Novel (Heteromolecular) π-Complexes of Aromatic Cation Radicals. Isolation and Structural Characterization
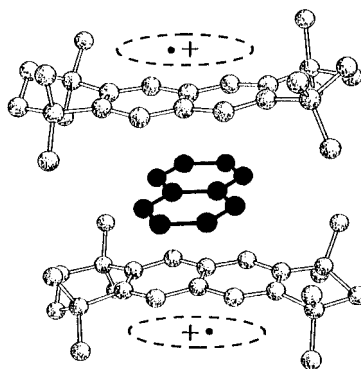
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ABSTRACT

Extensive (electron) delocalization in the novel heteromolecular π-complex of the hindered naphthalene cation radical (OMN[+]•) with naphthalene (NAP) accompanies the pronounced charge-transfer absorption band at ~1100 nm in the near-IR. X-ray crystallography establishes the viability of the unusual "club sandwich" structure despite the repulsive electrostatic forces inherent to the dicationic unit.

Cation radicals of organic donors are transient (reactive) intermediates in a variety of interesting redox reactions.[1–3] Despite intensive scrutiny, they remain generally extremely difficult to isolate owing to their high reactivity, even at low temperatures under an inert atmosphere.[4] Nevertheless, a number of aromatic cation radicals are sufficiently long-lived in solution to be characterized by UV–vis[5] and ESR[6] spectroscopy, and in some cases to be isolated in the solid state.[7,8] The few examples in which aromatic cation radicals have been successfully isolated as crystalline salts actually consist of mixed-valence units. For example, crystal-structure analysis showed that the naphthalene cation radical (**NAP**)[+]• exists as a mixed-valence dimer (**NAP**)$_2$[+]• in which the two components, crystallographically indistinguishable, are arranged face-to-face in π-stacks with an interplanar separation

(1) (a) Eberson, L. *Electron-Transfer Reactions in Organic Chemistry*; Springer: New York, 1987. (b) Yoshida, K. *Electrooxidation in Organic Chemistry. The Role of Cation Radicals as Synthetic Intermediates*; Wiley: New York, 1984. (c) Kochi, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227.

(2) (a) Bhattacharya, A.; DiMichele, L. M.; Dolling, U.-H.; Grabowski, E. J. J.; Grenda, V. J. *J. Org. Chem.* **1989**, *54*, 6118. (b) Kita, Y.; Tohma, H.; Hatanaka, K.; Takada, T.; Fujita, S.; Mitoh, S.; Sakurai, H.; Oka, S. *J. Am. Chem. Soc.* **1994**, *116*, 3864. (c) Rathore, R.; Kochi, J. K. *Acta Chem. Scand.* **1998**, *52*, 114. (d) Rathore, R.; Kochi. J. K. *J. Org. Chem.* **1996**, *61*, 627.

(3) For a recent review, see: Rathore, R.; Kochi J. K. *Adv. Phys. Org. Chem.* **2000**, *35*, 193.

(4) Cation radicals are transient species with strong electrophilic properties and subject to rapid proton loss, fragmentation, etc. See: (a) Schmittel, M.; Burghart, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2550. (b) Albini, A.; Fasani, E.; Dalessandro, N. *Coord. Chem. Rev.* **1993**, *125*, 269.

(5) (a) Badger; B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, *65*, 2576, 2582, and 2588. (b) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1970**, *66*, 2939. (c) Badger, B.; Brocklehurst, B. *Nature (London)* **1968**, *219*, 263. (d) Rodgers, M. A. J. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1278. (e) Inokuchi, Y.; Naitoh, Y.; Ohashi, K.; Saito, K. I.; Yoshihara, K.; Nishi, N. *Chem. Phys. Lett.* **1997**, *269*, 298. (f) Masnovi, J. M.; Kochi, J. K. *J. Phys. Chem.* **1987**, *91*, 1878. (g) Masnovi, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 6781.

(6) (a) Lewis, L. C.; Singer, L. S. *Chem. Phys.* **1965**, *43*, 2712. Also see: (b) Howarth, O. W.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1966**, *88*, 4514. (c) Howarth, O. W.; Fraenkel, G. K. *J. Chem. Phys.* **1970**, *52*, 6258. (d) Gerson, F.; Kaupp, G.; Okya-Nishiguchi, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 657.

significantly closer than van der Waals contacts. Such an intermolecular organization arises from the spontaneous association in solution of the aromatic cation radical with its neutral counterpart to form the stabilized *homomolecular* dimeric cation radical, as generically represented in eq 1.

$$\mathbf{Ar^{+\bullet} + Ar \rightleftharpoons \quad (Ar)_2^{+\bullet}} \qquad (1)$$
$$\text{(homomolecular)}$$
$$\pi\text{-complex}$$
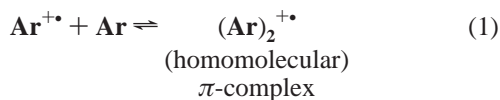
During the process of crystallization, these homomolecular dimers stack in infinite columnar structures characteristic of most mixed-valence aromatic cation-radical salts. Spectroscopically, the dimeric $(\mathbf{Ar})_2^{+\bullet}$ unit distinguishes itself from the monomeric constituent by an additional absorption band in the near-infrared (NIR) spectral range, which is attributed to charge-resonance or CR transitions within the cation-radical dimers[5] as schematically illustrated by the MO energy diagram (A) in Scheme 1. The resonance contributions


Scheme 1. Aromatic Cation-Radical π-Complexes

(A) Homomolecular **(B) Heteromolecular**
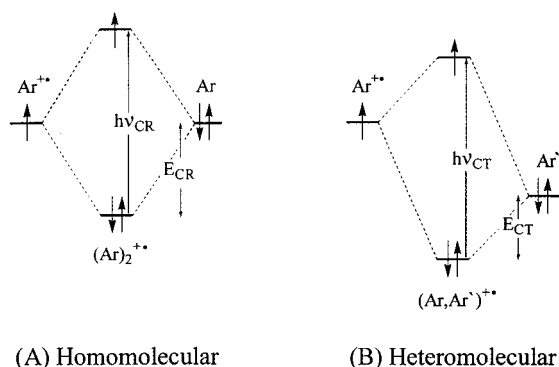
mainly arise from exchange interactions between the two (equal energy) HOMO's of **Ar** and **Ar$^{+\bullet}$** that are suitably oriented in the sandwich-like structure.

Cation-radical dimers constitute the smallest supramolecular unit that carries a delocalized positive charge, and this property has been extensively utilized to design various materials such as organic metals, (photo)conductors, ferromagnets, etc.[9] Nevertheless, the structural and electronic requirements that lead to intermolecular charge delocalization are not fully defined. We recently investigated the steric

requirements for charge-transfer or CT interactions to occur in various electron donor/acceptor or EDA complexes and clearly established that intermolecular contacts equal to or shorter than van der Waals contacts are necessary for charge transfer to be effective.[10] As such, our understanding of *charge-transfer* complexes led us to exploit an encumbered naphthalene analogue to investigate the steric requirements for *charge resonance*.[11] The facile annelation of the parent naphthalene donor into the hindered **OMN** renders its cation
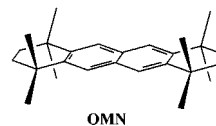
radical extremely persistent in solution at ambient temperatures for prolonged periods, as also shown by the cyclic voltammogram that is completely reversible over multiple scan rates as low as 10 mV/s. Interestingly, crystals of **OMN$^{+\bullet}$SbF$_6^-$** suitable for X-ray crystallography can be grown from a dichloromethane solution at -23 °C and the crystal structure shows that **OMN$^{+\bullet}$** cation radicals exist as isolated monomeric units separated by SbF$_6^-$ anions. These results demonstrate that dimerization of the hindered **OMN$^{+\bullet}$** with its neutral counterpart as in eq 1 is not possible. The UV–vis spectrum of **OMN$^{+\bullet}$**, both in solution and in the solid state, exhibits absorption bands at $\lambda_{max} = 672$ ($\epsilon_{672} = 9300$ M^{-1} cm^{-1}), 616, 503, and 396 nm that are readily assigned to the monomeric **OMN$^{+\bullet}$** cation radical by comparison of its characteristic fine structure with the cation radical of the parent naphthalene (**NAP$^{+\bullet}$**).[7f] Importantly, no new absorption is observed in the NIR region, confirming the absence of cation-radical dimers (**OMN**)$_2^{+\bullet}$ in solution. Such a direct relationship between steric hindrance and absence of CR absorption in the NIR spectral range for aromatic dimer cation radicals is quite similar to the one we previously observed for sterically encumbered organic CT complexes.[10]

To further investigate the nature of electronic interactions between π-systems, we embarked on the design of *heteromolecular* π-complexes of aromatic cation radicals, resulting from the complexation of an aromatic cation radical (Ar$^{+\bullet}$) with a different neutral aromatic donor (Ar$'$). However, such ionic π-heterocomplexes have to date only been observed as metastable species in the gas phase or in a freon matrix.[12,13] One of these studies (mass spectroscopy) has suggested that the dissociation energy of such heterodimers (Ar, Ar$'$)$^{+\bullet}$ is always smaller than that of either homodimer (Ar)$_2^{+\bullet}$ or (Ar$'$)$_2^{+\bullet}$.[12] The MO energy diagram in Scheme 1B qualita-

(7) (a) Enkelmann, V. In *Advances in Chemistry Series*; Ebert, L. B., Ed.; 1987; Vol. 217, p 177 and references therein. (b) Fritz, H. P.; Gebauer, H.; Friedrich, P.; Ecker, P.; Artes, R.; Schubert, U. *Z. Naturforsch.* **1978**, *33b*, 498. (c) Kröhnke, C.; Enkelmann, V.; Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 912. (d) Ayllón, J. A.; Santos, I. C.; Henriques, R. T.; Almeida, M.; Lopes, E. B.; Morgado, J.; Alcácer, L.; Veiros, L. F.; Duarte, M. T. *J. Chem. Soc., Dalton Trans.* **1995**, 3543 and references therein. (e) Keller, H.; Nöthe, D.; Pritzkow, H.; Wehe, D.; Werner, M.; Koch, P.; Schweitzer, D. *Mol. Cryst. Liq. Cryst.* **1980**, *62*, 181. (f) Kochi, J. K.; Rathore, R.; Le Maguerès, P. *J. Org. Chem.*, in press.
(8) (a) Rathore, R.; Le Maguerès, P.; Lindeman, S. V.; Kochi, J. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 809. (b) Rathore R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 5847. (c) Rathore, R.; Lindeman, S. V.; Kumar, A. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 6931.

(9) (a) Jerome, D.; Ribault, M.; Bechgaard, K. *J. Phys. Lett.* **1980**, L95. (b) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M. H. *Organic Superconductors. Synthesis, Structure, Properties and Theory*; Grimes, R. N., Ed.; Prentice Hall: Englewood Cliffs, NJ, 1992. (c) Kobayashi, H.; Tomita, N.; Naito, T.; Kobayashi, A.; Sakai, F.; Watanabe, T.; Cassoux, P. *J. Am. Chem. Soc.* **1996**, *118*, 368.
(10) Rathore, R.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 9393.
(11) (a) Rathore, R.; Kochi, J. K. *Acta Chem. Scand.* **1998**, *52*, 114. (b) Bruson, H. A.; Kroeger, J. W. *J. Am. Chem. Soc.* **1940**, *62*, 36.

tively illustrates the difference in the stabilization energy E_{CT} of the heteromolecular aromatic complex relative to that (E_{CR}) of the homomolecular analogue in Scheme 1A.[13] Probably because of this thermodynamic factor, the heteromolecular analogues have not been prepared pure in the condensed phase. To solve this problem, we utilized the sterically encumbered **OMN** described above to generate the cation-radical moiety of the heteromolecular complex. The (shallow) basket-like molecular structure of **OMN**$^{+\bullet}$ (with the methyl groups as handles) makes this cation radical a good candidate for pairing with a guest donor such as an electron-rich arene. After many attempts,[14] the parent naphthalene (**NAP**) appears to have the best steric fit to allow association with **OMN**$^{+\bullet}$ and form a heteromolecular complex. As such, cocrystallization of a dichloromethane solution of **OMN**$^{+\bullet}$SbCl$_6^-$ to which a large excess of solid **NAP** is added affords dark-green crystals of the desired salt of the heteromolecular cation-radical, which are surprisingly stable in air at room temperature for several days.

X-ray crystallography establishes the structure to be a 2:1 complex of **OMN**$^{+\bullet}$ and **NAP** (Figure 1). The naphthalene
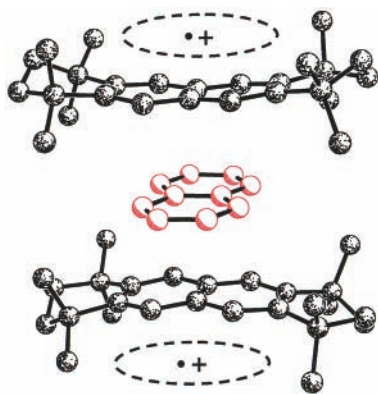

Figure 1. X-ray crystal structure of the trimeric unit **OMN**$^{+\bullet}$/**NAP**/**OMN**$^{+\bullet}$ showing the tightly sandwiched **NAP** donor between a pair of **OMN**$^{+\bullet}$ cation radicals. Hydrogens omitted for clarity.

donor is sandwiched between a pair of cation radicals to form the trinuclear complex. The **OMN**$^{+\bullet}$ and **NAP** units are rotated by 90°, leading to the same (cross-like) overlap (see Table S1, Supporting Information) as that in the mixed-valence homodimer salt of naphthalene (**NAP**)$_2^{+\bullet}$PF$_6^-$.[7b] Most importantly, the intermolecular contacts of 3.06 Å between **NAP** and **OMN**$^{+\bullet}$ are considerably shorter than the usual van der Waals separation of ~3.4 Å.
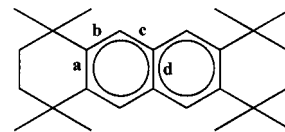
The effects of such short intermolecular contacts are reflected in the interatomic bond lengths within the **NAP** unit of the heterocomplex that show significant changes when

(12) (a). Meot-Ner, M. *J. Phys. Chem.* **1980**, *84*, 2724 and references therein. (b) Stone, J. A.;. Lin, M. S. *Can. J. Chem.* **1980**, *58*, 1666.

(13) Bally; T.; Roth, K.; Straub, R. *J. Am. Chem. Soc.* **1988**, *110*, 1639.

(14) From the standpoint of size/shape the naphthalenoid donors appear to be the best; but 2,3- and 2,6-dimethylnaphathalene both produce with **OMN**$^{+\bullet}$ weak complexes showing NIR absorptions at ~1150 nm and afford only small dark brown microcrystals.

Table 1. Interatomic Bond Lengths (Å) in the Hindered **OMN** as the Neutral Donor, in the Heteromolecular Cation-Radical Salt (**OMN**$^{+\bullet}$)$_2$(**NAP**)2SbCl$^-_6$, and in the Solvated Cation-Radical Salts **OMN**$^{+\bullet}$SbF$_6^- \cdot$CH$_2$Cl$_2$ and **OMN**$^{+\bullet}$SbCl$_6^- \cdot$2C$_7$H$_8$

bond	neutral	(**OMN**$^{+\bullet}$)$_2$(**NAP**)	(**OMN**$^{+\bullet}$)-(toluene)$_2$	**OMN**$^{+\bullet}\cdot$CH$_2$Cl$_2$
a	1.436(1)	1.414(8)	1.412(2)	1.399(6)
		−2.2 pm	−2.4 pm	−3.7 pm
b	1.382(1)	1.389(5)	1.419(2)	1.417(5)
		+0.7 pm	+3.7 pm	+3.4 pm
c	1.416(1)	1.409(4)	1.411(2)	1.406.(5)
		−0.6 pm	−0.4 pm	−0.9 pm
d	1.416(1)	1.418(7)	1.422(2)	1.418 (5)
		−0.2 pm	+0.6 pm	+0.2 pm

compared to the neutral and cation-radical species of naphthalene (Table 1 and Figure S1, Supporting Information). Thus, the various bonds in the **NAP** moiety follow the same trend (contraction or elongation) upon proceeding from the neutral **NAP** donor to the heteromolecular cation-radical salt and to the mixed-valence homodimer cation-radical salt (**NAP**)$_2^{+\bullet}$PF$_6^-$. Such a trend indicates that the same charge (removal) phenomenon from **NAP** takes place in heteromolecular as it does in homomolecular cation-radical salts.

The bond lengths in the **OMN**$^{+\bullet}$ moieties of the heteromolecular cation-radical salt are also compared in Table 1 with those in the neutral species and those in a solvated cation-radical salt (**OMN**$^{+\bullet}$)(toluene)$_2$ SbCl$_6^-$ that we recently obtained in the course of this work.[15] In all the **OMN**$^{+\bullet}$ units, bonds designated as **a** and **c** (Table 1) are contracted, whereas the bond **b** is elongated as compared to neutral **OMN**. The bond length changes are less dramatic in the heteromolecular cation-radical salt than those in the solvated cation-radical salts. This confirms our conclusion that negative charge is transferred from **NAP** to the **OMN**$^{+\bullet}$ units which in turn are no longer true monomeric cation radicals but are instead *partially* reduced.

To compare the spectroscopic properties of the hetero-complex with those of the (**NAP**)$_2^{+\bullet}$ homodimers, we compare the UV−vis spectrum of (**OMN**$^{+\bullet}$)$_2$(**NAP**), 2SbCl$_6^-$ in solution and in the solid state. The diffuse reflectance

(15) The crystal structure of the nonsolvated cation-radical salt **OMN**$^{+\bullet}$SbCl$_6^-$ is heavily disordered and prevents accurate analysis of the interatomic bond lengths.[6f] Nevertheless, we obtain ordered crystals of the "solvated" cation-radical salts **OMN**$^{+\bullet}$SbF$_6^- \cdot$ CH$_2$Cl$_2$ and **OMN**$^{+\bullet}$SbCl$_6^- \cdot$ 2C$_7$H$_8$ (see Supporting Information). The crystal structure of the toluene solvate consists of trimeric units of toluene/**OMN**$^{+\bullet}$/toluene that are separated by SbCl$_6^-$ anions. Owing to the poor donicity of toluene, the charge-transfer interactions between **OMN**$^{+\bullet}$ cation radicals and toluene may be neglected and the **OMN**$^{+\bullet}$ moieties may be viewed as isolated monomeric radical cations.
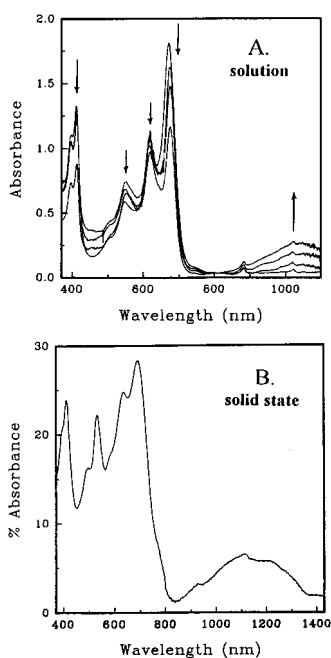
Figure 2. (A) Progressive growth of the charge-transfer description band at ∼1100 nm upon the incremental addition of naphthalene (**NAP**) to a 0.1 M solution of the hindered naphthalene cation radical **OMN**[+•] in dichloromethane at −78 °C. (B) Solid state diffuse reflectance spectrum of the heteromolecular CT salt (**OMN**[+•])$_2$-(**NAP**) 2SbCl$_6$[−] diluted in KPF$_6$ matrix.

spectrum of the heterocomplex shows a broad low-energy band at ca. 1100 nm (Figure 2B) that does not exist in any of the free (uncomplexed) components. The same band appears in solution when **NAP** is added to a dichloromethane solution of **OMN**[+•]SbCl$_6$[−] at −78 °C, and it continues to grow upon incremental additions of **NAP** (Figure 2A). This extra absorption band is reminiscent of the charge-resonance band in (**NAP**)$_2$[+•] dimers (λ_{max} = 1050 nm)[5a] and can be attributed to a partial charge transfer occurring in the heterocomplex from the close interaction of **OMN**[+•] and **NAP** in the crystal structure.

Annelation of the parent naphthalene into the sterically hindered **OMN** affords a novel aromatic hydrocarbon that can be readily oxidized in solution to a highly persistent cation radical. The steric encumbrance created by the eight methyl groups prevents the dimerization in solution of the cation radical **OMN**[+•] with its neutral counterpart **OMN**, as shown in the crystal structure of the cation-radical salt **OMN**[+•]SbF$_6$[−] in which **OMN**[+•] moieties exist as isolated monomeric units. Consequently, in contrast to its sterically accessible naphthalene analogue (which readily dimerizes and presents a charge-resonance band at 1050 nm), the UV−vis absorption spectrum of the cation radical salt of **OMN**[+•] does not show any new (low-energy) band, in accordance with a similar study performed on steric hindrance in organic charge-transfer complexes.[10] Further investigations on the nature of electronic interactions between aromatic systems led us to employ the basket-shaped cation radical **OMN**[+•] as an electron acceptor for the complexation with different electron-rich aromatics. In particular, the ready association of **OMN**[+•] with the parent naphthalene allows us to isolate for the first time in the solid state a heteromolecular π-complex cation radical (**OMN**[+•])$_2$(**NAP**), 2SbCl$_6$[−], as established by X-ray crystallography. Structurally, this complex appears similar to the parent dimeric cation-radical salt (**NAP**)$_2$[+•]PF$_6$[−•] in a face-to-face arrangement. The difference between the homomolecular and heteromolecular systems resides in the electronic properties of the component molecules. In (**NAP**)$_2$[+•]PF$_6$[−•], the electronic properties of both components are identical, whereas in the heterocomplex they are not—there being a ∼400 mV difference between the redox potentials of **OMN** (1.34 V vs SCE) and **NAP** (1.73 V vs SCE) as shown by B in Scheme I. Nevertheless, UV−vis spectroscopic studies on (**OMN**[+•])$_2$(**NAP**), 2SbCl$_6$[−] show an absorption band at ca. 1100 nm reminiscent of the charge-resonance band found at 1050 nm in the homodimer cation radical (**NAP**)$_2$[+•]PF$_6$[−•]. The reappearance of an extra absorption band on going from the monomeric cation-radical salt **OMN**[+•]SbCl$_6$[−] to the heteromolecular π-complex (**OMN**[+•])$_2$-(**NAP**), 2SbCl$_6$[−], together with the structural data, accounts for the charge-transfer nature of the title compound.[16] We hope that the successful isolation of the first crystalline heteromolecular (mixed valence) cation radical will now pave the way to prepare continuous stacks of different cation-radical salts showing novel physical properties. The electronic/magnetic properties of these interesting (paramagnetic) crystals are under active investigation, and their theoretical relationship as wholly organic analogues to the inorganic mixed-valence complexes[18] (both showing NIR sprectral bands) will be probed with the aid of Hush theory for intervalence transitions.[19]

Supporting Information Available: Preparation of cation-radical salts, electrocrystallization of (**NAP**)$_2$[+]PF$_6$[−], X-ray crystallographic analyses, Table S1, and Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) The *partial* transfer of (electron) charge in the heteromolecular complex relates to Mulliken charge-transfer theory[17] and is thus indicated as "CT" in Scheme 1B.

(17) (a) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811. (b) Mulliken, R. S.; Person, W. B. *Molecular Complexes. A Lecture and Reprint Volume*; Wiley: New York, 1969. (c) See also: Foster, R. *Organic Charge-Transfer Complexes*; Academic: New York, 1969.

(18) (a) Robin, M. B.; Day, D. *Adv. Inorg. Radiochem.* **1967**, *10*, 247. (b) Creutz, C.; Newton, M. D.; Sutin, N. *Photochem. Photobiol.* A. **1994**, *82*, 48.

(19) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391 and *Coord. Chem. Rev.* **1985**, *64*, 135.

(20) Sheldrick, G. M. *SHELXS-86. Program for Structure Solution*; University of Göttigen: Germany, 1986.

(21) The average geometry of naphthalene is from (a) Ponomarev, V. I.; Filipenko, O. S.; Atovmyan, L. O. *Kristallografy* **1976**, *21*, 392 and (b) Brock, C. P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1982**, *38*, 2218.