owing to the presence of the relatively large cesium cations separating the $IF_6^-$ anions. Therefore, the vibrational spectra observed for $IF_6^-$ are most likely due not to polymeric structures but either to a symmetry lower than $O_h$ or to very unusual electronic properties.[22,23]

**Acknowledgment.**—We thank Dr. A. C. Jones of Shell Development Co., Emeryville, Calif., for the use of the Cary 81 spectrophotometer.

[22] G. L. Goodman, paper presented at the Symposium on Inorganic Fluorine Chemistry, Argonne National Laboratory, Argonne, Ill., Sept 1963.

[23] L. S. Bartell, *J. Chem. Phys.*, **46**, 4530 (1967).

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# Correspondence

## The Absence of Steric Effects on the Proton Contact Shifts for $Co(C_5H_5N)_2X_2$ Complexes

*Sir:*

In a recent article,[1] the interpretation by Wayland and Drago[2] of the proton nmr contact shifts in the complexes $Co(C_5H_5N)_2X_2$ (where X = Cl, Br, or I) was criticized. Our interpretation suggested that the halide ion with the largest *Dq* would raise the energy of the $d_{z^2}$ orbital most in the $CoX_2$ fragment so that energy matching of the metal orbitals and pyridine (L) orbitals would be less effective in forming $CoL_2X_2$ when X is chloride. This effect would lead to the smallest spin delocalization due to covalency in the metal–pyridine (py) bond when X is chloride and would account for the observed decrease in the contact shifts for the series $Co(py)_2I_2 > Co(py)_2Br_2 > Co(py)_2Cl_2$.

This will be referred to subsequently as the mo model.[2] The claim is made[1] that there is a steric effect present in these complexes that has been neglected in our analysis. Such a steric effect would cause the metal ion and ligand orbitals to mix differently in the chloro and iodo complexes and negate our conclusion. The fact that the angles in $[(C_6H_5)_3P]_2NiCl_2$ indicate a $D_{2h}$ distortion was used to support this contention. The magnitude of the shift for a series of substituted pyridines was found to increase in the order: $\sim$4-$CH_2{=}CH$-py $\sim$ $C_5H_5N$ $\sim$ 4-$CH_3$-py $<$ 3-$CH_3$-py $\sim$ 3,4-$(CH_3)_2$-py $\sim$ 3-$C_2H_5$-py $<$ 3-5-$(CH_3)_2$-py. This order was proposed to result from increasing substituent steric effects. Since the size of the halides increases in the order $Cl^- < Br^- < I^-$, it was further proposed that the increase in ligand proton contact shift in the iodo complex compared to that in the chloro also results from a steric effect. Admittedly, our mo model is a qualitative rationalization of observed shifts and suffers from lack of a detailed theoretical analysis. In such instances it may be possible to say the same thing in different ways. Fortunately, this is not the case here. It is the purpose of this article to show that there is no real evidence for a steric effect dominating the trends in contact shifts for the complexes reported by either author.[1,2]

The first point that must be considered is whether the observed data support the contention that a steric effect is causing the trend in contact shifts for the series of substituted pyridine ligands. The argument presented[1] is that, as the steric requirements of the substituents increase, the spin delocalization to the ligand increases. The presence of an electronic substituent effect is dismissed because the electronic spectra for all of the complexes are very similar. This conclusion is clearly not justified, for electronic spectra are rather insensitive to small changes in the ligand electronic structure while contact shifts are sensitive to this property. An electronic substituent effect thus could cause large changes in contact shifts without having large effects on the electronic spectra. Figure 1 illustrates the near-linear relationship between the 2-H contact shift for the substituted pyridine ligands in the complexes $CoL_2X_2$ and the sum of the Taft $\sigma^*$ values for the 3,5 positions.[3,4] The 2-H contact shifts for the pyridine ligands which differ only in the 4 position substituent are also consistent with an electronic substituent effect. The presence of correlations with substituent constants is generally taken as evidence for the absence of significant steric effects.[3,4]

The precise character of the observed electronic substituent effects must be very complex and is not yet completely understood. The substituents not only modify the ligand donor properties, but also the electron distribution in each of the ligand molecular orbitals. The order of increasing ligand contact shifts is consistent with the substituent effect on the ligand donor properties, and this could well be the dominant effect for this series of closely related pyridine-type ligands. It must be stated, however, that it is virtually impossible to compare the contact shift in two different proton-containing ligands without a complete knowledge of the wave functions for the ligand orbitals. Simple replacement of an H by a methyl group may change the ligand wave functions involved in bonding in such a way that very different contact shifts are observed for essentially the same metal–ligand interaction (*vide infra*). If ligand substitution prevented free rotation of the ligand in the complex,

[1] G. N. LaMar, *Inorg. Chem.*, **6**, 1939 (1967).

[2] B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 4597 (1966).

[3] R. W. Taft, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

[4] P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

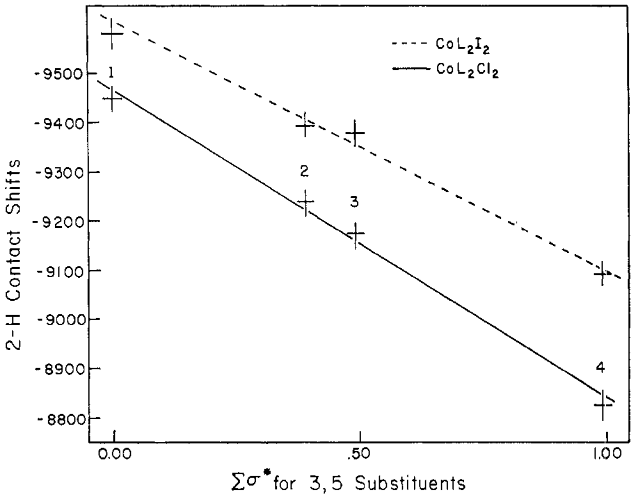

Figure 1.—Plot of 2-H contact shift *vs.* the sum of the Taft $\sigma^*$ values for the 3,5 substituents: (1) 3,5-$(CH_3)_2$-py; (2) 3-$C_2H_5$-py; (3) 3-$CH_3$-py; (4) py. The pertinent $\sigma^*$ values are: $CH_3$, 0.00; $C_2H_5$, −0.10; H, +0.49.

this could have a pronounced influence on the metal–ligand $\pi$-bonding interactions making interpretation of the contact shifts very difficult for the different proton containing ligands. For these reasons, Wayland and Drago held the proton-containing ligand constant in the series they compared.

The existence of the steric effect proposed[1] for Co(3-$CH_3$-py)$_2I_2$ was examined by employing molecular models.[5] For all orientations of the ring, there is no evidence of any steric repulsion resulting from the 3-methyl groups. As can be seen from models, there is no evidence of a steric effect even in the 3,5-$(CH_3)_2$-py complex. These findings are contrary to a reported investigation of the models, and we find the statement[1] that "molecular models indicate that 3 substituents could interfere with neighboring ligands..." to be incorrect for $CH_3$ groups. As can be seen from the models, substitution of the 2-H by 2-$CH_3$ would cause a steric effect in certain conformers. If there were a steric effect in any of these complexes, it would be present in this ligand. The contact shifts of Co(2-$CH_3$-py)$_2Cl_2$ have been examined[6] in the solvent acetone. According to the steric effect proposal, this ligand should have the largest contact shift for the steric effect should be greatest. As can be seen from the data in Table I, this prediction is not borne out. In fact, the proton contact shifts in Co(2-$CH_3$-py)$_2Cl_2$ are the smallest for any pyridine-type ligand. This is consistent with a steric effect causing a bond lengthening and, thus, decreased metal–ligand interaction. Therefore, it is apparent that when an authentic steric effect is present, the apparent metal–ligand covalency decreases which is directly opposed to the proposal of LaMar.

Another point that requires a brief comment is the use[1] of the known deviation from tetrahedral bond angles in Ni[$(C_6H_5)_3P]_2Cl_2$ to infer a similar deviation in $CoL_2X_2$ complexes. It is a well-known fact that strong field and $\pi$-bonding ligands give rise to square-planar geometry for nickel(II). The deviation of Ni[$(C_6H_5)_3P]_2Cl_2$ from planar $D_{2h}$ symmetry could be the result of the larger interligand repulsions in that geometry. Geometric considerations demonstrate that if all four ligands were identical or comparable in size, a distortion from tetrahedral angles toward planarity could not relieve strain. For the $C_{2v}$ complex Co(py)$_2Cl_2$ (local symmetry), $D_{2h}$ distortion would relieve strain only if pyridine–chloride repulsions were less than chloride–chloride or pyridine–pyridine repulsions. With four bulky groups of comparable size, as in Co(py)$_2Cl_2$, a steric effect is expected to be manifested through a lengthening of the metal–ligand bond distance with a retention of near-tetrahedral angles. It is very probable that bond lengthening would be reflected by reduced contact shifts. Thus if steric effects were operative, smaller ligand contact shifts would be anticipated in the iodo than in the chloro complex, contrary to the observed anion effect.

TABLE I

CONTACT SHIFTS FOR Co(2-$CH_3$-py)$_2Cl_2$ IN ACETONE[a]

| Proton | Co(2-$CH_3$-py)$_2Cl_2$[b] | Co(py)$_2Cl_2$[c,d] | Co(3,5-$(CH_3)_2$-py)$_2Cl_2$[d,e] |
|---|---|---|---|
| 2-$CH_3$ | −799 | ... | ... |
| 2-H | −8557 | −8820 | −9448 |
| 3-H | −2118 | −2220 | ... |
| 5-H | −2687 | | ... |
| 4-H | +194 | +208 | +302 |

[a] Contact shifts are reported in cps at 29° relative to the position of the free ligand resonance. The nmr spectrum of the 2-$CH_3$-py complex was measured at 34° and corrected to 29° by use of Curie's law. Co(2-$CH_3$-py)$_2Cl_2$ was also studied in excess ligand and found to be well behaved. The 3-H and 5-H resonances in the complex extrapolate to the single peak in the free ligand. (See S. S. Zumdahl and R. S. Drago, *J. Am. Chem. Soc.*, 89, 4319 (1967).) [b] See ref 6. [c] See ref 2. [d] The 2-H and 6-H are equivalent in py and 3,5-$(CH_3)_2$-py, and the 3-H and 5-H are equivalent in py. [e] See ref 1.

Contrary to what is reported,[1] the mo model does not require the structure of the complex to be invariant for different halides. Slight distortions from tetrahedral angles are expected in Co(py)$_2X_2$, because the nonequivalent ligands will cause a different distribution of the cobalt s, p, and d orbitals among them. This effect is well known in $CH_3X$ compounds where the $C^{13}$–H coupling constants[7] indicate different distribution of the carbon s and p orbitals as the electronegativity of X is varied. These hybridization changes result in slight distortions from tetrahedral angles for the $CH_3$ fragment and are expected to cause structural changes in $CoL_2X_2$ compounds. Consequently, the effects arising from different ligand donor strengths which are described by our mo model are expected to give rise to structural changes in the complexes. In the absence of appreciable ligand–ligand repulsion, the fundamental property is not the structural change but the electronic property of the ligands and metal ions that cause this change. Only when the geometry is determined

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(5) Courtauld molecular models.

(6) S. Zumdahl, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1968.

(7) R. S. Drago and N. A. Matwiyoff, *J. Organometal. Chem.* (Amsterdam), **3**, 62 (1965).

by ligand–ligand repulsion need the concern be with steric considerations and their effects on the bonding. To obtain evidence for a steric effect from structural data one must first sort out the geometrical changes due to these bonding considerations.

In conclusion, it is very satisfying that the mo model predicts the trend in contact shifts for any given proton-containing ligand when the halide is varied in all of the substituted pyridines reported. We should put the mo model in its proper context. Our claim is that this model accounts for the trends observed in the pyridine, substituted pyridine, and HMPA contact shifts when X is varied from Cl to Br to I in the cobalt(II) complexes in the solvent we employed. We do not claim that all contact shifts in $CoL_2X_2$ complexes will be dominated by this effect. In some complexes other effects (including steric and pseudo-contact effects) may exist that mask the changes from covalency. We must caution against using the mo model when comparing a series of different proton-containing ligands, or in complexes where rotation of the ligands is likely to be restricted by substituent changes. The model is also limited to metal–ligand interactions which result predominantly from ligand $\sigma$ and $\pi$ donation.

We also must conclude that the differences in the contact shift as the substiuted pyridine is varied in the compounds reported[1] cannot result from the type of steric effect described.[1] When an authentic steric effect is present, the contact shifts change oppositely to that predicted by LaMar (Table I). A complete understanding of these shifts is a very complex problem which will require both an analysis of the rotamers which can exist and good wave functions for all of the substituted pyridines. A simple change of a 2-H for a 2-$CH_3$ is seen to lead to a contact shift difference of 560 cps between the formerly equivalent 3- and 5-protons of $Co(2\text{-}CH_3\text{-}py)_2Cl_2$ (Table I). In other cases, substitution has relatively little effect on differences,[1] making qualitative predictions[1] of what will happen to the ligand wave functions on ring substitution dangerous.

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