TABLE I

RELATIVE ISOTROPIC SHIFTS IN COMPLEXED ANILINES

N subst		Aryl subst	Abs shift[a]	Relative shifts[b]						
				$N-CH_3$	N-H	*o*-H	*m*-H	$m-CH_3$	*p*-H	$p-CH_3$
CH_3	H	...	−5.4	−1.00	+2.5	+0.22[c]	−0.08	...	+0.24[c]	...
CH_3	CH_3	...	−0.63	−1.00	...	+0.27[c]	−0.08	...	+0.30[c]	...
CH_3	CH_3	$p-CH_3$	−0.77	−1.00	...	+0.25	−0.08	...	...	−0.22
CH_3	CH_3	$m-CH_3$	...	−1.00	...	+0.26[c]	−0.09	+0.08	+0.26[c]	...

[a] Observed shift in ppm from diamagnetic position for $N-CH_3$ protons at 0.8 *M* ligand and 0.3 *M* $Ni(AA)_2$ (0.1 *M* $Ni(AA)_2$ for N-methylaniline) concentrations in carbon tetrachloride using tetramethylsilane as an internal standard at 39–41°. The techniques were those used in ref 3. (Similar shifts were also observed in benzene solutions.) [b] Shifts are normalized in each case to the observed shift of the N-methyl resonance. [c] Positions somewhat uncertain owing to overlapping of peaks.

cant ionization of this proton but supports a positive spin density at the nitrogen and a π-type delocalization mechanism. Similar shifts were also observed for aniline itself. N,N-Dimethylanilines coordinate much less effectively with $Ni(AA)_2$, presumably owing to steric effects, but the observed isotopic shift ratios are almost the same as those observed for mono-N-methylaniline. In addition to the shift ratios, the similar magnitudes but opposite signs for the isotropic shifts of methyl group and directly attached proton resonances at a given phenyl position are characteristics of π-orbital delocalization predicted by the theory of McConnell.[4] The similarity in spin delocalization suggests that a single mechanism should account for the observed spin density in all of these anilines, and therefore the ionization mechanism appears unsatisfactory.

A reasonable molecular orbital description of this spin distribution can be made using the usual assumption that in octahedral nickel complexes the unpaired electrons are principally in the metal e_g orbitals which are involved in metal–ligand σ bonding. Positive spin density can therefore be delocalized onto the nitrogen atom through a σ mechanism similar to that previously proposed for the delocalization of spin in pyridine complexes.[5] For coordinated pyridine the metal–nitrogen bond involves an sp^2 atomic orbital on the nitrogen which is orthogonal to the ligand π orbitals. The observed spin-density distribution is therefore principally that associated with spin distribution through the σ system. However, in molecules such as aniline, the lone electron pair on nitrogen is either in a pure p or hybrid (sp^3) orbital[6a] which can overlap with the π atomic orbitals of the phenyl ring;[6b] *i.e.*, the lone pair used for σ bonding with the metal is also part of the ligand π-orbital network. Therefore spin which is delocalized onto the ligand through the metal–ligand σ bond may be distributed in the ligand in a typical π-orbital pattern. Such a mechanism for spin distribution in octahedral nickel complexes can account for the π type of spin distribution observed in other aromatic ligands such as phosphines[7] and pyridine oxides,[3] with no recourse to a metal–ligand π interaction.

For ligands such as the isonitriles[7] and nitriles,[3c] where the single ligand lone-pair orbital used for coordinate bond formation is effectively orthogonal to the ligand π system, this mechanism predicts a σ-type distribution in contrast to the observed π type of spin density distribution. This can be accounted for, without resort to metal–ligand π bonding, by assuming delocalization of positive spin density onto the ligand through the metal–ligand σ bond and delocalization of spin in the ligand π system by a π–σ spin polarization mechanism. As in pyridine, concurrent spin-density delocalization through the σ bonds in the aromatic ligand may also occur but this is not dominant owing to the increased number of intervening bonds between the metal atom and protons. Such a σ–π spin polarization mechanism has been suggested as one of two alternatives to explain π-type delocalization in octahedral imine nickel complexes.[8] The above results and considerations suggest that considerable caution should be exercised in using a π-type spin distribution in aromatic ligands as evidence for the presence of metal–ligand $d\pi$–$p\pi$ or $d\pi$–$d\pi$ formation.

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(4) H. M. McConnell, *J. Chem. Phys.*, **28**, 1188 (1958).

(5) J. A. Happe and R. L. Ward, *ibid.*, **39**, 1211 (1963).

(6) (a) A recent spectroscopic study [J. C. Brand, D. R. Williams, and T. J. Cook, *J. Mol. Spectry*, **20**, 194 (1966)] showed quite conclusively that aniline itself is *non*planar in its ground state; (b) the σ^+ values of H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958), quantitatively demonstrate this.

(7) W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *ibid.*, **86**, 3031 (1964).

(8) A. Chakravorty, J. P. Fennessey, and R. H. Holm, *Inorg. Chem.*, **4**, 26 (1965).

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Packing in Fluoride Complexes and Remarks Concerning Salts Containing Nitrogen Fluoride Cations[1]

Sir:

Zachariasen's 1948 paper[2] concerning alkali fluoride–uranium fluoride complexes brought to chemists' attention that it is possible to derive chemical formulas from the volume of the unit cells of such complexes by considering volumes of two constituents only: *the sum of the fluoride volumes and the alkali metal volume.*

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(1) This work was sponsored by the U. S. Atomic Energy Commission.

(2) W. H. Zachariasen, *J. Am. Chem. Soc.*, **70**, 2147 (1948); F. H. Ellinger and W. H. Zachariasen, *J. Phys. Chem.*, **58**, 405 (1954).

The volume of the smaller, highly charged heavy metal is neglected since it occupies interstices in the fluoride packing. This simple but elegant idea is very useful to the inorganic chemist, making it possible to check X-ray data on complex fluorides quickly for reasonableness, *i.e.*, for number of molecules per unit cell and for fit to trends within a series. In the case of uranium fluorides, Zachariasen used 18 A^3 as the average fluorine volume together with the following volumes (A^3) for cations: Na^+ (7), K^+ (21), NH_4^+ (26), and Rb^+ (28).[2] Lithium and cesium were not included in his compilation but using Li^+ as $\sim$0 and Cs^+ as $\sim$42 A^3 gives reasonable results. These volumes give for $LiUF_6$, 108 A^3 (111 obsd) and for $CsUF_6$, 150 A^3 (156 obsd).[3] See also Table I. [It is an interesting aside to note that such additive alkali metal ion and fluoride volumes can be obtained approximately by doubling the volume calculated using the ionic radius, and this is about the volume of a cube circumscribing a spherical ion, $8r^3 \approx (8/3)\pi r^3$.]

TABLE I

X-RAY DATA FOR SOME HEXAFLUORO M(V) COMPLEXES

	Volume, A^3			
	Formula unit	Cation	Anion	Av/F
$LiAsF_6$	95.3^a	$\sim$0	95.3	15.9
$NaAsF_6$	114.9^a	(7)	107.9	(18.0)
$KAsF_6$	116.0^b	21	95.0	15.8
$RbAsF_6$	122.7^b	28	94.7	15.8
$CsAsF_6$	138.1^b	42	96.1	16
NF_4AsF_6	169.9^c			17
$LiSbF_6$	$105.9^{a,d}$	$\sim$0	106	
$KSbF_6$	130^a	21	109	
NH_4SbF_6	131^e	26	105	
$RbSbF_6$	131^e	28	103	
$CsSbF_6$	148^e	42	106	

[a] Reference 6. [b] J. Cox, *J. Chem. Soc.*, 876 (1956); R. B. Roof, *Acta Cryst.*, **8,** 739 (1955). [c] Reference 5. [d] J. H. Burns, *Acta Cryst.*, **15,** 1098 (1962). [e] N. Schrewelius, *Arkiv Kemi*, [7] **B16,** 1 (1943); *Struct. Rept.*, **9,** 196 (1955).

It is worthwhile to recall Zachariasen's classic paper in view of the large amount of work being done on fluoride complexes, *e.g.*, the alkali metal–transition metal fluorides. It is especially intriguing to apply the approach to X-ray data on fluoride complexes containing the recently announced cation, NF_4^+.[4,5] Note: in NF_4SbF_6 and NF_4AsF_6, group V elements and fluorine occur in *both* the cation and anion.

The X-ray data for NF_4AsF_6 (tetragonal, a = 7.70 A, c = 5.73 A, Z = 2) yield a volume per formula weight of 170 A^3.[5] The average volume for each of the ten fluorines is therefore 17 A^3 which is quite reasonable although somewhat larger than the average volume of 16 A^3/fluorine found in the alkali metal–AsF_6^- salts listed in Table I.

Other comments can be made concerning the data in Table I.

(1) The As–Sb data show expected changes in size of MF_6^- with position of M(V) in the periodic table. The as yet undetermined NF_4SbF_6 cell volume should be $\gtrsim$10 A^3 larger than that of the analogous arsenic compound. This follows since the packing volume for SbF_6^- in the rhombohedral $MSbF_6$ compounds is slightly larger ($\sim$106 A^3) than for AsF_6^- ($\sim$96 A^3) in analogous compounds.

(2) The five alkali metal–hexafluoroarsenates form a series giving a consistent fluorine volume with the exception of $NaAsF_6$. *It is further found that $NaMF_6$ complexes of Ta(V), of U(V), and of group V(A) fluorides are all of higher volume.*[3,6] This is probably due to the unfortunate intermediate size of Na^+: too large to ignore and too small to pack efficiently.

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