

Cation–Cation Interactions

Cation-Cation Pairing by N-C-H-O Hydrogen Bonds

Waltraud Gamrad, Angelika Dreier, Richard Goddard, and Klaus-Richard Pörschke*

Dedicated to Professor Dr. Günther Wilke on the occasion of his 90th birthday

Abstract: The pairing of ions of opposite charge is a fundamental principle in chemistry, and is widely applied in synthesis and catalysis. In contrast, cation-cation association remains an elusive concept, lacking in supporting experimental evidence. While studying the structure and properties of 4-oxopiperidinium salts $[OC_5H_8NH_2]X$ for a series of anions X^- of decreasing basicity, we observed a gradual self-association of the cations, concluding in the formation of an isolated dicationic pair. In 4-oxopiperidinium bis(trifluoromethylsulfonyl)amide, the cations are linked by $N-H\cdots O=C$ hydrogen bonds to form chains, flanked by hydrogen bonds to the anions. In the tetra(perfluoro-tert-butoxy)aluminate salt, the anions are fully separated from the cations, and the cations associate pairwise by $N-C-H\cdots O=C$ hydrogen bonds. The compounds represent the first genuine examples of self-association of simple organic cations based merely on hydrogen bonding as evidenced by X-ray structure analysis, and provide a paradigm for an extension of this class of compounds.

In solution, ion pairing occurs when cations and anions associate in a solvent of low dielectric constant to form a distinct chemical entity. Depending on the degree of solvent participation, fully solvated ions, solvent-separated ion pairs, and contact ion pairs are usually distinguished.^[1] In contrast, cation–cation interactions of organic species appear as a rare and counterintuitive phenomenon which has been spectroscopically detected, for example, for NMe₄⁺ ions in aqueous K/CsBr solutions,^[2] for guanidinium ions in water,^[3] certain ionic liquids,^[4] and in the micellization of tetraalkylammonium surfactants,^[5] although there is no direct structural evidence to support this.

In quaternary tetraalkylammonium ions the positive charge is significantly delocalized onto the protons attached to the α -C atoms of the hydrocarbon chains,^[6] rendering these protons sufficiently acidic to engage in hydrogen bonds to anions. In N(C₂H₅)₄Br^[7a] and N(C₂H₅)₄I,^[7b] for example, most protons of the α - and β -C atoms form C–H···X hydrogen bonds to the halide X, which in turn functions as a hydrogen-bond acceptor. Reetz et al.^[8] have shown that the α protons of the NBu₄ cation form N–C–H···O=C hydrogen bonds^[9] to the enolate oxygen atoms of a malonic acid diester anion (C···O

[*] W. Gamrad, A. Dreier, Dr. R. Goddard, Prof. Dr. K.-R. Pörschke Max-Planck-Institut für Kohlenforschung Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr (Germany) E-mail: poerschke@kofo.mpg.de Homepage: http://www.kofo.mpg.de/poerschke.html

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201408278.

3.263(2)–3.391(2) Å) resulting in an overall neutral molecular entity. It seems reasonable to assume that the oxygen atoms of enolates are more basic than those of neutral ketones. We now wish to report the apparently unprecedented self-association of two secondary ammonium cations by N–C–H···O=C hydrogen bonding to neutral carbonyl groups with the formation of a dication.

The starting point of our investigation was our interest in the structural properties of 4-piperidone hydrate hydrochloride, a widely used feedstock in pharmaceutical chemistry. We show that the compound is actually 4,4-dihydroxypiperidinium chloride, $[(HO)_2C_5H_8NH_2]Cl(1a)$, in which the geminal diol is stabilized by hydrogen bonding to the chloride ion. The chloride ion serves as a fourfold hydrogen-bond acceptor^[1] to both hydroxy and ammonium protons in a three-dimensional network.^[10] The bromide $[(HO)_2C_5H_8NH_2]Br$ (1b) displays a similar 3D network structure. The corresponding iodide is unstable as a solid and dehydrates upon crystallization to give 4-oxopiperidinium iodide, $[OC_5H_8NH_2]I$ (2c). The analogous 4-oxopiperidinium chloride $[OC_5H_8NH_2]Cl$ (2a) can be prepared from 1a by dehydration with SOCl₂. Compound **2a** reacts with HBr by halide exchange to give $[OC_5H_8NH_2]Br$ (2b). The 4-oxopiperidinium halides 2a-c no longer have a typical three-dimensional ionic structure, but rather form parallel chains of alternating 4-oxopiperidinium cations and halide anions connected by NH…X…HN hydrogen bonds. These chains are closely packed, with the very weakly basic keto functions being barely involved in any hydrogen bonding.^[10] For the halide salts the carbonyl IR resonance occurs at about 1720 cm⁻¹, which corresponds to that of a typical neutral ketone (cyclohexanone, $\tilde{\nu}_{\rm CO} = 1717 \text{ cm}^{-1}$).

When **2a** is reacted with silver reagents AgX with a weakly or noncoordinating anion X⁻ such as $MeCO_2^-$, BF_4^- , CIO_4^- , $OSO_2CF_3^-$ (OTf⁻, triflate), $N(SO_2CF_3)_2^-$



 (NTf_2^{-}) , and $[Al\{OC(CF_3)_3\}_4]^-$ (= $[Al(PFTB)_4]^-$, Krossing's anion)^[11a] in diethyl ether or CH_2Cl_2 solution, chloride is replaced by these anions to give the $[OC_3H_8NH_2]X$ salts **2d**-i [Eq. (1)]. While **2d**-h crystallize without the inclusion of solvent, the aluminate **2i** separates from such solutions in the form of the solute compounds $[OC_5H_8NH_2(OEt_2)_2][Al-$

 $(PFTB)_4$] (2i·2Et₂O) and $[OC_5H_8NH_2][Al(PFTB)_4]\cdot CH_2Cl_2$ (2i·CH₂Cl₂).

In the solid state, the CO stretching frequency (wavenumber) of the 4-oxopiperidinium cation in compounds 2 depends on the counterion X and increases with the diminishing basicity of the anion in the series 2a-e (ca. 1720 cm^{-1}), **2f** (1725 cm⁻¹), **2g** (1741 cm⁻¹), and **2i**·2 Et₂O (1744 cm⁻¹). Compound **2h** (X = NTf₂) appears to be an exception, since it exhibits two $\tilde{\nu}_{CO}$ bands with frequencies expected for a typical ketone (1720, 1728 cm⁻¹) despite the low basicity of the anion. In analogy to related systems,^[12] we assume that a positive charge on the 4-oxopiperidinium ring results in a higher C=O bond strength and, consequently, an increase in the value of $\tilde{\nu}_{\rm CO}{}^{[13]}$ As expected, the effect is largest for 2i, which has the least basic anion (X = Al-(PFTB)₄). However, this explanation appears no longer applicable when the carbonyl lone electron pairs are bonded to a Lewis acid, as in the case for 2h, where the carbonyl group is hydrogen-bonded to acidic ammonium protons (see below).

When acetone was used as a solvent, variable amounts of the Schiff base $[OC_5H_8N=CMe_2]X$ (A) were formed as a byproduct, as a result of partial condensation. In addition,



the synthesis of **2i** was frequently accompanied by the formation of some viscous brownish byproducts which, according to ESI mass spectrometry, are polycation salts **B** formed by self-condensation of the 4-oxopiperidinium cation by water elimination.^[14,15] Such a condensation reaction appears to result from a linear head-to-tail association of 4-oxopiperidinium cations by N–H···O=C bonding in the absence of stabilization by the anions (**C**). This observation appears to verify the importance of the anions in the other compounds, such as **2h** (see below).

In order to investigate the possible role of the anion in the formation of hydrogen bonds involving the 4-oxopiperidinium cation in more detail, we studied the hydrogen bonding in the ammonium ketones **2a–i**. We reasoned that with decreasing basicity of the anions X in the sequence $Cl > Br > I \approx MeCO_2 > BF_4 > ClO_4 > OTf \ge NTf_2 \gg Al(PFTB)_4$ hydrogen bonds $NH \cdots X \cdots HN$ to the anion X would become less structure-determining and the weakly basic carbonyl group of the 4-oxopiperidinium ion should become increasingly involved in the bonding. Herein we describe essential features through the crystal structures of $2f (X^- = ClO_4^-), 2g (X^- = OTf^-), 2h (X^- = NTf_2^-), and 2i \cdot 2 Et_2O (X^- = [Al(PFTB)_4]^-).$

The 4-oxopiperidinium salts **2 f**, **2g**, and **2i**-2 Et₂O crystallize in the triclinic space group $P\overline{1}$ (no. 2). Each unit cell contains two cations and anions related by inversion centers. Compound **2h** crystallizes in the monoclinic space group $P2_1/c$ (no. 14). The main structural features of the 4-oxopiperidinium cations correspond to those of most other salts of this cation in our study (Cl⁻, Br⁻, I⁻, ClO₄⁻, OTf⁻, NTf₂⁻, and [Al(PFTB)₄]⁻; see Tables S1 and S2 in the Supporting Information). Based on the ring torsional angles, the cation adopts a chair conformation that is relatively steep around nitrogen and quite flat near the carbonyl group. As a result of this geometry, the axial and equatorial protons of the 4oxopiperidinium cation are electronically inequivalent. Protons on the nitrogen atoms were all located and refined.

The crystal structures of the perchlorate (2 f) and trifluoromethylsulfonate salts (2g) are remarkably similar and indicative of low but distinct basicity of the anions. In the crystal of 2 f eclipsed 4-oxopiperidinium cations alternate with perchlorate anions to form infinite chains along the *b* axis (Figure 1). The ammonium proton N1-H6_{ax} engages in



Figure 1. Crystal structure of 2f showing parallel chains of alternating 4-oxopiperidinium cations and perchlorate anions along the *b* axis (horizontal).

a single hydrogen bond with the O2 atom of a perchlorate anion (N1···O2 2.883(3) Å, N1–H6_{ax}···O2 160°), whereas the ammonium proton N1-H7_{eq} appears to participate in twofold hydrogen bonding to the O3 and O4 atoms of a neighboring anion (N1···O3 3.007(3) Å, N1–H7_{eq}···O3 137(1)° and N1···O4 3.107(3) Å, N1–H7_{eq}···O4 138(1)°). There is evidence of additional short N–C–H···O=C hydrogen-bonding interactions between the carbonyl O1 atom in one chain and the equatorial proton on C1, H1B_{eq}, of a neighboring chain (C1···O1 3.125(3) Å, C1–H1B_{eq}···O1 125(1)°). Otherwise, association of the chains appears to be mainly governed by close packing, since each parallel chain is surrounded by six nearest neighbors.

In the trifluoromethylsulfonate salt 2g, the 4-oxopiperidinium cations are similarly linked by N-H…O hydrogen bonds to the O atoms of triflate anions to form chains extending along the *b* axis (Figure 2). Thus, the axial





Figure 2. Crystal structure of 2g, showing parallel chains of alternating 4-oxopiperidinium cations and trifluoromethylsulfonate anions along the *b* axis (horizontal).

ammonium proton H6_{ax} attached to N1 of a 4-oxopiperidinium cation is hydrogen-bonded to O2 of a triflate anion in the chain (N1…O2 2.917(3) Å, N1–H6_{ax}…O2 170(1)°), whereas the equatorial ammonium proton, H7_{eq}, is hydrogen-bonded to O3 of a neighboring triflate anion (N1…O3 2.964(3) Å, N1–H7_{eq}…O3 174(1)°). As in **2 f**, in **2 g** parallel chains of N–H…O bonded anions and cations are each surrounded by six nearest neighbors in a close packing arrangement. Analogously, the carbonyl O1 atom appears to undergo an inter-chain N–C–H…O=C hydrogen-bonding interaction with the equatorial proton on C1, H1B_{eq}, of a neighboring chain (C1…O1 3.049(3) Å, C1–H1B_{eq}…O1 125(1)°).

Thus, all 4-oxopiperidinium salts 2a-g exhibit N⁺-H···X⁻ hydrogen-bonded chains of alternating ammonium centers and anions in the solid state. First indications of a change in the cation-anion bonding pattern occurred when we looked at the bis(trifluoromethylsulfonyl)imide salt. We chose the NTf₂ anion because of its low basicity and similarity to the triflate anion. 4-Oxopiperidinium bis(trifluoromethylsulfonyl)imide 2h was synthesized as described above and crystals of the salt were grown. Figure 3 summarizes the results of the crystal structure analysis of 2h. There are two independent cations and two independent anions in the asymmetric unit, as expected from the presence of two $\tilde{\nu}_{CO}$ absorptions. In contrast to 2a-g, in 2h both equatorial ammonium H atoms on the two 4-oxopiperidinium cations form short N-H-O=C hydrogen bonds^[16] to the carbonyl O atoms of the neighboring cations (N1--O2 2.783(3) Å, N1-H7eq--O2 161(1)°, and N2···O1 2.807(3) Å, N2-H12_{eq}···O1 153(1)°). In addition,



Figure 3. Crystal structure of **2h**, showing cation–cation N–H…O hydrogen-bonding and cation–anion N–H…N and N–H…O hydrogen-bonding interactions.

each cation forms a hydrogen bond between its axial H atom of the ammonium group and a NTf₂ anion. Whereas N1 forms a hydrogen bond to the sulfonyl O3 (N1···O3 2.765(3) Å, N1–H6_{ax}···O3 161(1)°), N2 hydrogen-bonds to the imide N4 (N2···N4 2.966(3) Å, N2–H11_{ax}···N4 166(1)°). Clearly, the use of an exceedingly weakly basic anion promotes hydrogen-bonding interactions between the cations.

Inspired by these results, we decided to investigate a 4-oxopiperidinium salt of a still less basic anion and selected the $[Al(PFTB)_4]^-$ anion in this case, since it is well known as a noncoordinating ion.^[11c] Its salt crystallizes from diethyl ether with

two solute molecules: 2i-2Et₂O. The compound comprises discrete perfluoroaluminate anions and 4-oxopiperidinium cations, whose ammonium protons are engaged in hydrogen bonds to the oxygen atoms of two ether molecules (N1--O2 2.776(2) Å, N1-H1C_{eq}···O2 168(1)° and N1···O3 2.815(2) Å, N1-H1D_{ax}...O3 168(1)°; Figure 4a). There are no obvious hydrogen-bonding interactions between the cations and the anions. Instead, pairs of solvated cations self-assemble around centers of symmetry. Association is based on N-C-H-O=C hydrogen bonding between the axial protons H1A_{ax} and H5B_{ax} on the α -C atoms (C1 and C5, respectively) of the ammonium group of one cation and the oxygen atom of the carbonyl group of a neighboring cation (C5…O1 3.142(2) Å, C5-H5B_{av}...O1 134° and C1...O1 3.392(2) Å, C1-H1A_{av}...O1 131°; Figure 4b). The C···O distances of the N-C-H···O=C bonds in $2i \cdot 2Et_2O$ (and also 2f,g) compare favorably with those of the bonds between ammonium groups and anionic carbonyl groups mentioned in the introduction^[8] and other literature data.^[9] In the crystal structure one can view 2i-2Et₂O as an AB₂-type salt whose molecular volume corresponds to the volume of the unit cell (2.241 nm³). From this and considering the known large thermochemical volume^[17a] of the [Al(PFTB)₄]⁻ anion ($V_{\text{therm}} = 0.758 \text{ nm}^3$),^[11b] we calculated the thermochemical volume of the tetrakis (diethylether)-di(4-oxopiperidinium) dication in 2i-2Et₂O at $V_{\text{therm}} = 0.725 \text{ nm}^3$. The comparable size of the dication and the anion suggests that a treatment of 2i-2Et₂O as an AB₂ salt of large close-packed ions is reasonable.

In addition to its size, the nature of the $[AI(PFTB)_4]^$ anion as an exceedingly weak base and weakest hydrogen-

bond acceptor^[11d,18] of the system appears critical for the formation of the dication in **2i**·2Et₂O. Unlike the other anions described in this paper, the perfluoroaluminate anion does not function as a hydrogen-bond acceptor for the 4-oxopiperidinium cation. Consistent with the rules put forward by Etter^[19b] that in complex systems involving various types of hydrogen bonding,^[19] the most acidic hydrogen atoms form H-bonds to the most basic donor atoms, the ammonium protons in **2i**·2Et₂O hydrogen-bond to the oxygen atoms of solvent diethyl ether. Such N–H…O(ether) hydrogen bonds appear unprecedented for diethyl ether,^[20] and even for the more basic THF only a few examples have been recorded.^[21] Thus, both





b)



Figure 4. Crystal and molecular structure of **2i**-2 Et₂O. a) View of the unit cell, showing the solvated self-associated cations and the surrounding $[Al(PFTB)_4]^-$ anions. b) Detail of the pairwise association of the 4-oxopiperidinium cations, solvated by diethyl ether molecules.

the cation-cation interaction and the ability of the cation to bond to ether molecules makes the structure of $2i \cdot 2Et_2O$ exceptional.

To shed light on the thermodynamics of the dication formation we carried out a Born–Fajans–Haber^[22] (BFH) cycle study on the dication salt as compared to the monocation salt at 298 K and 200 K in order to assess the stabilization of the dication by lattice effects (Scheme 1).^[23] Lattice



Scheme 1. BFH study of **2i**-2Et₂O (diethyl ether molecules are omitted from the formulae). The lattice enthalpies $\Delta_{latt}H_{298}$ of both salts were calculated by using volume-based thermodynamics,^[17] and the gas-phase dissociation enthalpy of the dication was determined by DFT calculations at the dispersion-corrected B3LYP/aug-cc-pVTZ and B3LYP/cc-pVQZ levels of theory.

Angew. Chem. Int. Ed. 2015, 54, 4482–4487

© 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

enthalpies $\Delta_{\text{latt}}H$ of the dicationic salt AB₂ and the monocationic salt AB were estimated to amount to $\Delta_{\text{latt}}H_{298} = +967 \text{ kJ mol}^{-1}$ and $\Delta_{\text{latt}}H_{298} = +323 \text{ kJ mol}^{-1}$, respectively (see the Supporting Information). Coulomb explosion of the gaseous dication was calculated by DFT methods to be exothermic by $\Delta H_{298} = -117 \text{ kJ mol}^{-1}$.^[24] As a result, dication formation in the crystal lattice is exothermic by $\Delta H_{298} = -204 \text{ kJ mol}^{-1}$ ($\Delta H_{200} = -214 \text{ kJ mol}^{-1}$). We have refrained from calculating the Gibbs energies, since entropic contributions can be assessed less precisely and for the solid state largely cancel each other out in the cycle. It becomes clear from the BFH cycle that the strong dication–anion attraction associated with the dication formation, overcompensating Coulomb repulsion.

There are various interesting aspects associated with the formation of the dicationic 2i-2Et₂O. 1) Cation-cation interactions in the solid state have been frequently observed for metal complexes, usually involving large metal ions such as the actinides (which provide ample coordination sites),^[25] but also for rhodium^[26] and silver^[27] complexes with smaller anions. 2) Of particular interest in the context of our results is the cation-cation binding observed in metal complexes of Ag,^[28a,29] Mo,^[28b] and $Tl^{[30]}$ involving large and noncoordinating counterions such as $[B\{C_6H_3(CF_3)_2\}_4]^{-,[30]}$ [Al- $(PFTB)_{4}^{-,[28]}$ and $[(\mu-F)Al_{2}\{(PFTB)_{6}^{-,[29]}]$ These for their part have precedent in the "lattice stabilization"[17a,b] of unusual dications such as E_4^{2+} (E = S, Se, Te)^[17b,c] and E_8^{2+} $(E = S, Se)^{[31]}$ by complex anions. BFH studies on the isolated AB₂ salts revealed stabilization of the dications by lattice forces, and a very similar situation appears to be the case for the organic dication salt 2i-2 Et₂O. 3) Organic dications held together solely by hydrogen bonds have been detected in gasphase studies^[32] and were also the topic of theoretical investigations.^[33,34] According to these results, metastable cation-cation complexes are viable species in the gas phase and show, although their dissociation enthalpies are exothermic due to Coulomb repulsion, distinct fragmentation barriers. Such organic dications have been suggested to become stabilized by "kinetic trapping in a sufficiently deep Hbonded well [which] should allow such species to be experimentally detected".^[34a] In the case of 2i-2Et₂O we have isolated such a metastable H-bonded cation-cation species in a crystal lattice, thus verifying the perception^[29a,35]

> that gas-phase cations can be effectively trapped in the solid state when combined with large noncoordinating anions.

> To summarize, we have studied the synthesis and solid-state structural properties of 4-oxopiperidinium salts $[OC_3H_8NH_2]X$ for a series of anions X of decreasing basicity. In these salts both the NH and NCH protons of the 4-oxopiperidinium cation engage in various forms of hydrogen bonding to available hydrogen-bond acceptors. For basic anions such as Cl⁻ and Br⁻ strong NH···X···HN hydrogen bonds are formed. These attenuate the positive charge on the 4-oxopiperidinium ring, and such salts exhibit an infrared CO stretching band of a typical neutral ketone at $\tilde{\nu}_{CO} \approx 1720$ cm⁻¹. As the



basicity of the anion diminishes, the positive charge of the 4oxopiperidinium cation increases and concurrently the carbonyl oxygen atom of the 4-oxopiperidinium cation gains in importance as a hydrogen-bond acceptor toward either the NH or NCH protons of a neighboring cation. For the NTf₂ salt 2h the 4-oxopiperidinium cations linearly associate by headto-tail N-H-O=C bonding to form oligomeric chains flanked by interactions with the NTf₂⁻ anions, with an associated almost unperturbed $\tilde{\nu}_{CO}$ frequency. In the $[Al(PFTB)_4]^-$ salt 2i-2Et₂O the anions are no longer able to hydrogen-bond with the cations. Here, the 4-oxopiperidinium cations not only bond to diethyl ether molecules by N-H-O bonding, but two such solvated 4-oxopiperidinium cations self-associate in cyclic head-to-tail fashion by N-C-H-O=C bonding to afford a dimeric dication, exhibiting an IR CO stretching band at a remarkable $\tilde{\nu}_{\rm CO} = 1744 \text{ cm}^{-1}$. The compound 2i-2Et₂O appears to be the first authentic example of the self-association of two organic cations to form a dication held together merely by hydrogen bonds. The trapping of the di(4oxopiperidinium) dication in an AB2-type crystal lattice containing large noncoordinating anions provides a paradigm for the creation of further elusive dications that are based on weak attractive forces.[36]

Keywords: hydrogen bonds · piperidine derivatives · polycations · structure elucidation

How to cite: Angew. Chem. Int. Ed. 2015, 54, 4482–4487 Angew. Chem. 2015, 127, 4564–4569

- C. Reichardt, T. Welton, Solvents and Solvent Effects in Organic Chemistry, 4th ed., Wiley-VCH, Weinheim, 2011.
- [2] M. Holz, K. J. Patil, Ber. Bunsen-Ges. 1991, 95, 107-113.
- [3] O. Shih, A. H. England, G. C. Dallinger, J. W. Smith, K. C. Duffey, R. C. Cohen, D. Prendergast, R. J. Saykally, J. Chem. Phys. 2013, 139, 035104.
- [4] A. Mele, G. Romanò, M. Giannone, E. Ragg, G. Fronza, G. Raos, V. Marcon, Angew. Chem. Int. Ed. 2006, 45, 1123–1126; Angew. Chem. 2006, 118, 1141–1144.
- [5] M. Benrraou, B. L. Bales, R. Zana, J. Phys. Chem. B 2003, 107, 13432–13440, and references therein.
- [6] a) M. T. Reetz, Angew. Chem. Int. Ed. Engl. 1988, 27, 994–998; Angew. Chem. 1988, 100, 1026–1030; b) V. B. Luzhkov, F. Österberg, P. Acharya, J. Chattopadhyaya, J. Åqvist, Phys. Chem. Chem. Phys. 2002, 4, 4640–4647.
- [7] a) M. Ralle, J. C. Bryan, A. Habenschuss, B. Wunderlich, *Acta Crystallogr. Sect. C* 1997, *53*, 488–490; b) B. R. Vincent, O. Knop, A. Linden, T. S. Cameron, K. N. Robertson, *Can. J. Chem.* 1988, *66*, 3060–3069.
- [8] M. T. Reetz, S. Hütte, R. Goddard, J. Am. Chem. Soc. 1993, 115, 9339–9340.
- [9] G. R. Desiraju, Acc. Chem. Res. 1991, 24, 290-296.
- [10] K.-R. Pörschke, W. Gamrad, R. Goddard, J. Breidung, H. Cui, in preparation.
- [11] a) I. Krossing, Chem. Eur. J. 2001, 7, 490-502; b) I. Krossing, H. Brands, R. Feuerhake, S. Koenig, J. Fluorine Chem. 2001, 112, 83-90; c) I. Krossing, I. Raabe, Angew. Chem. Int. Ed. 2004, 43, 2066-2090; Angew. Chem. 2004, 116, 2116-2142; d) I. Krossing, A. Reisinger, Eur. J. Inorg. Chem. 2005, 1979-1989.
- [12] Various effects may increase the carbonyl IR frequency, such as ring strain in cyclic compounds (e.g., cyclopentanone, $\tilde{v}_{\rm CO} = 1745 \text{ cm}^{-1}$) and electron-withdrawing substituents (e.g., hexa-chloroacetone, $\tilde{v}_{\rm CO} = 1780$, 1752 cm⁻¹).

- [13] The effect may also be compared to the observed change in IR frequencies for the C=O stretch in nonclassical metal carbonyl complexes: a) A. S. Goldman, K. Krogh-Jespersen, J. Am. Chem. Soc. 1996, 118, 12159–12166; b) H. Willner, F. Aubke, Organometallics 2003, 22, 3612–3633.
- [14] Organic polycations are relatively rare and have been realized in particular for dendrimeric^[14a,c] and cyclic^[14b] compounds in which the multiple onio centers are perforce confined to a single molecular entity: a) R. Weiss, B. Pomrehn, F. Hampel, W. Bauer, *Angew. Chem. Int. Ed. Engl.* 1995, *34*, 1319–1321; *Angew. Chem.* 1995, *107*, 1446–1448; b) A. Ito, Y. Ono, K. Tanaka, *Angew. Chem. Int. Ed.* 2000, *39*, 1072–1075; *Angew. Chem.* 2000, *112*, 1114–1117; c) A. W. Kleij, R. van de Coevering, R. J. M. Klein Gebbink, A.-M. Noordman, A. L. Spek, G. van Koten, *Chem. Eur. J.* 2001, *7*, 181–192.
- [15] For a polycationic ammonium-ammonia structure, see: T. Roßmeier, N. Korber, Z. Anorg. Allg. Chem. 2004, 630, 2665– 2668.
- [16] Intermolecular N-H+...O=C hydrogen bonding between ammonium and carbonyl groups of neutral molecules or anions is not uncommon and typical N-O distances are in the 2.69-3.00 Å range. For some relatively short distances (2.69-2.86 Å), see: a) J.-J. Brunet, R. Chauvin, J. Chiffre, B. Donnadieu, S. Huguet, P. Leglave, E. Mothes, Inorg. Chim. Acta 1999, 291, 300-310; b) F. A. R. Kaul, G. T. Puchta, H. Schneider, M. Grosche, D. Mihalios, W. A. Herrmann, J. Organomet. Chem. 2001, 621, 177-183; c) S. Amatori, G. Ambrosi, M. Fanelli, M. Formica, V. Fusi, L. Giorgi, E. Macedi, M. Micheloni, P. Paoli, R. Pontellini, P. Rossi, J. Org. Chem. 2012, 77, 2207-2218; d) S. Ahmed, L. A. Baker, R. S. Grainger, P. Innocenti, C. E. Quevedo, J. Org. Chem. 2008, 73, 8116-8119; e) A. R. Todorov, M. Nieger, J. Helaja, Chem. Eur. J. 2012, 18, 7269-7277; f) J. Zhou, S. J. Lancaster, D. A. Walker, S. Beck, M. Thornton-Pett, M. Bochmann, J. Am. Chem. Soc. 2001, 123, 223-237.
- [17] a) H. D. B. Jenkins, H. K. Roobottom, J. Passmore, L. Glasser, *Inorg. Chem.* **1999**, *38*, 3609–3620; b) T. S. Cameron, I. Dionne, H. D. B. Jenkins, S. Parsons, J. Passmore, H. K. Roobottom, *Inorg. Chem.* **2000**, *39*, 2042–2052; c) S. Brownridge, I. Krossing, J. Passmore, H. D. B. Jenkins, H. K. Roobottom, *Coord. Chem. Rev.* **2000**, *197*, 397–481; d) L. Glasser, H. D. B. Jenkins, *Chem. Soc. Rev.* **2005**, *34*, 866–874; e) L. Glasser, H. D. B. Jenkins, *J. Chem. Eng. Data* **2011**, *56*, 874–880.
- [18] For the protonated anion, H[Al(PFTB)₄], see: A. Kraft, J. Beck, G. Steinfeld, H. Scherer, D. Himmel, I. Krossing, Organometallics 2012, 31, 7485-7491.
- [19] a) A. C. Legon, D. J. Millen, *Chem. Soc. Rev.* 1987, *16*, 467–498;
 b) M. C. Etter, *Acc. Chem. Res.* 1990, *23*, 120–126; c) G. Gilli, P. Gilli, *The Nature of the Hydrogen Bond*, Oxford University Press, Oxford, UK, 2009; d) P. Gilli, L. Pretto, V. Bertolasi, G. Gilli, *Acc. Chem. Res.* 2009, *42*, 33–44.
- [20] F. H. Allen, Acta Crystallogr. Sect. B 2002, 58, 380-388.
- [21] a) W. J. Evans, M. A. Ansari, J. W. Ziller, *Inorg. Chem.* 1999, *38*, 1160–1164; b) M. K. Krepps, S. Parkin, D. A. Atwood, *Cryst. Growth Des.* 2001, *1*, 291–297; c) H. Kumagai, S. Kitagawa, M. Maekawa, S. Kawata, H. Kiso, M. Munakata, *J. Chem. Soc. Dalton Trans.* 2002, 2390–2396; d) T. C. Rosen, K. Kirschbaum, D. M. Giolando, *Dalton Trans.* 2003, 120–125; e) B. Kurscheid, B. Neumann, H.-G. Stammler, B. Hoge, *Chem. Eur. J.* 2011, *17*, 14935–14941.
- [22] a) M. Born, Verh. Dtsch. Phys. Ges. 1919, 21, 679-685; b) K.
 Fajans, Verh. Dtsch. Phys. Ges. 1919, 21, 714-722; c) F. Haber,
 Verh. Dtsch. Phys. Ges. 1919, 21, 750-768; d) D. F. C. Morris,
 E. L. Short, Nature 1969, 224, 950-952.
- [23] We thank Professor Ingo Krossing, Freiburg, for suggesting the BFH study to us.
- [24] We would like to thank Dr. Jürgen Breidung of our Max-Planck-Institute for performing the DFT studies.

4486 www.angewandte.org

© 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



- [25] N. N. Krot, M. S. Grigoriev, Russ. Chem. Rev. 2004, 73, 89-100.
- [26] S. Grimme, J.-P. Djukic, Inorg. Chem. 2011, 50, 2619-2628.
- [27] A. Vellé, A. Cebollada, M. Iglesias, P. J. Sanz Miguel, *Inorg. Chem.* 2014, 53, 10654–10659.
- [28] a) M. Scheer, L. J. Gregoriades, A. V. Virovets, W. Kunz, R. Neueder, I. Krossing, *Angew. Chem. Int. Ed.* 2006, *45*, 5689–5693; *Angew. Chem.* 2006, *118*, 5818–5822; b) M. Scheer, L. J. Gregoriades, M. Zabel, J. Bai, I. Krossing, G. Brunklaus, H. Eckert, *Chem. Eur. J.* 2008, *14*, 282–295.
- [29] a) I. Krossing, A. Reisinger, *Coord. Chem. Rev.* 2006, 250, 2721 2744; b) I. Raabe, S. Atonijevic, I. Krossing, *Chem. Eur. J.* 2007, 13, 7510–7522.
- [30] J. Cullinane, A. Jolleys, F. S. Mair, *Dalton Trans.* 2013, 42, 11971– 11975.
- [31] T. S. Cameron, R. J. Deeth, I. Dionne, H. Du, H. D. B. Jenkins, I. Krossing, J. Passmore, H. K. Roobottom, *Inorg. Chem.* 2000, 39, 5614–5631.
- [32] a) S.-W. Lee, J. L. Beauchamp, J. Am. Soc. Mass Spectrom. 1999, 10, 347-351; b) L. Feketeová, R. A. J. O'Hair, Chem. Commun. 2008, 4942-4944.

- [33] A. Shokri, M. Ramezani, A. Fattahi, S. R. Kass, J. Phys. Chem. A 2013, 117, 9252–9258.
- [34] a) F. Weinhold, R. A. Klein, Angew. Chem. Int. Ed. 2014, 53, 11214–11217; Angew. Chem. 2014, 126, 11396–11399; b) Corrigendum: F. Weinhold, R. A. Klein, Angew. Chem. Int. Ed. 2014, 53, 12992; Angew. Chem. 2014, 126, 13207.
- [35] T. S. Cameron, A. Decken, I. Dionne, M. Fang, I. Krossing, J. Passmore, *Chem. Eur. J.* 2002, *8*, 3386–3401.
- [36] Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/. Data for the single-crystal structure determinations of the compounds, including the CCDC deposition numbers, are contained in Tables S1 and S2 of the Supporting information. The detailled crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

Received: August 15, 2014 Revised: December 2, 2014 Published online: February 25, 2015