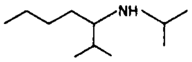
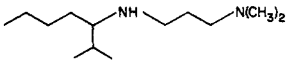
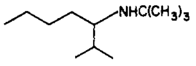
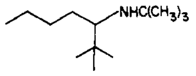
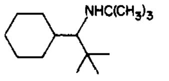
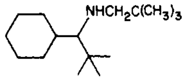
Table I. pK_a Values for Secondary Amines in THF

amine	reference acid	K_{eq}	pK_a
$(CH_3)_3SiNHSi(CH_3)_3$ (1)	2	0.0125	29.5
$(CH_3)_2CHNHSi(CH_3)_3$ (2)	thiophene[17]	0.028	31.4
$(CH_3)_3CCH_2NHSi(CH_3)_3$ (3)	4	0.44	33.2
$(CH_3)_3CNHSi(CH_3)_3$ (4)	7	0.008	33.6
$C_2H_5CH(CH_3)NHCH_2CH_2CH_3$ (5)	7	0.2	35.0
cis-2,6-dimethylpiperidine (6)	7	0.34	35.2
$(CH_3)_2CHNHCH(CH_3)_2$ (7)	9	0.025	35.7
dicyclohexylamine (8)	7	1	35.7
2,2,6,6-tetramethylpiperidine (9)	*a*	0.30	37.3
 10	$C_6H_5SCH_3$	0.30	37.6
 11	$C_6H_5SCH_3$	0.60	37.9
 12	$C_6H_5SCH_3$	1.6	38.3
 13	$C_6H_5SCH_3$	9.9	39.1
 14	$C_6H_5SCH_3$	27.6	39.5
 15	$C_6H_5SCH_3$	79	40.0

[a] We have previously measured a pK of 37.3 for TMP relative to the arbitrary standard 2-methyl-1,3-dithiane.[5]

bility to measure pK values well below 30. The most acidic of these is the bis(trimethylsilyl)amine (pK_a 29.5). For the other end of the scale, we have prepared amines more hindered than TMP, which exhibit still less acidity, as anticipated. Because of their reduced rates of transmetalation, their acidities have been measured by using thioanisole as the standard.[5,14] As seen in the table, these dialkylamines having two very bulky substituents possess pK's up to 40.[15] This total complement of amines having pK's of 29.5–40 extends the range of accessible pK measurements to 27–43 pK units.

It had been earlier recognized by Olofson and Dougherty that di-*tert*-butylamine and other very hindered amines offered additional potential but lacked availability. The work herein and that reported by Corey[9] now provide simple synthetic access to very hindered amines. During this investigation we have even encountered an overly hindered amine. Reduction of 2,6-di-*tert*-butylpyridine produced the corresponding piperidine,[16] an amine so hindered that it is inert to methyllithium, *n*-or *tert*-butyllithium in THF, with or without TMEDA or diethylamine as catalyst. Clearly, there is little scope for further increase in amine pK via increase in steric hindrance. There is, in contrast, a strong likelihood that the most highly hindered bases possess useful regioselectivities. For example, we have observed appreciably different rates of deprotonation of anisole, at the ortho position, and thioanisole at the methyl group. Although thioanisole is more acidic by a factor of 2,[18] its half-life for methyl group deprotonation is less than one sixth that for ring deprotonation of anisole.

We are now using the amines 1–15 in extending our measurements of acidity. For example, measurement of the metalation of thiophene in the presence of 4 has established its pK, previously unattainable in THF, as 33.3[17] (per hydrogen, compared to the value of 38.2 in cyclohexylamine[14]). Examination of the metalation of *p*-methylbiphenyl with 14 revealed appreciable lithiation, thereby providing a value of 40.4 (per hydrogen, compared to the value of 39.0 in cyclohexylamine[14]).

Supplementary Material Available: Procedures for the synthesis of all new amines along with their physical and spectral properties (5 pages). Ordering information is given on any current masthead page.

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[14] Streitwieser, A., Jr.; Guibé, F. *J. Am. Chem. Soc.* 1978, *100* 4532.

[15] Since, in general, alkyl groups increase acidity in the gas phase and decrease it in solution, the observed effects in our trends in amine acidities most likely reflect steric hindrance to solvation and aggregation (see Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1981; Chapter 3).

[16] Day, J. C. *J. Org. Chem.* 1978, *43*, 3646.

[17] Its pK of 33.3, per hydrogen, determined in equilibrium with 4 was confirmed by a second measurement vs. 1. Its pK per molecule is 33.0.

[18] The acidities per hydrogen, in pK units are 39.0 and 38.6 for anisole and thioanisole, respectively (values revised slightly from the initial report[5]).

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Stable and Explosive Alkali Metal–Anion Radical–Ammonia Complexes

Summary: Solid crystalline Rb and Cs salts with the composition $M^+{}_2(NH_3)(naphthalene^{-}\cdot)_2$ have been generated and are found to hold the ammonia molecule endothermically, and similar salts involving alkaline earth metals or alkali metals with other anion radicals detonate upon crystallization due to the exothermic release of ammonia.

Sir: Relatively little importance has been given to the coordination chemistry of alkali metal cations due to the fact that the complexing ability of these cations is much weaker than those of the transition-metal ions, and the complexes of the alkali metals are thought to be simple and understandable in terms of the ionic model.[1,2] However, salts of the small cations possess the ability to hold various types of solvents in the crystal lattice.[1] This is especially true of the hydrogen-bonding solvents, which can interact strongly with the anion of a salt. For example, $Na_2SO_4\cdot10H_2O$ is a common solvent complex wherein the cation is within the $Na(H_2O)_6$ octhedron.[3] We have made use of the strong affinity of the lone pair of electrons for alkali metals and the hydrogen bond that forms between ammonia and organic anion radicals[4] to generate a novel series of compounds containing two alkali metal cations, two naphthalene anion radicals, and one molecule of ammonia.

When 1 mol of naphthalene (NP) is reacted with 1 mol of K, Rb, or Cs in very dry liquid ammonia and the solvent (NH_3) is removed under reduced pressure, a solid is left that has the formula $M_2(NH_3)(NP)_2$. When a similar

Scheme I

$$2M^+NP^{-}\cdot(s) + 2H_2O(l) \longrightarrow 2MOH(aq) + NP(s) + NPH_2(s) \quad \Delta H^\circ = \begin{cases} -78.2 & M = K \\ -52.6 & M = Rb \\ -55.2 & M = Cs \end{cases}$$

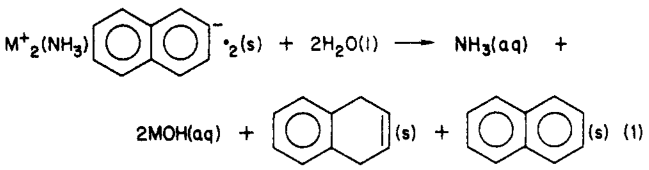
$$NPH_2(s) + NP(s) + 2MOH(aq) + NH_3(aq) \longrightarrow M^+{}_2(NH_3)(NP^{-}\cdot)_2(s) + 2H_2O(l) \quad \Delta H^\circ = \begin{cases} +59.4 & M = K \\ +65.2 & M = Rb \\ +67.9 & M = Cs \end{cases}$$

$$NH_3(g) \longrightarrow NH_3(aq) \quad \Delta H^\circ = -8.5$$

$$2M^+NP^{-}\cdot(s) + NH_3(g) \longrightarrow M^+{}_2(NH_3)(NP^{-}\cdot)_2(s) \quad \Delta H^\circ = \begin{cases} -27.3 \pm 2.9 & M = K \\ +4.0 \pm 1.5 & M = Rb \\ +4.1 \pm 1.4 & M = Cs \end{cases}$$

process is carried out utilizing sodium metal, the salt detonates upon crystallization. These detonations can be violent. Further, attempts to synthesize the analogous compound with sodium and anthracene (AN) again leads to a detonation upon crystallization of the salt. Thus, the sodium naphthalene– and sodium anthracene–ammonia complexes are kinetically unstable. This is in strong contrast to the kinetic and thermodynamic stability of the uncoordinated sodium and potassium salts of the polyacenes (i.e., $Na^+AN^{-}\cdot$).[5]

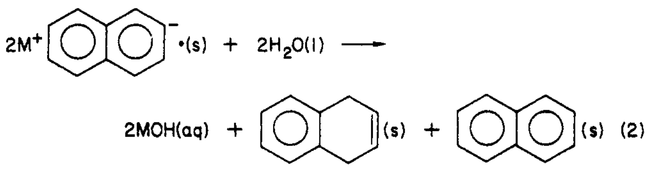
Samples of the $M^+{}_2(NH_3)(NP^{-}\cdot)_2$ solid salts (M = K, Rb, and Cs) were reacted with water (reaction 1) in a modified calorimeter as previously described[5-7] in order to quantitatively determine the affinity that the metal naphthalenides have for ammonia and to find the thermodynamic stability of these novel coordination compounds.



(1)

$$\Delta H^\circ = -59.4 \pm 0.7 \text{ kcal/mol for } M = K$$
$$= -65.2 \pm 0.5 \text{ kcal/mol for } M = Rb$$
$$= -67.9 \pm 0.2 \text{ kcal/mol for } M = Cs$$

The heats of reaction 1 can be compared to those for the uncomplexed salts of metal naphthalene (reaction 2) in order to determine the affinity that $M^+NP^{-}\cdot$ has for ammonia, Scheme I.



(2)

$$\Delta H^\circ = 2(-39.1 \pm 1.1 \text{ kcal/mol}) \text{ for } M = K$$
$$= 2(-36.3 \pm 0.5 \text{ kcal/mol}) \text{ for } M = Rb$$
$$= 2(-27.6 \pm 0.6 \text{ kcal/mol}) \text{ for } M = Cs$$

From Scheme I it is clear that the cesium naphthalene complexes ammonia endothermically (+4.1 kcal/mol of ammonia). This is the opposite of the results from the alkaline earth metal polyacene systems.[7] The stoichiometry of these new salts also contrasts dramatically with those of the analogous salts of the group two elements, which have the general formula $M^{2+}(NH_3)_2(\text{polyacene}^{-}\cdot)_2$.

After exposure of the alkali metal–naphthalene complexes, crystallized from ammonia, to high vacuum for 24 h, the ammonia molecule is still associated with two cations and two anions. Neither further exposure to open vacuum nor warming to 100 °C alters this composition. However, heating of the salts under vacuum with a burner liberates a half a mole of ammonia per mole of metal in the in the salt. This pyrolysis does result in some charring.

As the salt is crystallizing from ammonia, the number of moles of ammonia associated with the salt is decreasing until it reaches its final value of half of an NH_3 for each metal and naphthalene. When sodium serves as the cation and anthracene as the anion, the crystal lattice energy of $Na^+(NH_3)_n(AN^{-}\cdot)$ must be less than that for $Na^+AN^{-}\cdot$. This is evidenced by the fact that as the pressure of ammonia decreases over the salt, a point is reached where the crystal geometry rearranges exothermically and "spits" out the ammonia molecules. This results in the observed explosions.

The generation of the potassium anthracene salt does not result in an explosion, but no ammonia is incorporated into the final salt. Only $K^+AN^{-}\cdot$ is left after the removal of the ammonia. This salt reacts with water exothermically, liberating 31.0 kcal/mol of heat, which is identical with that previously reported for the salt crystallized from tetrahydrofuran (THF).[5] This material, evidently, liberates the ammonia slowly as the pressure of ammonia is decreased, and the structure of the resulting salt is identical with that obtained from THF.

The alkaline earth metal–ammonia–polyacene complexes that have been observed so far all contain 2 mol of ammonia per mol of polyacene, rendering them stable. However, when the same synthetic procedure was carried out utilizing Ba, ammonia, and nitrobenzene, only one ammonia was left in the crystalline complex. A 5-day-old sample of the dark green solid $Ba^{2+}(NH_3)(\text{nitrobenzene}^{-}\cdot)_2$ exploded violently upon agitation.

We feel that there are probably many stable ammonia–alkali metal–anion radical complexes, and we intend to search for more examples of this new series organic compounds. But, due to the violent behavior already observed, we must proceed with caution.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. $K^+{}_2(NH_3)(NP^{-}\cdot)_2$, 91410-64-9; $Rb^+{}_2(NH_3)(NP^{-}\cdot)_2$, 91410-65-0; $Cs^+{}_2(NH_3)(NP^{-}\cdot)_2$, 91410-66-1; $K^+NP^{-}\cdot$, 4216-48-2; $Rb^+NP^{-}\cdot$, 34488-92-1; $Cs^+NP^{-}\cdot$, 34474-70-9; $Ba^{2+}(NH_3)(C_6H_5NO_2{}^{-}\cdot)_2$, 91410-67-2; anthracene, 120-12-7.

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(6) (a) Stevenson, G. R.; Zigler, S. S.; Reiter, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 6057. (b) The solid salts were reacted with 100 mL of water in the calorimeter. Plots of the change in the temperature of the calorimeter vs. the mmoles of salt are linear, and the slopes of the lines are proportional to the enthalpies of reactions 1 and 2. The errors reported for the enthalpies are propagated from the standard deviations in the slopes of the lines (see ref 5, 6a, and 7).
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