derive a general expression for the interaction constants in terms of the primary force constants.

Let $\Delta r_{CX} = +1$. From hypothesis 2, the CX bond order decreases by $\alpha_{CX} = -1/P_{CX}$. This leads to an increase in CY bond order of $-\gamma\alpha_{CX}$ and a corresponding decrease in CY distance of $\Delta r_{CY} = \gamma\alpha_{CX}P_{CY}$. Combining these relations

$$\frac{\Delta r_{CY}}{\Delta r_{CX}} = (S_{CY})_{CX} = -\gamma\frac{P_{CY}}{P_{CX}}$$

With eq 1 this shows that $\gamma = \beta$ and

$$F_{CX,CY} = +\beta\frac{P_{CY}}{P_{CX}}F_{CY} = +\beta\frac{P_{CX}}{P_{CY}}F_{CX}$$

The last equality arises because by symmetry $F_{CX,CY} = F_{CY,CX}$, and leads to the relation $P_{CY}/P_{CX} = (F_{CX}/F_{CY})^{1/2}$. We then find

$$F_{CX,CY} = +\beta(F_{CX}F_{CY})^{1/2} \qquad (2)$$

Thus, from eq 2 if we know approximate values for F_{CX} and F_{CY} and a value for β, which by hypothesis 1 is constant for all X and Y, we can calculate $F_{CX,CY}$ for the ten molecules we are considering.

The fundamental harmonic frequencies for CO_2 are known[9,10] much better than those for the other nine molecules. Therefore they have been used to calculate the CO_2 force constants from which β was evaluated as 0.0788 using eq 1. Approximate values for F_{CS} and F_{CSe} were calculated from the frequencies of CS_2 and CSe_2. Since frequencies were not available for CTe_2, an approximate value of 4.6 mdynes/A, given by Wentink,[2] was used for F_{CTe}. Because of the noted similarity in bonding, it is reasonable to assume these primary force constants do not change appreciably among the different molecules considered. The procedure followed here was to calculate the harmonic frequencies of the ten molecules from β and the approximate values for the primary stretching force constants and to compare them with observed frequencies. Table I gives the results.

TABLE I

INTERACTION CONSTANTS AND HARMONIC STRETCHING FREQUENCIES FOR LINEAR XCY

		Calcd[a]		Obsd[b]		
Molecule	$F_{CX,CY}$	ω_1	ω_3	ω_1	ω_3	Ref
CO_2	1.263	1354.6	2396.6	1354.5	2396.4	*c*
CS_2	0.62	671	1560	672	1559	*d*
CSe_2	0.48	376	1308	373 ± 6	1323 ± 10	*e*
CTe_2	0.36	257	1121	. . .	. . .	. . .
OCS	0.88	889	2111	876 ± 6	2091 ± 10	*f*
OCSe	0.77	679	2070	650 ± 6	2045 ± 10	*f*
OCTe	0.67	567	2042	. . .	. . .	. . .
SCSe	0.54	515	1451	516 ± 6	1457 ± 10	*e*
SCTe	0.47	435	1385	431 ± 6	1386 ± 10	*e*
SeCTe	0.41	312	1222	. . .	. . .	. . .

[a] For the calculation the values $\beta = 0.0788$, $F_{CO} = 16.025$ mdynes/A, $F_{CS} = 7.86$, $F_{CSe} = 6.1$, and $F_{CTe} = 4.6$ were used. [b] Unfortunately, except for CO_2, and perhaps CS_2, the accuracy of the observed frequencies is poor, partially owing to Fermi resonance perturbations. The limits of error are rather arbitrary but should encompass the true values. [c] See ref 9 and 10. [d] D. Agar, E. K. Plyler, and E. D. Tidwell, *J. Res. Natl. Bur. Std.*, **66A,** 259 (1962). [e] These "observed" harmonic values are calculated from the observed frequencies in ref 1 with application of approximate anharmonic corrections analogous to those for CO_2 and CS_2. [f] See ref 2; these are approximate harmonic frequencies, accuracy unknown. For discussion of OCS see A. G. Maki, E. K. Plyler, and E. D. Tidwell, *J. Res. Natl. Bur. Std.*, **66A,** 163 (1962).

The interaction constants in Table I are not greatly different from those given by Wentink; however, the derivation behind them is more realistic chemically. The agreement is quite good considering the approximations involved. The calculated values for SCSe and SCTe are well within the experimental accuracy of the observed values. The results of Table I do indicate that F_{CO}, F_{CS}, and F_{CSe} are somewhat lower in OCS and OCSe than in CO_2, CS_2, and CSe_2. It is gratifying that the 14 observed frequencies can be approximated so well using only five parameters (β, F_{CO}, F_{CS}, F_{CSe}, and F_{CTe}).

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[9] C. P. Courtoy, *Ann. Soc. Sci. Bruxelles, Ser. I,* **73,** 5 (1959).

[10] H. R. Gordon and T. K. McCubbin, Jr., *J. Mol. Spectry.*, **19,** 137 (1966).

Spin Delocalization in Substituted Anilines Complexed with Bis(2,4-pentanedionato)nickel(II)[1]

Sir:

Recently it was reported that the spin delocalized in mono-N-substituted anilines octahedrally coordinated with salicylaldimine complexes is typical of that expected for delocalization involving a π-orbital mechanism.[2] As spin delocalized from the metal to the phenyl group by a π mechanism through an sp^3 hybridized nitrogen appeared unfeasible, these authors adopted the suggestion of LaMar that π delocalization occurs through an ionic form involving ionization of the N–H proton leaving the nitrogen with a p orbital available for π bonding with the metal.

As a part of an investigation involving the use of paramagnetic complexes to determine diamagnetic resonance positions,[3] isotropic shifts of substituted aniline proton resonances due to complexing with metal 2,4-pentanedionates, $M(AA)_2$, were observed. The nmr spectra of solutions containing an excess of monomethylaniline and $Ni(AA)_2$ show isotropic shift ratios, Table I, similar to those previously reported for the salicylaldimine complexes.[2] In addition, the N–H proton resonance was observed to be broadened and shifted strongly upfield. This militates against signifi-

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[1] Most of this work was carried out at Princeton University and was supported by the National Science Foundation through Grant No. GP-3397.

[2] J. D. Thwaites and L. Sacconi, *Inorg. Chem.*, **5,** 1029 (1966).

[3] (a) R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **88,** (1966); (b) *ibid.*, **87,** 5350 (1965); (c) R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, **5,** 152 (1966).

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