

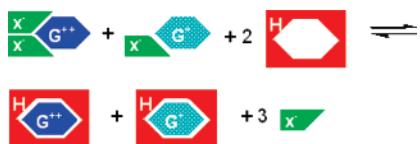
Competitive Interactions of Two Ion-Paired Salts with a Neutral Host To Form Two Non-Ion-Paired Complexes

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It is demonstrated that our reported equilibrium treatments that take into account ion-paired guest and non-ion-paired complexes can be applied to competitive complexations. Satisfactory results were obtained for a system with two cationic guests [*N,N'*-dimethyl-4,4'-biyridinium bis(hexafluorophosphate) (**1**) and dibenzylammonium hexafluorophosphate (**2**)] having a common counterion and a single neutral host dibenzo-24-crown-8 (**3**), even though for this system one exchange process is slow and the other fast on the ¹H NMR time scale. The competitive complexation protocol presented here provides a convenient method for the determination of $K_{ap}K_{ipd}$ (the product of the ion-pair dissociation constant of the guest salt and the association constant for the host with the resultant free cation) for new systems from ion-paired guests that form complexes that are not ion paired.

Applications of ionic compounds in supramolecular chemistry can be dated to Pederson's discovery of the alkalai metal templated synthesis of crown ethers.¹ Paraquat derivatives² and secondary ammonium salts³ are two types of the most commonly used guests in supramolecular chemistry. Ion pairing has been a subject of much recent interest in supramolecular chemistry.⁴ Our group demonstrated that the concentration dependence of the association constant of a slow-exchange system, dibenzo-24-crown-8/dibenzylammonium salts, in low dielectric constant solvents can be attributed to ion pairing of the salts and the dissociated nature of the complex.⁵ Later we demonstrated that analogous paraquat-based fast-exchange host–guest systems which exhibit variations in the apparent association constant

($K_{a,exp}$, defined below) with concentration involve dissociated complexes, while those whose $K_{a,exp}$ are invariant with concentration involve ion-paired complexes.⁶ The study of ion pairing in competitive complexation is important because many complicated supramolecular systems contain more than two ionic species.⁷ Some examples include self-assembly of pseudorotaxanes and pseudopolyrotaxanes,^{7a} acid–base controlled molecular shuttles,^{7b} photoinduced electron-transfer triads,^{7c} and a molecular elevator.^{7d} Here we report a successful application of our equilibrium treatments to a competitive complexation system involving two guests, *N,N'*-dimethyl-4,4'-biyridinium bis-

(2) Colquhoun, H. M.; Goodings, E. P.; Maud, J. M.; Stoddart, J. F.; Williams, D. J.; Wolstenholme, J. B. *J. Chem. Soc., Chem. Commun.* **1983**, 1140–1142. Ashton, P. R.; Fyfe, M. C. T.; Martinez-Diaz, M.-V.; Menzer, S.; Schiavo, C.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1998**, 4, 1523–1534. Huang, F.; Fronczeck, F. R.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, 125, 9272–9273. Huang, F.; Gibson, H. W.; Bryant, W. S.; Nagvekar, D. S.; Fronczeck, F. R. *J. Am. Chem. Soc.* **2003**, 125, 9367–9371. Chen, L.; Zhao, X.; Chen, Y.; Zhao, C.-X.; Jiang, X.-K.; Li, Z.-T. *J. Org. Chem.* **2003**, 68, 2704–2712. Huang, F.; Fronczeck, F. R.; Gibson, H. W. *Chem. Commun.* **2003**, 1480–1481. Huang, F.; Zhou, L.; Jones, J. W.; Gibson, H. W.; Ashraf-Khorassani, M. *Chem. Commun.* **2004**, 2670–2671. Huang, F.; Switek, K. A.; Zakharov, L. N.; Fronczeck, F. R.; Sledobnick, C.; Lam, M.; Golen, J. A.; Bryant, W. S.; Mason, P.; Rheingold, A. L.; Ashraf-Khorassani, M.; Gibson, H. W. *J. Org. Chem.* **2005**, 70, 3231–3241. Huang, F.; Guzei, I. A.; Jones, J. W.; Gibson, H. W. *Chem. Commun.* **2005**, 1693–1695. Huang, F.; Switek, K. A.; Gibson, H. W. *Chem. Commun.* **2005**, 3655–3657. Han, T.; Chen, C.-F. *Org. Lett.* **2006**, 8, 1069–1072. Huang, F.; Gantzel, P.; Nagvekar, D. S.; Rheingold, A. L.; Gibson, H. W. *Tetrahedron Lett.* **2006**, 47, 7841–7844. Huang, F.; Nagvekar, D. S.; Zhou, X.; Gibson, H. W. *Macromolecules* **2007**, 40, 3561–3567.

(3) Fyfe, M. C. T.; Stoddart, J. F. *Adv. Supramol. Chem.* **1999**, 5, 1–53. Bryant, W. S.; Guzei, I.; Rheingold, A. L.; Gibson, H. W. *Org. Lett.* **1999**, 1, 47–50. Huang, F.; Zakharov, L. N.; Rheingold, A. L.; Jones, J. W.; Gibson, H. W. *Chem. Commun.* **2003**, 2122–2123. Hung, W.-C.; Liao, K.-S.; Liu, Y.-H.; Peng, S.-M.; Chiu, S.-H. *Org. Lett.* **2004**, 6, 4183–4186. Lowe, J. N.; Fulton, D. A.; Chiu, S.-H.; Elizarov, A. M.; Cantrill, S. J.; Rowan, S. J.; Stoddart, J. F. *J. Org. Chem.* **2004**, 69, 4390–4402. Hou, H.; Leung, K. C.-F.; Lanari, D.; Nelson, A.; Stoddart, J. F.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, 128, 15358–15359. Zong, Q.-S.; Zhang, C.; Chen, C.-F. *Org. Lett.* **2006**, 8, 1859–1862. Rogez, G.; Ferrer-Ribera, B.; Credi, A.; Ballardini, R.; Gandolfi, M. T.; Balzani, V.; Liu, Y.; Northrop, B. H.; Stoddart, J. F. *J. Am. Chem. Soc.* **2007**, 129, 4633–4642.

(4) Montalti, M. *Chem. Commun.* **1998**, 14, 1461–1462. Baik, M.-H.; Schauer, C. K.; Ziegler, T. *J. Am. Chem. Soc.* **2002**, 124, 11167–11181. Rekharsky, M.; Inoue, Y.; Tobey, S.; Metzger, A.; Anslyn, E. *J. Am. Chem. Soc.* **2002**, 124, 14959–14967. Perry, J. L.; Christensen, T.; Goldsmith, M. R.; Toone, E. J.; Beratan, D. N.; Simon, J. D. *J. Phys. Chem. B* **2003**, 107, 7884–7888. Markusson, H.; Beranger, S.; Johansson, P.; Armand, M.; Jacobsson, P. *J. Phys. Chem. A* **2003**, 107, 10177–10183. Nakanishi, T.; Yilmaz, I.; Nakashima, N.; Kadish, K. M. *J. Phys. Chem. B* **2003**, 107, 12789–12796. Tobey, S. L.; Anslyn, E. V. *J. Am. Chem. Soc.* **2003**, 125, 10963–10970. Naidoo, K. J.; Lopis, A. S.; Westra, A. N.; Robinson, D. J.; Koch, K. R. *J. Am. Chem. Soc.* **2003**, 125, 13330–13331. Credi, A.; Dumas, S.; Silvi, S.; Venturi, M.; Arduini, A.; Pochini, A.; Secchi, A. *J. Org. Chem.* **2004**, 69, 5881–5887. Boswell, P. G.; Buhlmann, P. *J. Am. Chem. Soc.* **2005**, 127, 8958–8959. Schmuck, C.; Rehm, T.; Grohn, F.; Klein, K.; Reinhold, F. *J. Am. Chem. Soc.* **2006**, 128, 1430–1431. Cheng, K.-W.; Lai, C.-C.; Chiang, P.-T.; Chiu, S.-H. *Chem. Commun.* **2006**, 2854–2856. Ng, K.-Y.; Cowley, A. R.; Beer, P. D. *Chem. Commun.* **2006**, 3676–3678. Clemente-Leon, M.; Pasquini, C.; Hebbe-Viton, V.; Lacour, J.; Dalla Cort, A.; Credi, A. *Eur. J. Org. Chem.* **2006**, 1, 105–112. Cametti, M.; Nissinen, M.; Dalla Cort, A.; Mandolini, L.; Rissanen, K. *J. Am. Chem. Soc.* **2007**, 129, 3641–3648. Vickers, M. S.; Beer, P. D. *Chem. Soc. Rev.* **2007**, 36, 211–225.

(5) Jones, J. W.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, 125, 7001–7004.

(6) Huang, F.; Jones, J. W.; Sledobnick, C.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, 125, 14458–14464.

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[§] Present address: E. I. duPont de Nemours and Company, Jackson Laboratory, Deepwater, NJ 08023.

(1) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, 89, 7017–7036.

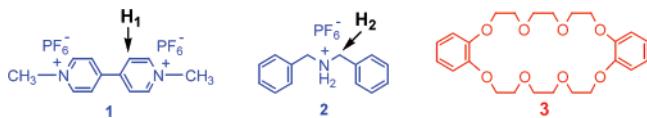
(hexafluorophosphate)⁸ (**1**) and dibenzylammonium hexafluorophosphate⁹ (**2**), and one host, dibenzo-24-crown-8 (**3**), both of whose 1:1 complexes are not ion paired.^{5,6} This serves as a further test of these treatments and provides a convenient method for the determination of $K_{\text{ap}}K_{\text{ipd}}$, the product of the ion-pair dissociation constant and the association constant for the host with the resultant free cationic guest, for ion-paired guests that form complexes that are not ion paired through use of competitive complexation systems.

The association constants for 1:1 host–guest complex formation in the literature are generally not explicitly defined, but since the units are M^{-1} , it is assumed that they are of the form

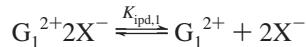
$$K_{\text{a,exp}} = [\text{Complex}] / [\text{Host}]_{\text{uc}} [\text{Guest}]_{\text{uc}}$$

where $[\text{Complex}] = [\text{Host}]_{\text{c}} = [\text{Guest}]_{\text{c}}$, $[\text{Host}]_{\text{uc}} = [\text{Host}]_0 - [\text{Complex}]$, and $[\text{Guest}]_{\text{uc}} = [\text{Guest}]_0 - [\text{Complex}]$. Here the subscripts “c” and “uc” denote complexed and uncomplexed species, respectively.

The following treatment is based on the assumptions that (a) the monocationic or dicationic guest exists in solution as a monomer, G^+X^- or $\text{G}^{2+}\text{2X}^-$, which is predominantly ion paired, (b) upon dissociation of the guest salt, it is the free monocation G^+ or dication G^{2+} that forms the complex, which is not ion paired, and (c) there are no other species present in the solutions.



For a dicationic guest $\text{G}^{2+}\text{2X}^-$ and host H we derive



$$K_{\text{ipd},1} = [\text{G}^{2+}\text{2X}^-]^2 / [\text{G}^{2+}\text{2X}^-][\text{X}^-]^2$$

$$[\text{G}^{2+}] = K_{\text{ipd},1} [\text{G}^{2+}\text{2X}^-] / [\text{X}^-]^2$$

$$K_{\text{ap},1} = [\text{HG}^{2+}] / [\text{H}][\text{G}^{2+}]$$

(7) (a) Ashton, P. R.; Glink, P. T.; Martinez-Diaz, M.-V.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1930–1933. (b) Ashton, P. R.; Ballardini, R.; Balzani, V.; Baxter, I.; Credi, A.; Fyfe, M. C. T.; Gandolfi, M. T.; Gómez-López, M.; Martínez-Díaz, M.-V.; Piersanti, A.; Spencer, N.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 11932–11942. (c) Ballardini, R.; Balzani, V.; Clemente-León, M.; Credi, A.; Gandolfi, M. T.; Ishow, E.; Perkins, J.; Stoddart, J. F.; Tseng, H.-R.; Wenger, S. *J. Am. Chem. Soc.* **2002**, *124*, 12786–12795. (d) Badjic, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845–1849. (e) Loeb, S. J. *Chem. Soc. Rev.* **2007**, *36*, 226–235.

(8) Allwood, B. L.; Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1058–1061.

(9) Ashton, P. R.; Campbell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1865–1869.

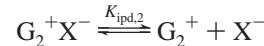
$$K_{\text{ap},1} = [\text{HG}^{2+}][\text{X}^-]^2 / K_{\text{ipd},1} [\text{G}^{2+}\text{2X}^-][\text{H}]$$

$$K_{\text{a,exp},1} = [\text{HG}^{2+}] / [\text{G}^{2+}\text{2X}^-][\text{H}] = K_{\text{ap},1} K_{\text{ipd},1} / [\text{X}^-]^2 \quad (\text{eq 1})$$

Equation 1 can be rewritten as¹⁰

$$K_{\text{a,exp},1}^{0.5} = [\text{HG}^{2+}]^{0.5} / [\text{G}^{2+}\text{2X}^-]^{0.5} [\text{H}]^{0.5} = K_{\text{ap},1}^{0.5} K_{\text{ipd},1}^{0.5} / [\text{X}^-] \quad (\text{eq 2})$$

For a monocationic guest G_2^+X^- and the same host H we derive



$$K_{\text{ipd},2} = [\text{G}_2^+][\text{X}^-] / [\text{G}_2^+\text{X}^-]$$

$$[\text{G}_2^+] = K_{\text{ipd},2} [\text{G}_2^+\text{X}^-] / [\text{X}^-]$$

$$K_{\text{ap},2} = [\text{HG}_2^+] / [\text{H}][\text{G}_2^+]$$

$$K_{\text{ap},2} = [\text{HG}_2^+] / K_{\text{ipd},2} [\text{G}_2^+\text{X}^-][\text{H}]$$

$$K_{\text{a,exp},2} = [\text{HG}_2^+] / [\text{G}_2^+\text{X}^-][\text{H}] = K_{\text{ap},2} K_{\text{ipd},2} / [\text{X}^-] \quad (\text{eq 3})$$

For the competitive situation involving both guests $\text{G}_1^{2+}\text{2X}^-$ and G_2^+X^- with the common host H, the free counterions X^- arise from dissociation of both guest salts and also from both complexation processes. That is, the extent of complexation of both guests is reduced relative to simple binary complexations not only by the competitive binding of the other guest, but also because of increased concentration of the common counterion as a result of the dissociation of the guest salts and their competitive complexation. The effect on the dicationic guest will be greater because the extent of complexation depends on the square of the concentration of the anion (eq 1), while the complexation of the monocation depends only on the first power of the anion concentration (eq 3). From eqs 2 and 3, we derive

(10) An astute reviewer suggested that the intermediate salt $\text{G}_1^{2+}\text{X}^-$ might be involved in this process. We have considered this possibility from several points of view. First, generation of X^- via formation of the intermediate $\text{G}_1^{2+}\text{X}^-$ but without its complexation by the crown ether can be shown not to significantly alter the mathematical analysis under certain plausible conditions (see the Supporting Information). Another possibility is that ionization yields only $\text{G}_1^{2+}\text{X}^-$ and not G_1^{2+} and that complexation of $\text{G}_1^{2+}\text{X}^-$ to form $\text{HG}_1^{2+}\text{X}^-$ occurs, this being the only complex that exists; this situation corresponds exactly to the complexation of dibenzylammonium salts with dibenzo-24-crown-8, i.e., the formation of a free “cation” that is complexed as a non-ion pair, as previously reported.⁵ This possibility can be ruled out, since the equations for that situation⁵ are not obeyed by the **1**·**3** system. Other more complicated possibilities include the latter scenario augmented by ionization of $\text{G}_1^{2+}\text{X}^-$ to G_1^{2+} , with either no complexation of the latter or additional complexation of the latter free dication; the mathematical treatments of these scenarios are complex and not readily solved in closed form. Therefore, in accord with Einstein’s statement that “Everything should be made as simple as possible, but not simpler.” (<http://www.fys.ku.dk/~raben/einstein/>) and the fact that eq 2 provides a reasonably satisfactory fit of the rather extensive data for **1**·**3** over a broad range of concentrations and ratios,⁶ we consider the present treatment to be adequate for evaluation of competitive experiments as described herein.

$$[\text{HG}_2^+]/[\text{HG}_1^{2+}]^{0.5} = (K_{\text{ap},2} K_{\text{ipd},2} / K_{\text{ap},1}^{0.5} K_{\text{ipd},1}^{0.5}) \{[\text{G}_2^+ \text{X}^-] [\text{H}]^{0.5} / [\text{G}_1^{2+} \text{X}^-]^{0.5}\} \quad (\text{eq 4})$$

and

$$K_{\text{a,exp},2} / K_{\text{a,exp},1}^{0.5} = K_{\text{ap},2} K_{\text{ipd},2} / K_{\text{ap},1}^{0.5} K_{\text{ipd},1}^{0.5} \quad (\text{eq 5})$$

In the present study with paraquat guest **1**, dibenzylammonium guest **2**, and dibenzo-24-crown-8 (**3**) as the common host $[\text{HG}_1^{2+}] = [\mathbf{1}]_{\text{c}}$, $[\text{HG}_2^+] = [\mathbf{2}]_{\text{c}}$, $[\text{G}_1^{2+} \text{X}^-]_{\text{o}} - [\mathbf{1}]_{\text{c}} = [\mathbf{1}]_{\text{uc}}$, $[\text{G}_2^+ \text{X}^-]_{\text{o}} - [\mathbf{2}]_{\text{c}} = [\mathbf{2}]_{\text{uc}}$, and $[\text{H}] = [\mathbf{3}]_{\text{o}} - [\mathbf{1}]_{\text{c}} - [\mathbf{2}]_{\text{c}} = [\mathbf{3}]_{\text{uc}}$, and eq 4 can be rewritten as

$$[\mathbf{2}]_{\text{c}} / [\mathbf{1}]_{\text{c}}^{0.5} = (K_{\text{ap},2} K_{\text{ipd},2} / K_{\text{ap},1}^{0.5} K_{\text{ipd},1}^{0.5}) \{[\mathbf{2}]_{\text{uc}} [\mathbf{3}]_{\text{uc}}^{0.5} / [\mathbf{1}]_{\text{uc}}^{0.5}\} \quad (\text{eq 6})$$

For solutions with various concentrations of guests **1** and **2** and host **3**, a plot of $[\mathbf{2}]_{\text{c}} / [\mathbf{1}]_{\text{c}}^{0.5}$ vs $[\mathbf{2}]_{\text{uc}} [\mathbf{3}]_{\text{uc}}^{0.5} / [\mathbf{1}]_{\text{uc}}^{0.5}$ should yield a straight line with the slope of $K_{\text{ap},2} K_{\text{ipd},2} / K_{\text{ap},1}^{0.5} K_{\text{ipd},1}^{0.5}$ and an intercept of zero based on eq 6. This slope is also equal to $K_{\text{a,exp},2} / K_{\text{a,exp},1}^{0.5}$ based on eq 5.

Our previous study of complexation of paraquat guest **1** with dibenzo-24-crown-8 (**3**) showed that $K_{\text{ap},1} = 106 (\pm 42) \text{ M}^{-1}$ and $K_{\text{ipd},1} = 4.64 (\pm 1.86) \times 10^{-4} \text{ M}^2$ in acetone- d_6 .⁶

$K_{\text{a,exp},3 \cdot 2}$ values (Table 1) were calculated on a point-by-point basis from $K_{\text{a,exp},3 \cdot 2} = [\mathbf{3}]_{\text{c}} / \{[\mathbf{3}]_{\text{uc}} [\mathbf{2}]_{\text{uc}}\}$. $K_{\text{a,exp},3 \cdot 2}$ varied up to 3.7-fold and decreased when initial concentrations of **1** or **2** increased, in accord with eq 3. A log-log plot of eq 7⁵ for the complexation between dibenzylammonium salt **2** and crown ether **3** in acetone- d_6 is shown in Figure 1. The slope, 0.998, of the best fit line at low concentrations of host **3** is very close to the ideal value, 1, for the case where the complex is 100% dissociated and $K_{\text{ap},2}[\mathbf{3}] \ll 1$. The slope, 0.534, of the best fit line at high concentrations of **3** is close to the ideal value, 1/2, for the case where the complex is completely dissociated and $K_{\text{ap},2}[\mathbf{3}] \ll 1$. From the intercepts of these two lines, $K_{\text{ap},2}$ and $K_{\text{ipd},2}$ were calculated to be $123 (\pm 21) \text{ M}^{-1}$ and $3.03 (\pm 0.74) \times 10^{-2} \text{ M}$, respectively, in acetone- d_6 .¹¹ In less polar 3:2 CDCl_3 : CD_3CN we previously found $K_{\text{ap},2} = 5.6 (\pm 0.6) \times 10^2 \text{ M}^{-1}$ and $K_{\text{ipd},2} = 2.6 (\pm 0.7) \times 10^{-2} \text{ M}$.⁵ These data indicated that the association constant for the complex is more sensitive to the polarity of the solvent than dissociation constant of the guest salt. Previously it was observed that PF_6^- salts were generally the most dissociated so dissociation constants of PF_6^- salts are relatively less sensitive to the polarity of the solvent than those with other counteranions.^{5,12}

$$[\mathbf{3}]_{\text{c}} / [\mathbf{2}]_{\text{uc}}^{0.5} = K_{\text{ap},2} K_{\text{ipd},2}^{0.5} [\mathbf{3}]_{\text{uc}} / (1 + K_{\text{ap},2} [\mathbf{3}]_{\text{uc}})^{0.5} \quad (\text{eq 7})$$

For the study of competitive complexation of guests **1** and **2** with host **3**, nine solutions were prepared with the constant initial concentration of paraquat **1** and varied initial concentrations of secondary ammonium salt **2** and crown ether **3**. The percentage

(11) According to eq 7,⁵ the intercepts of the two lines in Figure 1 give $\log(K_{\text{ap},2} K_{\text{ipd},2}^{0.5}) = 1.33 (\pm 0.12)$, $K_{\text{ap},2} K_{\text{ipd},2}^{0.5} = 21.4 (\pm 1.0) \text{ M}^{-0.5}$ and $\log(K_{\text{ap},2}^{0.5} K_{\text{ipd},2}^{0.5}) = 0.286 (\pm 0.015)$, $K_{\text{ap},2}^{0.5} K_{\text{ipd},2}^{0.5} = 1.93 (\pm 0.07)$. From these values $K_{\text{ap},2}$ and $K_{\text{ipd},2}$ were determined. Errors are based on errors of the intercepts.

(12) Schmid, R.; Kirchner, K.; Dickert, F. L. *Inorg. Chem.* **1988**, 27, 1530–1536. Nelson, S. F.; Ismagilov, R. F. *J. Phys. Chem. A* **1999**, 103, 5373–5378.

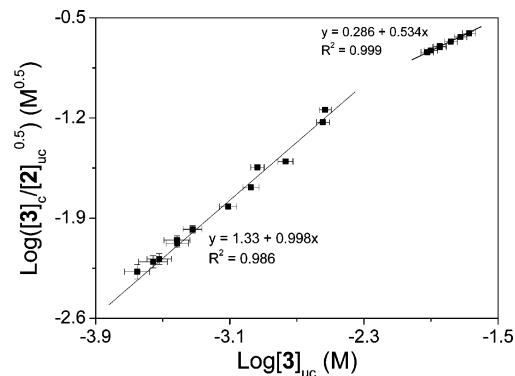


FIGURE 1. Log–log plot of eq 7 for the complexation between dibenzylammonium guest **2** and dibenzo-24-crown-8 host **3** in acetone- d_6 at 22 °C.

TABLE 1. $K_{\text{a,exp},2}$ Values at Different Initial Concentrations for the Complexation between Guest **2** and Host **3** in Acetone- d_6 at 22 °C

$[\mathbf{2}]_0$ (mM)	$[\mathbf{3}]_0$ (mM)	% 3 complexed ^a	$[\mathbf{2}]_{\text{c}}$ or $[\mathbf{3}]_{\text{c}}^b$ (mM)	$[\mathbf{2}]_{\text{uc}}^c$ (mM)	$[\mathbf{3}]_{\text{uc}}$ (mM)	$K_{\text{a,exp},3 \cdot 2}$ (M^{-1})
6.00	6.00	0.544	3.27	2.73	2.73	437
6.00	3.00	0.633	1.90	4.10	1.10	421
3.00	1.50	0.482	0.723	2.28	0.777	409
3.00	2.00	0.469	0.938	2.06	1.06	428
3.00	1.00	0.523	0.523	2.48	0.477	444
3.00	0.500	0.544	0.272	2.73	0.228	438
12.0	1.20	0.623	0.747	1.13	0.453	147
3.00	6.00	0.337	2.02	0.977	3.98	521
3.00	3.00	0.431	1.29	1.71	1.71	444
6.67	20.0	0.289	5.77	0.895	14.2	454
6.67	18.3	0.310	5.67	0.997	12.6	450
10.0	30.0	0.292	8.77	1.23	21.2	336
10.0	27.5	0.314	8.64	1.36	18.9	335
10.0	25.0	0.335	8.39	1.61	16.6	313
10.0	22.5	0.371	8.35	1.65	14.2	357
10.0	20.0	0.401	8.03	1.97	12.0	339
10.0	8.00	0.644	5.15	4.85	2.85	373
1.50	0.500	0.397	0.199	1.30	0.301	507
1.33	0.670	0.369	0.247	1.08	0.423	539
1.00	1.00	0.282	0.282	0.718	0.718	545
2.40	0.600	0.459	0.275	2.12	0.325	399
2.25	0.750	0.440	0.330	1.92	0.420	409
2.00	1.00	0.391	0.391	1.61	0.609	398

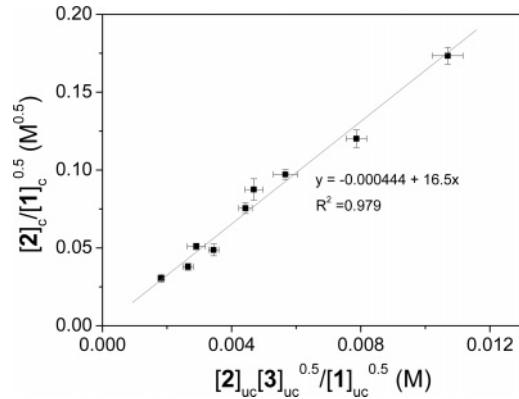
^a Calculated from integrations of peaks of aromatic protons of complexed and uncomplexed **3**. ^b “c” means complexed. ^c “uc” means uncomplexed.

of complexed paraquat **1** was calculated based on chemical shift change of H_1 (fast exchange),⁶ while the percentage of complexed dibenzylammonium salt **2** was calculated based on integrations of peaks corresponding to H_2 of complexed and uncomplexed species (slow exchange)⁵ (Table 2). On the basis of these data, a plot of eq 6 for this competitive complexation was made (Figure 2). The intercept of the plot is zero within experimental error, while the slope, $16.5 (\pm 1.0) \text{ M}^{-0.5}$, agrees with the value of $K_{\text{ap},2} K_{\text{ipd},2} / K_{\text{ap},1}^{0.5} K_{\text{ipd},1}^{0.5}$, $16.8 (\pm 3.3) \text{ M}^{-0.5}$, calculated from the results of individual complexations between **3** and **1** and between **3** and **2**. Stated another way, from our knowledge of $K_{\text{ap},2}$ and $K_{\text{ipd},2}$ from Figure 1 and the slope of Figure 2 we calculate $K_{\text{ap},1} K_{\text{ipd},1} = 5.11 (\pm 1.07) \times 10^{-2} \text{ M}$; the directly measured value was $4.92 (\pm 3.92) \times 10^{-2} \text{ M}$.⁶ This study provides a further test of these equations and demonstrates that they are also appropriate for competitive complexations of two ion-paired salts with a common counterion that both produce non-ion-paired complexes.

TABLE 2. Percentages of Complexed Guests **1** and **2** at Different Initial Concentrations for the Competitive Complexation by Host **3** in Acetone-*d*₆ at 22 °C

[1] ₀ (mM)	[2] ₀ (mM)	[3] ₀ (mM)	fraction 1 complexed ^a	fraction 2 complexed ^b
1.00	2.00	2.00	0.366	0.289
1.00	2.00	4.00	0.541	0.441
1.00	2.00	8.00	0.719	0.683
1.00	4.00	2.00	0.311	0.215
1.00	4.00	4.00	0.485	0.416
1.00	4.00	8.00	0.678	0.633
1.00	8.00	2.00	0.247	0.172
1.00	8.00	4.00	0.404	0.302
1.00	8.00	8.00	0.567	0.501

^a Based on chemical shift changes of H₁ and Δ₀ = 1.32 ppm.⁶ ^b Based on integrations of peaks corresponding to H₂ of complexed and uncomplexed **2**.⁵

**FIGURE 2.** Plot of eq 6 for the competitive complexation of paraquat guest **1** and dibenzylammonium guest **2** by dibenzo-24-crown-8 host (**3**) in acetone-*d*₆ at 22 °C.

It should be noted that $K_{\text{ap},2}K_{\text{ipd},2}/(K_{\text{ap},1}K_{\text{ipd},1})^{0.5}$ is a constant in the competitive situation, even though individually $K_{\text{a,exp},2}$ and $K_{\text{a,exp},1}$ have different values at different initial host and guest concentrations. This provides a new and very facile method for the determination of $K_{\text{ap},1}K_{\text{ipd},1}$ values, which are more difficult to determine, since in a fast-exchange system such as **1**·**3** the chemical shift changes at different initial host and guest concentrations would have to be obtained for determinations in the normal way. Here from a plot of eq 6 by using integrations of peaks corresponding to complexed and uncomplexed states of **2**·**3**, a slow-exchange system, the value of

$K_{\text{ap},1}K_{\text{ipd},1}$ for the fast exchange system can be easily obtained from the slope if $K_{\text{ap},2}K_{\text{ipd},2}$ is known.

In summary, we demonstrated that our equilibrium treatments of individual complexations involving ion-paired mono- and dicationic guests with neutral hosts in formation of non-ion-paired complexes are also appropriate for competitive complexation studies. The research presented here provides a convenient method for the determination of $K_{\text{ap},1}K_{\text{ipd}}$ for new systems from ion-paired guests that form complexes that are not ion paired through use of competitive complexation studies.

Experimental Section

3 was purchased and used as received. All other compounds were prepared by literature procedures.¹³ All solutions were prepared as follows. Precisely weighed amounts of dried compounds were added into screw cap vials. Acetone-*d*₆ was added with to-deliver volumetric pipets. Then specific volumes of each fresh solution were mixed to yield the desired concentrations. For example, to prepare a solution of 1.00/2.00/2.00 mM **1**/**2**/**3**, 0.500 mL of 3.00 mM **1**, 0.500 mL of 6.00 mM **2**, and 0.500 mL of 6.00 mM **3** were added into a screw cap vial with 0.500 mL to-deliver pipets. ¹H NMR data were collected on a temperature-controlled 400 MHz spectrometer. Acetone-*d*₆ was chosen as the solvent because all compounds used here have good solubilities in it. Error bars were calculated by using a ±5% deviation in percent complexation. Linear regressions were performed with the entire error range (abscissa and ordinate) at each data point; standard errors in both the intercept and slope coefficients based on regression were used to determine errors in association constants of host–guest complexes and dissociation constants of salts.

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Supporting Information Available: More discussion on eq 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) Synthesis of **1**: Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790–5795 and references therein. Synthesis of **2**: Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 709–728.