

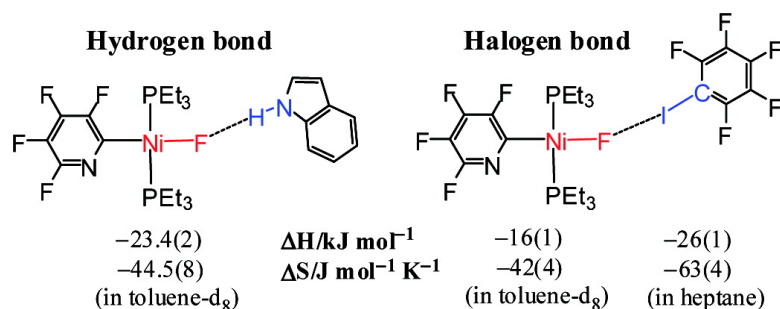
Communication

Metal Fluorides Form Strong Hydrogen Bonds and Halogen Bonds

Stefano Libri, Naseralla A. Jasim, Robin N. Perutz, and Lee Brammer

J. Am. Chem. Soc., **2008**, 130 (25), 7842-7844 • DOI: 10.1021/ja8020318 • Publication Date (Web): 29 May 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 2 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Metal Fluorides Form Strong Hydrogen Bonds and Halogen Bonds: Measuring Interaction Enthalpies and Entropies in Solution

Stefano Libri,[†] Naseralla A. Jasim,[‡] Robin N. Perutz,^{*,‡} and Lee Brammer^{*,†}

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K., and Department of Chemistry, University of York, Heslington, York YO10 5DD, U.K.

Received March 21, 2008; E-mail: lee.brammer@sheffield.ac.uk; rnp1@york.ac.uk

Although much research has been devoted in recent years to the study of intermolecular interactions of halogens, knowledge of energetics has lagged behind knowledge of structure. Halogens are common constituents of a wide range of organic and inorganic molecules and are frequently found in their monovalent state at the periphery of these molecules, where they are readily available for noncovalent interactions. Depending upon their coordination environment, halogens can exhibit Lewis basic or acidic character enabling them to participate in two classes of strong, directional intermolecular interaction, namely hydrogen bonds¹ and halogen bonds.² Interest in hydrogen bonding involving halogens spans coordination and organometallic chemistry,^{3–6} supramolecular chemistry and crystal engineering,⁷ and biochemistry,⁸ whereas halogen bonding has seen applications in areas such as crystal design,⁹ molecular recognition,¹⁰ topochemical reactions,¹¹ molecular conductors,¹² and liquid crystals;¹³ their role in structural biology has also been examined.¹⁴

Structural studies have demonstrated that metal halide complexes are excellent acceptors of hydrogen bonds¹ and halogen bonds.¹⁵ However, support for this assertion from experimental determinations of interaction energies is very limited for hydrogen bonding^{3a,c,4} and entirely absent for halogen bonding. Without such data in the form of equilibrium constants or enthalpies of interaction, opportunities for informed design are limited and calculations cannot be compared to experiments. Metal fluoride complexes, specifically, are now widely studied because of their unusual reactivity and their relevance in C–F activation of organic molecules;¹⁶ they are also well known hydrogen bond acceptors.^{3–6,8,17} Indirect evidence based upon complexes of other metal halides¹⁸ and on fluoride ions¹⁹ suggests that fluoride ligands will also serve as halogen bond acceptors.

Indicators of the strength of hydrogen bonding for metal fluoride complexes can be found in structural data on their adducts of HF^{3b,5a,b} or water.^{6,8} In the case of *cis*-[Ru(PMe₃)₄(FHF)₂]^{5b} the distance between fluorine atoms of the coordinated bifluoride in the crystal structure is almost unchanged from that of free (FHF)[–].

The objective of this study is to compare the strength of hydrogen and halogen bonds formed by a metal fluoride complex in the condensed phase, focusing on species analogous to those with potential applications in supramolecular chemistry and crystal engineering (Figure 1).

The fluoride ligand provides a direct NMR spectroscopic handle free of spectral overlap that is very sensitive to its environment. The metal fluoride complex chosen is *trans*-(tetrafluoropyrid-2-yl)bis(triethylphosphine)fluoronickel(II)²⁰ (**NiF**), which is convenient for the ease of synthesis, high solubility in most organic solvents, and the presence of a single fluoride ligand. The hydrogen

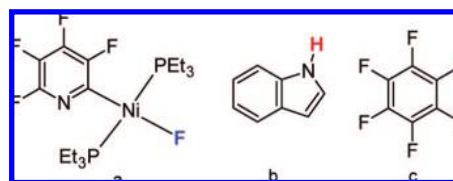


Figure 1. Species used in this work: (a) nickel fluoride complex (**NiF**), (b) indole, (c) iodopentafluorobenzene.

bond donor is indole, which is a good hydrogen bond donor but importantly not a good hydrogen bond acceptor,²¹ nor a potential nitrogen donor ligand. Iodopentafluorobenzene is a very good halogen bond donor due to the fluorination of the ring, which greatly increases the electrophilicity of the iodine atom.²² This compound (C₆F₅I) has already found applications in liquid crystal design¹³ and is a convenient precursor to a great variety of halogen bond donors, due to the ease with which it undergoes regioselective aromatic nucleophilic substitution in the position *para* to the iodine.^{2,11,23}

Formation of the hydrogen-bonded adduct between **NiF** and indole was analyzed by multinuclear NMR spectroscopy.²⁴ For indole, there is a downfield shift of the pyrrolic hydrogen in the ¹H NMR spectrum characteristic of hydrogen bond formation and smaller shifts of the signals of the other hydrogen atoms (Figure 2a). The fluoride ligand of the metal complex shows a substantial downfield shift in the ¹⁹F NMR spectrum at δ –371.4 rising by ca. 20 ppm at high concentrations of indole (Figure 2b);²⁵ very small variations (<0.3 ppm) in the ¹⁹F chemical shifts of the organic fluorine atoms of the tetrafluoropyridyl ligand and in the ³¹P chemical shifts (ca. 0.1 ppm) of the triethylphosphine ligands also arise. These changes demonstrate the retention of the fluoride, phosphine, and fluoropyridyl ligands and provide direct evidence for selective interaction with the fluoride ligand. Coordination at nickel is excluded by the properties of indole and the lack of change in other NMR parameters. No further spectroscopic changes are observed within 48 h, indicating the stability of the system.

The variation with concentration of the signal for the coordinated fluoride in the ¹⁹F NMR spectrum was used to determine the equilibrium constant for adduct formation and its temperature dependence in deuterated toluene (Figures 3 and S4).

The titration curves are fitted well by the following model:



where *D* = indole, that is, the sequential formation of 1:1 and 1:2 complexes. The same measurement was made for the adduct

[†] University of Sheffield.

[‡] University of York.

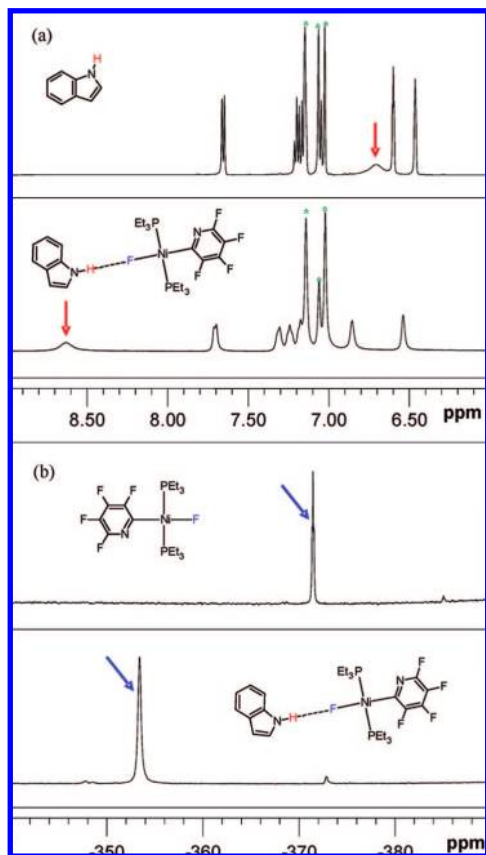


Figure 2. (a) Indole signals in the ^1H NMR spectrum (500 MHz, toluene- d_8) for pure indole (top) and for the indole/ NiF mixture (bottom). Solvent peaks are marked with an asterisk. (b) Fluoride signals in the ^{19}F NMR spectrum in toluene- d_8 for pure NiF (top) and for the indole/ NiF mixture (bottom). Both spectra were measured at a temperature of 300 K.

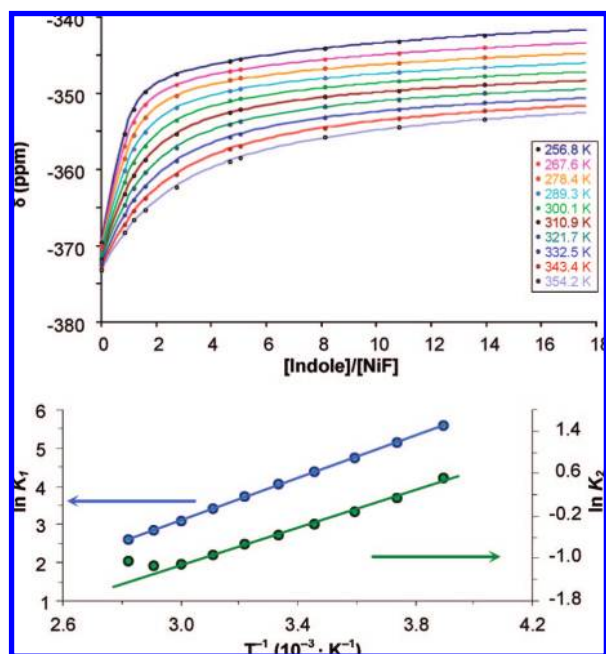


Figure 3. (a) Fit of the titration curves at different temperatures, showing observed δ_{F} versus ratio of molar concentrations of indole and NiF in toluene- d_8 ; (b) Van't Hoff plot.

between NiF and iodopentafluorobenzene in deuterated toluene. The effect of the presence of the halogen bond donor on the NMR

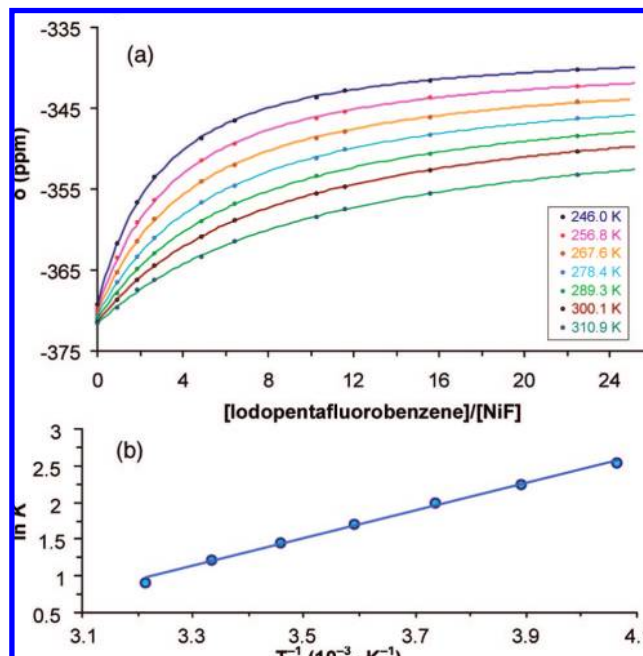


Figure 4. (a) Fit of the titration curves at different temperatures, showing observed δ_{F} versus ratio of molar concentrations of iodopentafluorobenzene and NiF in toluene- d_8 . (b) Van't Hoff plot.

Table 1. Summary of Thermodynamic Parameters Determined^a

Lewis acid	solvent	K_1^b	ΔH_1^0 (kJ·mol ⁻¹)	ΔS_1^0 (J·mol ⁻¹ ·K ⁻¹)	K_2^b	ΔH_2^0 (kJ·mol ⁻¹)	ΔS_2^0 (J·mol ⁻¹ ·K ⁻¹)
$\text{C}_8\text{H}_8\text{NH}$	toluene- d_8	57.9(3)	-23.4(2)	-44.5(8)	0.58(4)	-14.8(8)	-53(3)
$\text{C}_6\text{F}_5\text{I}$	toluene- d_8	3.41(9)	-16(1)	-42(4)			
$\text{C}_6\text{F}_5\text{I}$	heptane	21.8(2)	-26(1)	-63(4)	0.22(4)	-21(1)	-83(5)

^a Errors are provided at the 95% confidence level. ^b At 300.1 K.

signals of NiF is very similar to that observed in the case of indole: a substantial downfield shift of the coordinated fluoride signal and small shifts for other nuclei. The iodopentafluorobenzene shows small changes in the fluorine chemical shifts. In this case, only the 1:1 adduct appears to be present (equation 1, $\text{D} = \text{C}_6\text{F}_5\text{I}$; Figure 4). The measurement for the NiF /iodopentafluorobenzene system has been repeated in heptane. The change of solvent has the remarkable effect of allowing the formation of the 1:2 adduct, along with the 1:1 adduct (Figures S7, S8, and S9). The values of the equilibrium constant, standard enthalpy, and entropy for the formation of all adducts are provided in Table 1.

Each process exhibits negative values of the enthalpy and entropy in accordance with the models proposed. Where two sequential steps are observed, the standard enthalpy change for the second process is significantly smaller than for the first process, as expected. The halogen bond interaction is very sensitive to the change in solvent from toluene to heptane, showing increased values of K , $|\Delta H|$ and $|\Delta S|$ for the latter. A plausible explanation is that, despite its low polarity, toluene may interact quite strongly with iodopentafluorobenzene since fluorinated arenes are known to form stable π -stacked adducts with nonfluorinated arenes.²⁶ Weaker interactions via $\text{C}-\text{I}\cdots\pi$ halogen bonds also cannot be excluded.²⁷ Analogous investigation of the solvent dependence of the hydrogen bond cannot be accomplished since indole is insoluble in heptane. However, interactions of indole with toluene via π -stacking or $\text{N}-\text{H}\cdots\pi/\text{C}-\text{H}\cdots\pi$ interactions²⁸ are expected to be weaker than the solvent interactions involving iodopentafluorobenzene.

In conclusion, we have established that enthalpies of halogen bonds formed by donors such as iodopentafluorobenzene with Lewis bases (here NiF) may be as large as those for hydrogen bonds formed by that Lewis base with indole. The energy of these intermolecular interactions indicates that coordinated fluoride is a strong hydrogen bond and halogen bond acceptor. Implicit in the strong hydrogen bond is that the Ni–F bond is highly polar. The hydrogen bond enthalpy is comparable with that determined by Crabtree for intramolecular N–H···F(Ir) hydrogen bonds involving an aniline hydrogen bond donor,^{3c,29} whereas to our knowledge the entropy of such an interaction is previously unreported. The strength of the halogen bond is consistent with our previous assertion that M–X···X'–C halogen bonds are predominantly electrostatic in character, with stronger halogen bonds expected for lighter halide ligands.¹⁸ Important prior experimental studies of the energetics of halogen bonds are limited to binding constant determinations for iodoacetylene adducts with Lewis bases³⁰ and to extensive gas phase studies involving interhalogens as halogen bond donors.³¹ However, computational studies include recent calculations for gas phase halogen-bonded PhBr···X[–] adducts which determine interaction energies to be greater for X = F > Cl > Br, with magnitudes as high as 64 kJ mol^{–1} for the halogen bond involving a free fluoride ion.³²

The strength of both classes of interaction, hydrogen bonds and halogen bonds underlines their general importance in supramolecular chemistry and suggests their utility for the development of supramolecular control in transition-metal catalysts³³ and for the introduction of functional metal centers in the design of molecular crystals. In particular, these results are important in the application of hierarchical principles for supramolecular synthons,³⁴ used in designing crystalline materials, as recently reported by Aakeröy³⁵ in discussing the competition between halogen and hydrogen bonds in organic molecules.

Acknowledgment. We are grateful to Professor Chris Hunter for provision of a macro used in calculation of the equilibrium constants. S.L. is supported by a studentship from the White Rose Consortium under the network project “Molecular Engineering”.

Supporting Information Available: Complete experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Brammer, L.; Bruton, E. A.; Sherwood, P. *Cryst. Growth Des.* **2001**, *1*, 277.
- (2) (a) Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G. *Acc. Chem. Res.* **2005**, *38*, 386. (b) Metrangolo, P.; Resnati, G., Eds. *Halogen Bonding: Fundamentals and Applications, Structure & Bonding*; Springer: Berlin, 2007.
- (3) (a) Richmond, T. G. *Coord. Chem. Rev.* **1990**, *105*, 221. (b) Murphy, V. J.; Hascall, T.; Chen, J. Y.; Parkin, G. *J. Am. Chem. Soc.* **1996**, *118*, 7428. (c) Lee, D.-H.; Kwon, H. J.; Patel, B. P.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H. *Organometallics* **1999**, *18*, 1615.
- (4) Yandulov, D. V.; Caulton, K. G.; Belkova, N. V.; Shubina, E. S.; Epstein, L. M.; Khoroshum, D. V.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 12553.
- (5) (a) Jasim, N. A.; Perutz, R. N. *J. Am. Chem. Soc.* **2000**, *122*, 8685. (b) Jasim, N. A.; Perutz, R. N.; Foxon, S. P.; Walton, P. H. *J. Chem. Soc., Dalton Trans.* **2001**, *11*, 1676.
- (6) Jasim, N. A.; Perutz, R. N.; Whitwood, A. C.; Braun, T.; Izundu, J.; Neumann, B.; Rothfeld, S.; Stammler, H. G. *Organometallics* **2004**, *23*, 6140.
- (7) Brammer, L.; Swearingen, J. K.; Bruton, E. A.; Sherwood, P. *Proc. Nat. Acad. Sci. U.S.A.* **2002**, *99*, 4956.
- (8) Emsley, J.; Reza, N. M.; Dawes, H. M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 313.
- (9) Zhu, S.; Xing, C.; Xu, W.; Li, Z. *Tetrahedron Lett.* **2004**, *45*, 777.
- (10) Farina, A.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 2433.
- (11) Caronna, T.; Liantonio, R.; Logothetis, T. A.; Metrangolo, P.; Pilati, T.; Resnati, G. *J. Am. Chem. Soc.* **2004**, *126*, 4500.
- (12) Yamamoto, H. M.; Maeda, R.; Yamaura, J. I.; Kato, R. *J. Mater. Chem.* **2001**, *11*, 1034.
- (13) Nguyen, H. L.; Horton, P. N.; Hursthouse, M. B.; Legon, A. C.; Bruce, D. W. *J. Am. Chem. Soc.* **2004**, *126*, 16.
- (14) Auffinger, P.; Hays, F. A.; Westhof, E.; Ho, P. S. *Proc. Nat. Acad. Sci. U.S.A.* **2004**, *101*, 16789.
- (15) Brammer, L.; Mínguez Espallargas, G.; Adams, H. *CrystEngComm* **2003**, *5*, 343.
- (16) (a) Doherty, N.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553. (b) Grushin, V. V. *Chem. Eur. J.* **2002**, *8*, 1007. (c) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25. (d) Mayer, J. M. *Comments Inorg. Chem.* **1988**, *8*, 125. (e) Macgregor, S. A.; Roe, D. C.; Marshall, W. J.; Bloch, K. M.; Bakhtmutov, V. I.; Grushin, V. V. *J. Am. Chem. Soc.* **2005**, *127*, 15304. (f) Braun, T.; Perutz, R. N. Transition-Metal Mediated C–F Bond Activation. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Amsterdam, 2006.
- (17) Brammer, L.; Bruton, E. A.; Sherwood, P. *New J. Chem.* **1999**, *23*, 965.
- (18) (a) Mínguez Espallargas, G.; Brammer, L.; Sherwood, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 435. (b) Jordan, F.; Brammer, L.; Sherwood, P. *J. Am. Chem. Soc.* **2005**, *127*, 5979.
- (19) (a) Ghassemzadeh, M.; Harms, K.; Dehnicke, K. *Chem. Ber.* **1996**, *129*, 115. (b) Drews, T.; Marx, R.; Seppelt, K. *Chem. Eur. J.* **1996**, *2*, 1303.
- (20) Cronin, L.; Higgitt, C. L.; Karch, R.; Perutz, R. N. *Organometallics* **1997**, *16*, 4920.
- (21) (a) Peris, E.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 2179. (b) Wessel, J.; Lee, J.-C.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed.* **1995**, *34*, 2507. (c) Desmurs, P.; Kavallieratos, K.; Yao, W.; Crabtree, R. H. *New J. Chem.* **1999**, *23*, 1111.
- (22) Valerio, G.; Raos, G.; Meille, S. V.; Metrangolo, P.; Resnati, G. *J. Phys. Chem. A* **2000**, *104*, 1617.
- (23) (a) Xu, J.; Liu, X.; Kok-Peng Ng, J.; Lin, T.; He, C. *J. Mater. Chem.* **2006**, *16*, 3540. (b) Bertani, R.; Chau, F.; Gleria, M.; Metrangolo, P.; Milani, R.; Pilati, T.; Resnati, G.; Santosera, M.; Vanzo, A. *Inorg. Chim. Acta* **2007**, *360*, 1191.
- (24) ¹³C NMR chemical shifts have been used to identify C–1···N halogen bonds but not used to determine interaction energies, see: Bouchmella, K.; Boury, B.; Dutremez, S. G.; van der Lee, A. *Chem. Eur. J.* **2007**, *13*, 6130.
- (25) An upfield ¹⁹F chemical shift has been observed as a result of hydrogen bonding involving tungsten(II) and titanium(IV) fluoride complexes.^{3a}
- (26) (a) Williams, J. H. *Acc. Chem. Res.* **1993**, *26*, 593. (b) Reichenbaecher, K.; Süß, H. I.; Hulliger, J. *Chem. Soc. Rev.* **2005**, *34*, 22. (c) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641.
- (27) Lu, Y. X.; Zou, J. W.; Wang, Y. H.; Yu, Q. S. *Chem. Phys.* **2007**, *334*, 1.
- (28) Nishio, M. *CrystEngComm* **2004**, *6*, 130.
- (29) (a) The indole to fluoride ligand hydrogen bond enthalpy also exceeds that reported (16.7 kJ mol^{–1}) from solid state IR spectroscopic measurements for an indole–PPh₃O adduct,^{21a} and that for a gas-phase measurement of an indole to water hydrogen bond (20(1) kJ mol^{–1}).^{29b} (b) Mons, M.; Dimicoli, I.; Tardivel, B.; Piuze, F.; Brenner, V.; Millié, P. *J. Phys. Chem. A* **1999**, *103*, 9958.
- (30) (a) Laurence, C.; Queignec-Cabanatos, M.; Dziembowska, T.; Queignec, R.; Wojtkowiak, B. *J. Am. Chem. Soc.* **1981**, *103*, 2567. (b) Laurence, C.; Queignec-Cabanatos, M.; Wojtkowiak, B. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1605.
- (31) Legon, A. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2686.
- (32) Lu, Y.-X.; Zou, J.-W.; Wang, Y.-H.; Jiang, Y.-J.; Yu, Q.-S. *J. Phys. Chem. A* **2007**, *111*, 10781.
- (33) (a) Das, S.; Brudvig, G. W.; Crabtree, R. H. *Chem. Commun.* **2008**, 413. (b) Natale, D.; Mareque Rivas, J. C. *Chem. Commun.* **2008**, 425.
- (34) (a) Desiraju, G. R. *Angew. Chem., Int. Ed.* **1995**, *34*, 2311. (b) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120.
- (35) Aakeröy, C. B.; Fasulo, M.; Schultheiss, N.; Desper, J.; Moore, C. *J. Am. Chem. Soc.* **2007**, *129*, 13772.

JA8020318