no binding occurs. Thus, one-electron oxidation of the metal causes a series of carbon-carbon single bond rotations that expose a site for guest binding. The overall change in ligand conformation is reminiscent of the blossoming of a flower (anthesis).

A strong dependence of the redox potential on the size and shape of the solvent was also observed. It was concluded that the complex preferentially binds small solvent molecules. However, in all solvents, a more positive redox potential (more stable Cu(I) state) was observed in the tppa complex than the tpa complex. In view of these findings, two questions arose: (1) Why do the phenyl substituents increase the redox potential of the complex in all solvents studied? and (2) What is the magnitude of each contributing factor? The purpose of this paper is to address these questions.

Our interest in metal complexes of tppa relates in part to the role of active-site amino acids in metalloproteins that contribute to binding and catalysis by means other than metal coordination. For example, blue copper proteins (e.g. azurin, plastocyanin) are efficient electron shuttles involved in photosynthesis. They greatly stabilize the Cu(I) redox state by two mechanisms: (a) by enforcing ligand geometries complementary to the Cu(I) state, resulting in a distorted Cu(II) state of the metallo-



1 R_1=R_2=R_3=H; tpa
2 R_1=Ph; R_2=R_3=H; Phtpa
3 R_1=R_2=Ph; R_3=H; Ph_2tpa
4 R_1=R_2=R_3=Ph; tppa

5 [Cu(tpa)(AN)]$(ClO_4)_2$
6 [Cu(Phtpa)(AN)]$(ClO_4)_2$
7 [Cu(Ph_2tpa)(AN)]$(ClO_4)_2$
8 [Cu(tppa)(AN)]$(ClO_4)_2$
9 [Cu(tppa)]BPh_4

*To whom correspondence should be addressed.

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protein;[16] and (b) by mediating the effective local dielectric to favor the Cu(I) state, by using hydrophobic amino acid side chains.[17] In the case of complexes **8** and **9**, mechanism (a) does not operate since the distortion of the copper ion coordination sphere is opposite from that of blue copper proteins; the Cu(I) state is distorted while the Cu(II) state is not. Thus, studies of **4** may provide an opportunity to probe the magnitude of the effect of local dielectric, mechanism (b). In order to probe further the basis of the increased redox potential of **8**, we prepared $Cu(ClO_4)_2$ complexes of Phtpa **2** and Ph_2tpa **3**. We reasoned that, if the increased redox potential was attributable to environmental effects, then an increase directly proportional to the number of phenyl substituents would be observed. A nonlinear response would suggest that other factors contribute to the effect, particularly those related to inner-sphere coordination or a change in the mechanism of the redox process.

RESULTS

Synthesis. Compound **2** was prepared (Figure 1) beginning with the Suzuki coupling of aldehyde **10** with phenylboronic acid[18,19] to form biaryl **11**. The primary amine **12** was prepared via the phthalimide. Reaction of **12** with commercially available picolyl chloride provided **2** in 83% yield. This reaction fails in aqueous NaOH[20], but $NaHCO_3$/MeOH conditions provide satisfactory yield. For **3**, excess **11** was reacted with picolyl amine and $NaCNBH_3$. Crystals of **6** and of **7** were isolated as AN complexes from reaction of $Cu(ClO_4)_2$ with the free ligand in AN/water. Tpa **1** and tppa **4** were prepared as described, as were the $[Cu(tpa)(AN)](ClO_4)_2$ **5**, $[Cu(tppa)(AN)](ClO_4)_2$ **8**, and $[Cu(tppa)]BPh_4$ **9**.[15,20]

Cyclic Voltammetry. Cyclic voltammetry experiments were carried out in a standard three-electrode apparatus with a glassy carbon working electrode, a nonaqueous reference electrode (0.1 M $AgNO_3$ in AN), and a Pt wire auxiliary electrode. Experiments were run in 0.1 M n-Bu_4NPF_6 as supporting electrolyte in AN, DMF, DMA, and IBN with scan rates of 50 mV or 100 mV. The observed potentials are listed in Table 1, as are the potentials previously determined for **5** and **8**. The complexes all undergo quasi-reversible one-electron oxidation with current ratios i_c/i_a approaching unity. The electrochemical experiments were conducted at least twice. The positions of the waves were compared to the potential of the ferrocenium/ferrocene (Fc^+/Fc) couple (E°=0.400 V vs NHE). Observed potentials for the tppa complexes were the same regardless of initial oxidation state (Cu(I) or Cu(II) complex).

Table 1 Redox Potentials (mV, vs. N.H.E.)

Compound	*AN**	*IBN*	*DMF*	*DMA*
$[Cu(tpa)](ClO_4)_2$**	0.00	-260	-230	-230
$[Cu(Phtpa)](ClO_4)_2$***	90	-60	-140	-110
$[Cu(Ph_2tpa)](ClO_4)_2$***	200	100	-40	20
$[Cu(tppa)](ClO_4)_2$**	300	220	120	240

*AN=CH_3CN, IBN=$(CH_3)_2CHCN$, DMF=$(CH_3)_2NCHO$, DMA=$(CH_3)_2NCOCH_3$
**Reference 15.
***This work.

DISCUSSION

Structures. We recently reported x-ray crystal structures of $[Cu(tppa)(AN)](ClO_4)_2$ **8** and $[Cu(tppa)]BPh_4$ **9** (Figure 2).[15] These structures are crucial to understanding the present chemistry and will be summarized here. The x-ray structure of $[Cu(tpa)(AN)](ClO_4)_2$ was reported previously[21] and is very similar to that of **8**.

In the Cu(I) complex **9**, two phenyl rings stack in a "T" configuration as observed in solid benzene and protein side chains (Figure 3).[22] The Cu(I) is completely en-

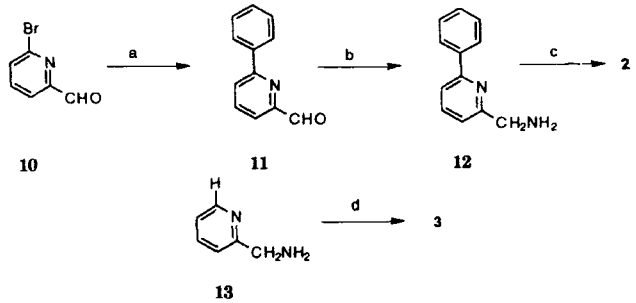

Figure 1 a) $PhB(OH)_2$, $Pd(PPh_3)_4$, 65–90%. b) $NaCNBH_3$, 67%; $SOCl_2$, 90%; potassium phthalimide, Na_2CO_3, 78%; 6 N HCl, 80%. c) 2 eq. picolyl chloride hydrochloride, $NaHCO_3$, MeOH/H_2O, 83%. d) 2 eq. compound **11**, $NaCNBH_3$, 30%.

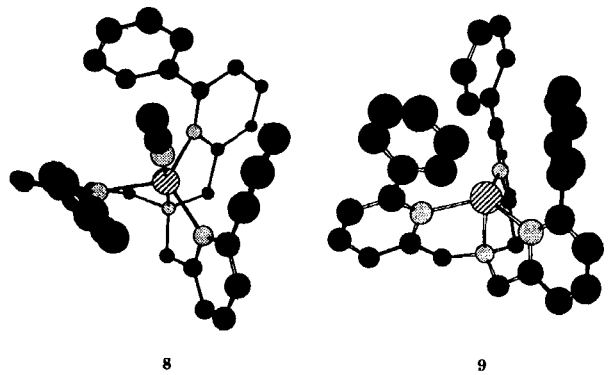

Figure 2 Molecular models of cationic portions of complexes **8** and **9**, as observed in x-ray crystal structures.[15] View is from above the phenyl substituents looking down upon the coordination sphere of the copper ion. The copper ion in **9** is ligated by four nitrogens of the tppa ligand. The copper ion in **8** is ligated by the same tppa nitrogen atoms as well as by the nitrogen atom of an AN molecule.

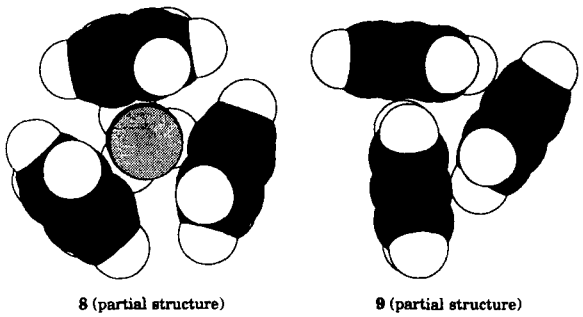

Figure 3 Space-filling models of the phenyl substituents (view directly opposite that shown in Figure 2; much of the complex has been z-clipped for clarity) as observed in the x-ray structures of complexes **8** and **9**.[15] In **9**, the phenyl groups are arranged in an imbricate fashion, with a slight distortion to allow T-stacking. In **8**, the phenyl groups are valvate, and fully enclose the metal-coordinated acetonitrile guest.

capsulated by the tppa ligand. In **8**, the ligand contains a cavity in which an AN solvate molecule is bound (Figure 3). To create the cavity, the ligand undergoes a helical twist. The average angle between the best axis of the pyridine-phenyl "arms" and the Cu-N1 bond in **9** is 14.8°; in **8** it is 36.3°. There is little change in the dihedral angles defined by the planes of the pyridines and phenyls in the two complexes (average 40° vs. 38°). The overall change in the ligand structure in going from **9** to **8** is reminiscent of anthesis, the blossoming of a flower. Indeed, the arrangement of the phenyl substituents in the two complexes is analogous to the packing of petals in a flower blossom. In **8**, the phenyl groups are arranged in an imbricate fashion, each overlapping another while being overlapped by a third. In **9**, the phenyl substituents are arranged edge-to-edge, or valvate.

Electrochemistry. Our study originated with the observation that Cu(II) complexes of tppa were easily reduced during electrospray ionization for mass spectral analysis. We were quite surprised that reduction would occur during the positive ion mode of electrospray ionization, which involves electrochemically oxidizing conditions. However, others have also reported that coordination complexes can be reduced during mass spectral analysis under these conditions,[23,24] with the electrons apparently originating from the decomposition of substances in the solution being analyzed. In any case, the published reports suggest that reduction under ESI conditions can roughly correlate with the redox potential of the coordination complex.[23,24] We therefore examined the redox behavior by established methods.

Since redox potentials of Cu(II) complexes of **1** have been reported to be quite negative,[25] we were surprised to find that **8** was easily reduced. Figure 4a shows the redox potential for the $Cu(ClO_4)_2$ complexes Ph_ntpa (n=0–3) in AN. The observed linear relationship is apparently possible because of the small size of the AN molecule and its ability to accommodate the steric re-

Figure 4a

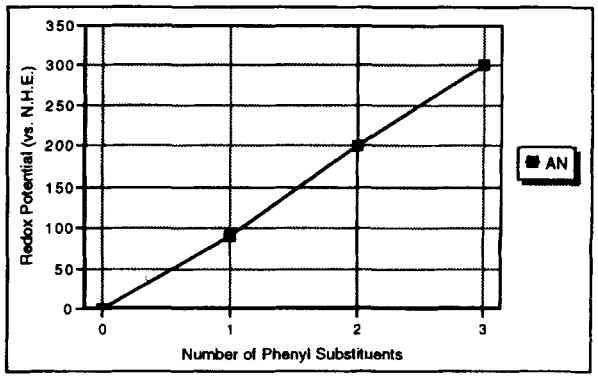

Figure 4b

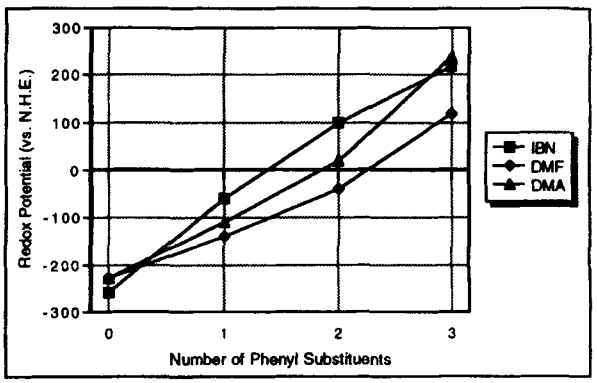

Figure 4 Plots of the observed redox potential vs. the number of ligand phenyl substituents in several solvents. In AN (Fig. 4a), addition of one phenyl group to the ligand results in a redox potential increase of 90±5 mV. Such a generalization cannot be made for the other solvents, since the relationship between the number of phenyl substituents and redox potential is not linear (Fig. 4b). In IBN, a larger difference is observed between $[Cu(tpa)]^{2+}$ and $[Cu(Phtpa)]^{2+}$ than between $[Cu(Ph_2tpa)]^{2+}$ and $[Cu(tppa)]^{2+}$. In DMF and DMA, the opposite trend occurs. These differences correspond to expected size, shape and structure/electronic parameters involved in solvent coordination.

strictions imposed by the phenyl substituents. All of the other solvents investigated gave distinctly different results. There is clearly no direct relationship with bulk solvent, since AN, DMF, and DMA have nearly equal dielectric constants.[26] Figure 4b shows the data for IBN, DMF, and DMA. Clearly, changes in oxidation state in these solvents are affected by steric interactions between the tripodal ligand and the coordinated solvent molecule. Examination of molecular models indicated that none of these solvents could replace the AN molecule in **8** without significantly distorting the coordination geometry of the metal ion.

The increase in redox potential with the number of ligand phenyl groups can occur due to either relative stabilization of the Cu(I) state or destabilization of the Cu(II) state. The specific mechanisms considered here include: 1) steric interaction between the phenyl groups of the tripodal ligand and coordinated solvent molecules in the

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Cu(II) state; 2) inductive effect of phenyl groups; and 3) shielding of the metal ion charge from solvent dielectric by the nonpolar phenyl substituents.

After obtaining redox data on **5** and **8** but prior to obtaining crystallographic data,[15] it seemed likely that the positive redox potential of **8** could be attributable to a *distortion of the* Cu(II) state by the sterically demanding phenyl substituents. Cu(II) complexes of tpa were known to be five-coordinate, whereas Cu(I) complexes were expected to be four-coordinate, as has been observed with related ligands.[27] If the phenyl groups occluded the fifth coordination site, the complex should be easier to reduce. However, while some close contacts are observed in the x-ray structure of **8**,[15] the nitrogen-copper bond lengths and angles appear unperturbed compared with the x-ray structure of **5**.[21] If anything, the x-ray structures of **8** and **9** indicate that is the Cu(I) ion that appears to be distorted in this redox couple.

Another possible influence is the electron withdrawing effect of the phenyl substituents on the pyridine rings. Electron withdrawing groups can reduce the σ-donor ability of the ligand, which would increase the redox potential. However, these effects have been examined in bipyridyl ligands, and phenyl groups are known to exert only small inductive effects as substituents.[28] Sorrell studied structurally related tripodal ligand/copper complexes,[29] and found that alkyl group substitution on the ligand resulted in redox changes similar to those observed with phenyl groups in this study.

A third possible explanation is the reduction in the local dielectric due to shielding of the copper atom from the polar solvent by the nonpolar phenyl groups.[29,30] A less polar environment near the metal atom would favor a lower atomic change. In **5–8**, the phenyl groups only shield one hemisphere around the metal ion. However, the remaining hemisphere is already somewhat shielded by the tripodal ligand. Unfortunately, the complexes are not sufficiently soluble for studies in a wider variety of solvents.

There may be other small contributing factors to the change in redox potential. For example, the phenyl substituents may stablilize the Cu(I) state of the redox couple by T-stacking in the complexes of tppa and Ph_2tpa (although this would not explain the stabilization that is also observed in Phtpa). Furthermore, our discussion thus far has been limited to the data obtained in AN, in which a nearly linear change was observed. In the other three solvents studied, a detailed analysis cannot be made due to insufficient structural data on the complexes.

From these experiments, we conclude that environmental effects are the most likely explanation for the positive reduction potential of **8** in AN. Each phenyl substituent in Ph_ntpa contributes 100 mV toward the stability of the Cu(I) state under the experimental conditions. However, the redox behavior in the other solvents is more complex and probably involves inner-sphere effects.

MATERIALS AND METHODS

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. The following were distilled under nitrogen before use: methanol from $Mg(OCH_3)_2$; DMF and DMA from sodium (distilled under reduced pressure); AN and IBN from CaH_2. Melting points were obtained with a MEL-TEMP II apparatus and are uncorrected. Analytical glassware was soaked in a concentrated H_2SO_4 bath and rinsed with deionized water before use. Electoanalytical measurements were performed using a EG&G Model 273 potentiostat. ESI-MS experiments were performed on a Vestec Model 200 Electrospray Mass Spectrometer. The general conditions of ESI-MS were: needle voltage = 2.2 kV, ESI chamber temp = 55°C, repeller voltage = 200 V, lens temp = 120°C, block temp = 250°C. Syringe pump injection, flow rate = 4 µl/min. All mass spectra are reported as the tallest peak of the isotope envelope with relative intensities in parentheses. All observed masses correspond to calculated masses ±1 mass unit. Impurities were consistently observed corresponding to [Cu(ligand)X]$^+$ where X=F, Cl, $OCOCH_3$. Control experiments indicate that the mass species derive from salts present in the source of the spectrometer.

[Cu(tpa)AN](ClO$_4$)$_2$ **5**. The complex was synthesized as described[21] except that it was purified by recrystallization from methanol/ether. The presence of $[Cu(tpa)Cl]ClO_4$ was checked by UV/Vis spectroscopy, since only the latter complex shows a band at 330 nm. (**Caution**: Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantity and with caution.)[31] UV (AN, nm): λ_{max} = 298 (2100), 853 (360). Electrospray MS: 261 (46), 412 (100).

[Cu(Phtpa)(AN)](ClO$_4$)$_2$ **6**. A solution of $Cu(ClO_4)_2$ (50.3 mg) in water (2 mL) was added dropwise via pipet to a solution of **2** in AN (7 mL). Methanol (2–3 drops) was added to facilitate dissolution. Upon standing at ambient temperature, blue crystals formed (mp >180°C). Anal. (mass %): Calculated for $C_{26}H_{25}N_5O_8Cl_2Cu$: C 46.61 H 3.76 N 10.45. Found: C 46.86 H 3.64 N 10.70. UV (AN, nm): λ_{max} = 305 (2900), 835 (240). Electrospray MS: 428 (100), 464 (34), 488 (70), 505 (70).

[Cu(Ph$_2$tpa)(AN)](ClO$_4$)$_2$ **7**. A solution of $Cu(ClO_4)_2$ (50.3 mg) in water (2 mL) was added dropwise via pipet to a solution of **3** in AN (7 mL). Upon standing at ambient temperature, blue-green crystals formed. The rate of precipitation could be accelerated by dilution of the solu-

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tion with water. Anal. (mass %): Calculated for $C_{32}H_{29}N_5CuCl_2O_8$: C 51.52 H 3.92 N 9.39. Found: C 51.15 H 4.27 N 9.42. UV (AN, nm): λ_{max} = 300 (5900), 819 (300). Electrospray MS: 504 (100), 540 (9), 564 (22), 604 (12). mp 196°C.

[Cu(tppa)(AN)](ClO$_4$)$_2$ **8**. This compound was prepared as previously described.[15] Electrospray MS: 519 (88), 580 (100), 600 (58), 616 (4), 640 (26).

ACKNOWLEDGMENTS

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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