[n-Bu₄N][TrisO₃]. Metathesis of LiTrisO₃ (19.5 mmol) with [n-Bu₄N]I (19.5 mmol) in MeOH for 4 h followed by filtration, concentration of the filtrate by rotary evaporation, and addition of hexane produced the product [n-Bu₄N][TrisO₃], mp 300 °C dec, in 50% yield. Anal. Calcd for C₅₅H₆₆O₃NP₃: C, 74.19; H, 7.75; P, 10.83. Found: C, 72.99; H, 7.80; P, 10.79.

Li{[Ph₂P(O)]₂[Ph₂P(S)]C}, Li⁺TrisO₂S⁻. HTrisO₂S (16.7 g, 26.9 mmol) reacted as described above with LiOMe. Addition of Et₂O gave the desired product, mp >360 °C, in 82% yield. Anal. Calcd for C₃₇H₃₀LiO₂P₃S: C, 69.59; H, 4.74; P, 14.55. Found: C, 68.91; H, 4.99; P, 14.48.

[n-Bu₄N][TrisO₂S]. Metathesis of LiTrisO₂S and [n-Bu₄N]I in MeOH gave the product, mp 335 °C, in 51% yield. Anal. Calcd for C₅₃H₆₆NO₂P₃S: C, 72.83; H, 7.61; P, 10.63. Found: C, 72.59; H, 7.81; P, 10.61.

Li{[Ph₂P(O)][Ph₂P(S)]₂C}, Li⁺TrisOS₂⁻. HTrisOS₂ (9.42 g, 14.5 mmol) and LiOMe (0.82 g, 22 mmol) reacted as described above. Addition of Et₂O gave the desired product, mp >360 °C, in 73% yield. Anal. Calcd for C₃₇H₃₀LiOP₃S₂: C, 67.89; H, 4.62; P, 14.20. Found: C, 67.39; H, 4.91; P, 14.23.

[(MePh₂P)₃C]I₂, TrisMe₃²⁺I⁻₂. HTris (2.23 g, 3.94 mmole was dissolved in 100 mL of CH₂Cl₂, and the mixture was slowly added under N₂ to a suspension of LiOMe (0.224 g, 50% excess) in 3 mL of MeOH.

All solvents were thoroughly deoxygenated. After the mixture was stirred for 2 h at room temperature, MeI (4 mL, 5-fold excess) was added. The reaction vessel was tightly closed, and the mixture was stirred for about 20 h. The mixture was filtered to remove excess LiOMe, and the filtrate was concentrated via rotary evaporation to a yellowish oil. Addition of CH₂Cl₂/hexane produced colorless crystals, mp 298 °C dec, in 66% yield. ³¹P NMR (ppm): 19.3 (s (lit.²⁷ 19.9), ²J(P–P) = 22 ± 0.5 Hz (from ¹³C AXX′₂ spin system)). ¹H NMR (ppm): CH₃, 2.76 ("filled in" doublet, N = 12.5 Hz (lit.²⁷ 2.62, N = 19.2 Hz)). ¹³C NMR (ppm): CP₃, 6.7 (q, ¹J(P–C) = 84 Hz (lit.²⁷ 10.8 q, J = 82 Hz))); PCH₃, 17.8 (¹J(P–C) = 60.6 Hz); PhC₁, 123.5 (¹J(P–C) = 88.7 Hz, ³J(P–C) = 2.6 Hz); PhC₂,₆, 133.6 (²J(P–C) = 10.8 Hz); PhC₃,₅, 130.4 (3J(P–C) = 12.7 Hz); PhC₄, 134.1.

(32) N = (ⁿJ + ⁿ⁺²J), where n = 2 for the ortho carbons and n = 3 for the meta carbons of the phenyl group: Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; p 141.

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A Chronoamperometric and Cyclic Voltammetric Study of the Sequential Two-Electron-Transfer Process Induced in Binuclear Copper(II) 1,3,5-Triketonates by Simple Cations. Effect of Cation Variation and Ligand Substitution on the Transfer of Two Electrons at Very Similar Potentials

R. L. Lintvedt,* B. A. Schoenfelner, and K. A. Rupp

Simple cations of the alkali and alkaline-earth metals have been shown to induce the reversible, sequential transfer of two electrons at nearly the same potential in bis(1,3,5-triketonato)dicopper(II) complexes and their diamine Schiff bases. They also cause a positive shift in redox potentials of 300–400 mV. These effects are interpreted as being due to the complexation of the cations to the electron pairs of the terminally coordinated oxygens in the reduced species, [CuᴵᴵCuᴵL₂]⁻ and [CuᴵCuᴵL₂]²⁻. This is supported by the fact that no cation effect is observed when a terminal ketonate oxygen is replaced by an imine nitrogen from C₂H₅NH₂, for example. Presence of the amine group precludes electron-pair donation to the added cation. The potential shift is highly correlated to the size/charge ratio of the cations such that Ba²⁺ > Li⁺ > Na⁺ > K⁺ > Rb⁺ > Cs⁺. This is also consistent with a complexation phenomenon.

Introduction

In previous papers[1] we reported the observation that, in the absence of alkali-metal cations, bis(1,3,5-triketonato)dicopper(II) complexes undergo the reversible transfer of one electron at about −0.9 V vs. SCE, with no further reduction before about −1.8 V. Addition of Na⁺ or Li⁺ to the electrochemical cell results in two significant changes in the electrochemistry of these binuclear Cu(II) molecules. First, the electron transfer is switched from simple one-electron transfer to the sequential, reversible transfer of two electrons at very nearly the same potential, i.e. $E_1 - E_2 \cong 30$ mV. Second, the reduction potential is shifted to more positive values by about 300–400 mV and the shift is a function of the cation, with Li⁺ > Na⁺. These effects are consistent with some type of complexation/association of the added cation with the reduced complex. The present study was undertaken to in-

vestigate the nature of this interaction.

Experimental Section

Compounds. The bis(1,3,5-triketonato)dicopper(II) complexes used in this study have been prepared and characterized previously.[2]

Cu₂(PAAea)₂. The ligand was prepared by adding 1.5 mL (8.3 mmol) of 2,2-dimethyl-3,5,7-octanetrione[3] (H₂PAA) and one drop of concentrated H₂SO₄ to 100 mL of refluxing methanol. Ethylamine (9.6 mmol) was added and the solution refluxed for 0.33 h. Slow evaporation of the solvent yielded a yellow oil, which was used without further purification. The oil was dissolved in 10 mL of methanol and added dropwise to a refluxing solution of 1.66 g (8.3 mmol) of Cu₂C₂H₃O₂·H₂O in 100 mL of methanol. Upon addition of 2.0 mL (14.0 mmol) of triethylamine, a

(1) (a) Lintvedt, R. L.; Ranger, G.; Schoenfelner, B. A. *Inorg. Chem.* **1984**, *23*, 688. (b) Lintvedt, R. L.; Kramer, L. S. *Inorg. Chem.* **1983**, *22*, 796.

(2) Lintvedt, R. L.; Glick, M. D.; Tomlonovic, B. K.; Gavel, D. P. *Inorg. Chem.* **1976**, *15*, 1633. Heeg, M. J.; Mack, J. L.; Glick, M. D.; Lintvedt, R. L. *Inorg. Chem.* **1981**, *20*, 833.

(3) Wishart, J. F.; Ceccarelli, C.; Lintvedt, R. L.; Berg, J. M.; Foley, D. P.; Frey, T.; Hahn, J. E.; Hodgson, K. O.; Weis, R. *Inorg. Chem.* **1983**, *22*, 1667.
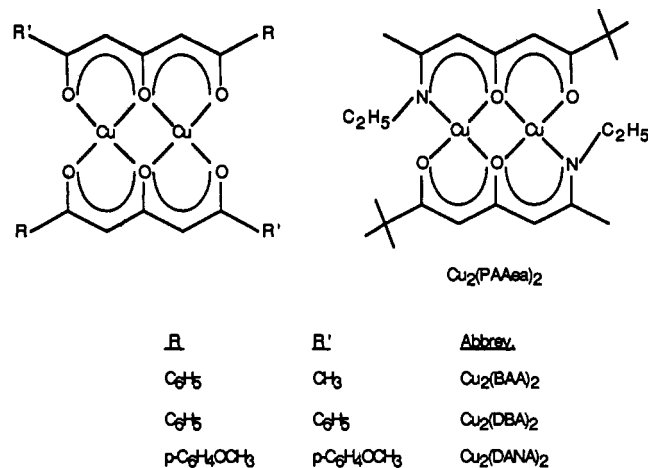
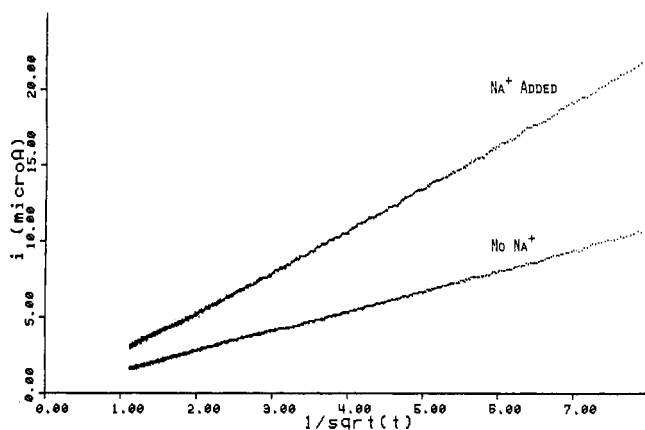**Figure 1.** Schematic drawing of the compounds and abbreviations used.

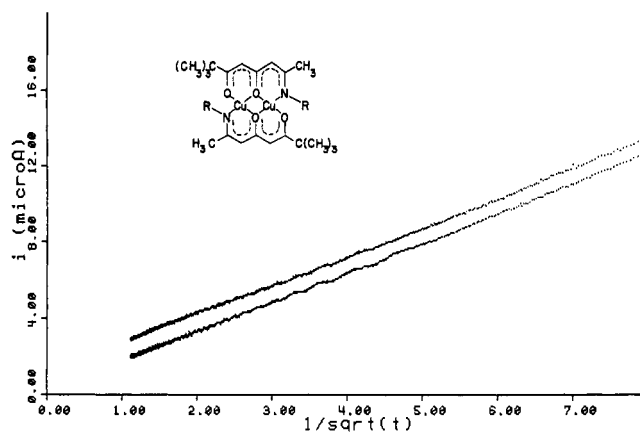**Figure 3.** Chronoamperometric results for $Cu_2(PAAea)_2$ with and without Na^+ at a HMDE working electrode and a SSCE reference in DMF with 0.100 M TEAP supporting electrolyte. The concentration of $Cu_2(PAAea)_2$ is 0.50 mM. For the upper curve, 5.0 mM $NaClO_4$ was added.

Figure 2. Chronoamperometric results for $Cu_2(BAA)_2$ with and without Na^+ at a HMDE working electrode and a SSCE reference in DMF with 0.100 M TEAP supporting electrolyte. The concentration of $Cu_2(BAA)_2$ is 0.50 mM. For the "Na^+ added" case, Na^+ concentration is 5.0 mM.

dark green precipitate formed. The mixture was refluxed for 0.33 h and filtered, and the precipitate was collected, washed with methanol, and air-dried. The product was isolated as dark green microcrystals. Anal. Calcd for $C_{24}H_{38}N_2O_4Cu_2$: C, 52.83; H, 7.02; N, 5.13; Cu, 23.29. Found: C, 52.53; H, 6.98; N, 5.03; Cu, 23.06.

Electrochemistry. Cyclic voltammetric (CV) procedures and apparatus have been recently described.[1] Electrochemical measurements were made in Omni Solv grade (MCB Reagents) *N,N*-dimethylformamide (DMF), which was used without further purification. Chronoamperometric experiments were carried out at a HMDE of area 2.2×10^{-2} cm^2. The metal cations were added as their nitrate or perchlorate salts. The same apparatus used in the CV experiments was utilized to obtain the chronoamperometric response data. The data were transferred from the digital oscilloscope to a Data General Eclipse S-130 minicomputer for analysis and plotting.

The chronoamperometric curves obtained were the average of at least three potential steps from before the foot of the CV wave to at least 150 mV more negative of E_{pc}. The data used were from approximately 15 to 800 ms after the potential step. Data before 15 ms were discarded due to non-Cottrell behavior caused by double-layer and induced Faradaic charging.

Results

Cyclic voltammetric and chronoamperometric experiments have been carried out to probe the unusual electrochemical behavior previously reported for binuclear copper(II) 1,3,5-triketonates and their Schiff base derivatives.[1] Structural representations and abbreviations of the compounds are given in Figure 1.

The change from one- to two-electron redox behavior upon addition of simple alkali-metal cations is confirmed by chronoamperometry. This is evidenced by the doubling of the slope of the i vs. $1/\tau^{1/2}$ plot as shown in Figure 2 for $Cu_2(BAA)_2$ in the absence and presence of a 10-fold excess of Na^+. The current–time behavior of $Cu_2(BAA)_2$, $Cu_2(DBA)_2$, and $Cu_2(DANA)_2$

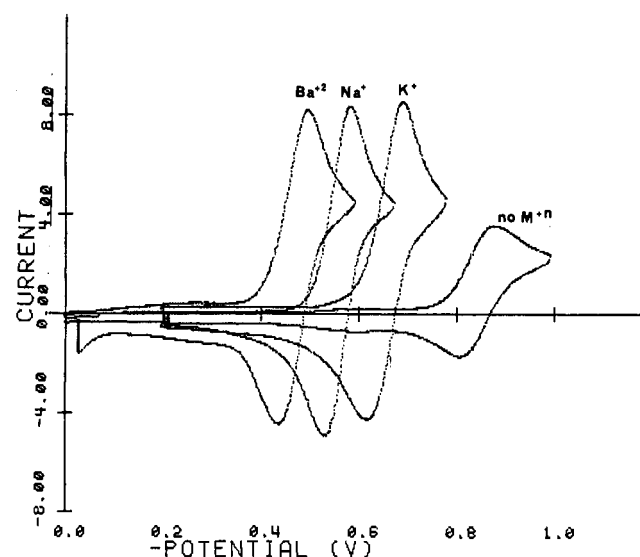**Figure 4.** Cyclic voltammograms of 0.80 mM $Cu_2(BAA)_2$ in DMF with 0.100 M TEAP as supporting electrolyte at a HMDE working electrode vs. SSCE. Scan rate is 100 mV/s. The solutions used to obtain cyclic voltammograms labeled K^+, Na^+, and Ba^{2+} contain, in addition, 8.0 mM $KClO_4$, $NaClO_4$, and $Ba(ClO_4)_2$, respectively.

in the presence of alkali- and alkaline-earth-metal cations is consistent with the Cottrell equation[4] (1) in the time window

$$i(\tau) = nFAC_0^*D_0^{1/2}/\pi\tau \tag{1}$$

15–800 ms after the potential step at the HMDE. By chronoamperometry, each of the bis(1,3,5-triketonato)dicopper(II) complexes undergoes one-electron redox in the absence of the cations and two-electron redox in the presence of a molar excess of the cations (proven by the doubling of the i vs. $1/\tau^{1/2}$ slope upon addition of the cations).

To further examine the role of the metal cations in the shift from one- to two-electron redox processes in these complexes, the amine Schiff base H_2PAAea and its binuclear Cu(II) complex, $Cu_2(PAAea)_2$, have been prepared. This Schiff base derivative does not exhibit the one- to two-electron redox change upon addition of metal cations. This can be seen in Figure 3, where the slope of i vs. $1/\tau^{1/2}$ does not change upon addition of a 10-fold molar excess of Na^+ ions.

The effect of some of these cations on the CV of $Cu_2(BAA)_2$ is shown graphically in Figure 4. All the individual cyclic voltammograms in this figure were recorded at the same con-

(4) Bard, A. J; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York.

Table I. Variation of Redox Potential Shift as a Function of the Metal Cation Added for Three Bis(1,3,5-triketonato)dicopper(II) Complexes[a]

complex	$\Delta E_{1/2}$, mV[b]					
	Ba^{2+}	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
Cu$_2$(BAA)$_2$	384	339	292	197	140	c
Cu$_2$(DBA)$_2$	383	350	292	197	182	124
Cu$_2$(DANA)$_2$	390	365	304	194	205	145

[a] [M^{n+}]/[complex] $\geq$ 10/1. [b] All values are an average of three cyclic voltammograms each at 100, 200, and 500 mV/s scan rate. [c] Distorted.
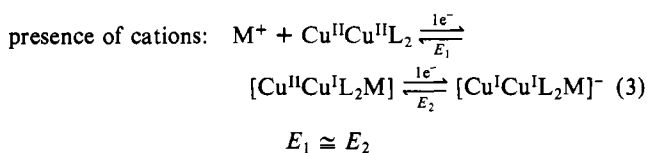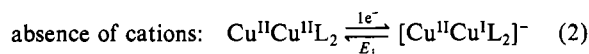
centration of complex and same electrode surface area, but with different or no metal salts added. The four overlayed cyclic voltammograms are for the cases in which no M$^+$, K$^+$, Na$^+$, and Ba^{2+} were added, with $E_{1/2}$ values of −0.81, −0.62, −0.53, and −0.44 V vs. SSCE, respectively. In addition to the positive potential shift upon addition of metal cations, a large increase in peak currents is observed when compared to the cyclic voltammogram with no metal cations present. This is consistent with the change from a one- to a two-electron process in the presence of metal cations. Similar results are obtained for Cu$_2$(DBA)$_2$ and Cu$_2$-(DANA)$_2$.

Figure 5 shows an excellent correlation between $\Delta E_{1/2}$ (the magnitude of the shift between the $E_{1/2}$ in the absence of added cations and the $E_{1/2}$ values recorded in the presence of various cations) and the size/charge ratio of the cation. The ionic size/charge ratios used in this correlation are derived from the Shannon–Prewitt effective ionic radii for six-coordinate ions.[5] The $E_{1/2}$ shift results for various cations at different scan rates are presented in Table I. These values are derived from the average of at least three $E_{1/2}$ measurements at each scan rate.

Table II shows the variation in ΔE_p values at different scan rates for the copper complexes in the presence of Ba^{2+}, Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$. All complexes show an increase in ΔE_p with increasing scan rate, indicating that the redox process is quasireversible. It is clear from these data that the redox process tends to become less reversible with increasing size of the cation. For all the complexes, the greatest reversibility is observed when Na$^+$ is the added cation.

Discussion

We have previously described the two important effects on the redox properties of binuclear copper(II) triketonate complexes brought about by simple cations.[1] The first is to convert the reversible, one-electron-transfer redox to an electron-transfer process characterized as the nearly reversible, sequential transfer of two electrons at very similar potentials. In other words, the cations act as a switch between a one-electron and a two-electron transfer. The second is to bring about a very large positive shift in the reduction potential. The behavior in the presence and absence of simple cations may be summarized by the following equations:

absence of cations: $\quad Cu^{II}Cu^{II}L_2 \underset{E_1}{\overset{1e^-}{\rightleftharpoons}} [Cu^{II}Cu^{I}L_2]^- \quad$ (2)

presence of cations: $\quad M^+ + Cu^{II}Cu^{II}L_2 \underset{E_1}{\overset{1e^-}{\rightleftharpoons}}$

$$[Cu^{II}Cu^{I}L_2M] \underset{E_2}{\overset{1e^-}{\rightleftharpoons}} [Cu^{I}Cu^{I}L_2M]^- \quad (3)$$

$$E_1 \cong E_2$$

In addition, the results presented in Tables I and II show clearly that the shift in the reduction potential is a function of the size and charge of the added cation. This is graphically illustrated in Figure 4, which shows the cyclic voltammograms occurring at more and more positive potentials as the size/charge ratio of the cations decreases. The very strong correlation between the cation

size/charge ratio and the potential shift is illustrated in Figure 5. The magnitude of the potential shift and the dependence of the potential on size/charge ratios suggest that the cation is strongly associated with the binuclear complex, i.e. coordinated to all or some of the species present, Cu^{II}Cu^{II}L$_2$, [Cu^{II}Cu^{I}L$_2$]$^-$, and [Cu^{I}Cu^{I}L$_2$]$^{2-}$.

It has not been possible to electrochemically evaluate the equilibrium constants for cation association since at low concentrations of cation one observes only electron transfer of the "free" binuclear complex and the "cation-associated" binuclear complex (see Figure 1b in ref 1b). Thus, the formation constant is sufficiently large that effectively (at least to the limit of electrochemical detection) all of the cation is associated. In other words, the cyclic voltammograms of the cation-free and cation-associated species shown in Figure 1b of ref 1b simply change in relative peak currents until at a 1/1 cation-to-complex ratio the more negative cation-free wave disappears entirely. At no point are there a smooth transition and shift in potential as a function of cation concentration. This implies a large formation constant, large enough to preclude the usual $E_{1/2}$ vs. [cation] experiments to determine its value.

Coordination or association of these cations to the oxidized complex, Cu^{II}Cu^{II}L$_2$, does not appear too appreciable. There are no obvious spectral indications of cation coordination of the type observed for a variety of Schiff base type complexes[6] as in eq 4.

$$(4)$$
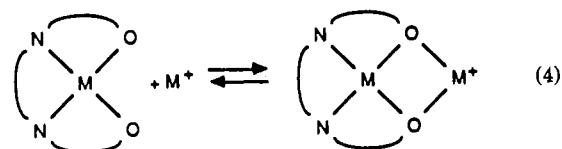
From this evidence and the fact that we have not been able to isolate such complexes, we conclude that cation association with the electron pairs on the terminal oxygens of the oxidized complex is very weak (K_f is less than about 10^{-3}). It stands to reason that association with the reduced species, [Cu^{II}Cu^{I}L$_2$]$^-$ and [Cu^{I}Cu^{I}L$_2$]$^{2-}$, would be much stronger due to the negative charges on these redox products. This interpretation of the experimental results is consistent with complexes of the following type for the first reduction product.
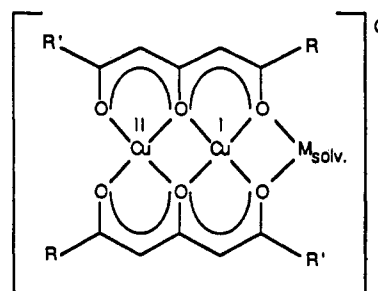
Strong complexation of the cation creates an effectively neutral species of the first reduction product. The overall similarity in charge between the initial oxidized complex, [Cu^{II}Cu^{II}L$_2$]^0, and the first reduction product in the presence of cations, [Cu^{II}Cu^{I}L$_2$M]^0, may partially explain why $E_1 \cong E_2$ in the two-electron reduction, eq 3.

Complexation of the simple cations is further implicated by the fact that tetraalkylammonium cations do not cause the two-electron transfer to take place and do not shift the potentials to the positive values observed for the simpler cations. The R$_4$N$^+$ cations are, of course, not capable of forming electron-pair bonds and are too large to be effective polarizers. In other words, the possibility for true coordination does not exist for R$_4$N$^+$ cations, which are present in large excess as the supporting electrolyte in all the electrochemical measurements reported.

In order to investigate the nature of the cation complexation, simple Schiff base complexes were prepared in which one terminal

(5) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 925.

(6) Gracomelli, A.; Rotunno, T.; Senatore, L. *Inorg. Chem.* **1985**, *24*, 1303.

Table II. ΔE_p Variation with Scan Rate for Various Metal Cations with $Cu_2(BAA)_2$, $Cu_2(DBA)_2$, and $Cu_2(DANA)_2$

scan rate, mV/s	$Cu_2(BAA)_2$					$Cu_2(DBA)_2$						$Cu_2(DANA)_2$					
	Ba^{2+}	Li^+	Na^+	K^+	Rb^{2+}	Ba^{2+}	Li^+	Na^+	K^+	Rb^+	Cs^{2+}	Ba^{2+}	Li^+	Na^+	K^+	Rb^+	Cs^{2+}
20	a	46	41	44	64	42	42	39	42	41	68	47	42	43	46	52	64
50	46	45	41	47	77	46	45	44	45	45	80	56	54	46	51	64	77
100	51	45	46	53	85	53	50	45	51	50	93	42	61	50	57	69	81
200	56	55	49	62	93	58	57	49	54	57	111	69	71	56	61	76	98
500	61	92	57	76	110	63	63	51	60	64	132	80	81	63	67	91	127

^{a} Distorted.
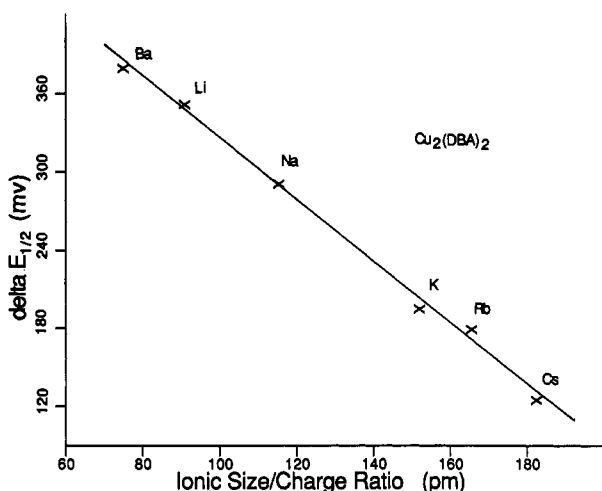
Figure 5. Plot of the magnitude of the shift in $E_{1/2}$ upon addition of various cations as a function of the cation size/charge ratio.

carbonyl oxygen is replaced by N–R, for example, $Cu_2(PAAea)_2$. The single-crystal structure determination of $Cu_2(PAAea)_2$ has been completed,[7] and the imine groups are trans with each Cu(II) bound to three ketonate oxygens and one imino nitrogen. As a result, interaction by the cations with the terminal donor atoms is unlikely for two reasons. First, the ethyl groups on the imine nitrogen present a considerable steric problem. Second, there are no available electron pairs on the imine nitrogen in these complexes and, therefore, no opportunities to chelate the cations in the terminal positions. Thus, binding of the cations in the manner illustrated above is impossible. It is significant that the redox properties of these Schiff base complexes are entirely unaffected by the presence of the simple cations. That is, addition of the cations does not shift the redox potentials and does not convert

(7) Lintvedt, R. L.; Rupp, K. A., unpublished results.

the one-electron reduction to a two-electron-transfer process. This, of course, is in sharp contrast to the electrochemical results of adding cations to the electrochemical cell containing the binuclear copper(II) triketonates. This difference in redox behavior is also observed when the effect of cations on the diamine Schiff base binuclear complexes is compared with their effect on the simple monoamine Schiff bases. Diamine Schiff bases such as Cu_2-$(BAA)_2$en exhibit cation effects that are identical with those of triketonates, e.g. $Cu_2(BAA)_2$.[1] That is, cations shift the redox potentials to more positive values and cause the two-electron transfer to occur. While approach of the cation to the closed diamine end of these molecules is obviously blocked, chelation at the "open" end is clearly possible since there are two ketonate oxygens with available electron pairs.

Inasmuch as the cation effects for molecules such as $Cu_2(BAA)_2$ and $Cu_2(BAA)_2$en are the same (only the absolute value of the redox potentials differ), one can conclude that only one set of terminal oxygens is required to cause the potential shift and the two-electron-transfer process. A reasonable conclusion based upon the results for $Cu_2(BAA)_2$, $Cu_2(BAA)_2$en, and $Cu_2(PAAea)_2$ is that the cation is bound to the electron pairs of two terminal oxygens of the reduced complexes. The exact manner by which this binding facilitates the sequential transfer of two electrons is not known. The fact that the potentials, E_1 and E_2, for the two transfers are very nearly the same may be partially due to the charge similarity between the reactant, $Cu^{II}Cu^{II}L_2$, and the first reduction product, $[Cu^{II}Cu^{II}L_2M]^0$. The shift in the potentials caused by the cations, $Ba^{2+} > Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, is entirely consistent with an increase in the formation constant, K_f, in going from Cs^+ to Ba^{2+}.

$$[Cu^{II}Cu^{I}L_2]^- + M^{n+} \overset{K_f}{\rightleftharpoons} [Cu^{II}Cu^{I}L_2M] \qquad (5)$$