It has been found that this reaction constitutes a rapid and convenient synthesis of chlorine nitrate. The reaction occurs on contact of the $ClF$ with $HNO_3$ at temperatures down to −112° in 85–95% yield. The product $ClNO_3$ was purified by vacuum fractionation. The vapor pressure was measured over a considerably broader range (−80 to 26°) than that in the literature (−70 to −25°). The temperatures and vapor pressures are: −79.8°, 1 mm; −63.9°, 6 mm; −46.2°, 22 mm; −25.9°, 75 mm; 0.0°, 302 mm; 13.0°, 526 mm; and 26.1°, 866 mm. The vapor pressure–temperature relationship is described by $\log P(\text{mm}) = 7.9892 - (1509.4/T)$.

Chlorine nitrate has a boiling point of 22.3° (*vs.* literature extrapolation of 18°) with a heat of vaporization of 6.9 kcal/mole and a Trouton constant of 23.4. The compound is stable in stainless steel systems after pretreatment with some $ClNO_3$. Long-term storage in stainless steel or glass at approximately −40° has not resulted in any significant decomposition. Unlike $FNO_3$[2] and the chlorine oxides, no explosive incidents have been experienced with $ClNO_3$. However, the material should be handled with care in the absence of sensitivity test reports.

### Experimental Section

Chlorine monofluoride and nominally anhydrous $HNO_3$ (distilled from $H_2SO_4$) were separately condensed at −196° into a stainless steel or Kel-F cylinder attached to a stainless steel–Teflon vacuum line. The cylinder was closed and the temperature was changed to some higher constant temperature in the range −112 to 0°. The reactor was then held at −78° and the product pumped out rapidly and trapped at −95°. Little or no HF was removed from the reactor in this manner as evidenced by the failure to generate $SiF_4$ when the product was subsequently handled in glass. Sometimes HF was removed by allowing the products to stand over NaF for a period. The identity of the product was established by its infrared spectrum[3] and molecular weight from vapor density measurements. Vapor phase chromatography, using a column packed with 50% w/w of Halocarbon oil 4-11V and Kel-F low-density molding powder according to Dayan and Neale,[4] gave an analysis of 98.4% $ClNO_3$ and 1.6% $Cl_2$. This sample was taken after 2 days in the metal vacuum system at temperatures up to ambient temperature. The $Cl_2$ impurity is a decomposition product which probably arose during this period or subsequent handling in the gas chromatograph. For the purpose of determining the stoichiometry, the more accurately measurable $ClF$ was used as the limiting reagent. Typically, 11.9 mmoles of $ClF$ was allowed to react with approximately 14 mmoles of $HNO_3$ and yielded 10.6 mmoles of $ClNO_3$ (89%). In an alternative procedure, the $HNO_3$ was maintained at −78° while $ClF$ gas was gradually admitted to the reactor. When the pressure ceased to drop, the reaction was complete. Work-up was as above. The synthesis has been successfully conducted on a scale of several liters.

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# Correspondence

## Structural *vs.* Ligand Field Strength Effects on Covalency in Pseudo-Tetrahedral Complexes of Cobalt(II) and Nickel(II) Dihalides, as Determined by Proton Magnetic Resonance

*Sir:*

There have appeared recently a number of publications[1-6] concerning the proton magnetic resonance shifts for pseudo-tetrahedrally coordinated cobalt(II) and nickel(II) dihalide complexes, abbreviated $L_2M^{II}X_2$, where X = Cl, Br, or I, and L = pyridine-type ligand, py;[4-6] triarylphosphine, $(\text{aryl})_3P$;[1-3] or hexamethylphosphoramide, HMPA.[6] Most of the attention has been focused on ascertaining the ligand orbital containing the unpaired spin.[1,3,5,6] For some of these complexes, it has been observed[3,6] that the contact shifts and hence presumably also the extent of spin delocalization from the metal depend upon the halide ion, increasing in the order $Cl < Br < I$. To explain this effect, Wayland and Drago[6] invoked a molecular orbital picture of the complexes, where the metal dihalide fragment for variable halogen would have antibonding orbitals of varying energy, $Cl > Br > I$, reflecting their ligand field strengths, such that when the neutral ligands are added, the extent of metal–ligand covalency increases $Cl < Br < I$.

However, an important factor was neglected in this analysis,[6] this being that there is no assurance that the structure of a complex is invariant for different halides. In the absence of proof for identical structures, the observed trends cannot be taken as evidence for an electronic anion effect. Indeed, X-ray work on $((\text{phen})_3P)_2NiCl_2$ has shown[7] that both the Cl–Ni–Cl and P–Ni–P angles deviate appreciably from 109°, having been attributed to differences in ligand–ligand repulsions,[7] though other effects could also be operative. In view of the fact that halide–halide repulsions vary, the

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TABLE I

ISOTROPIC SHIFTS FROM THE COMPLEXES $L_2Co^{II}X_2$[a]

| L | Position | Cl | Br | I | Ref |
|---|---|---|---|---|---|
| py | 2-H | −8820[b] | −8970 | −9090[b] | 10, 11 |
| | 3-H | −2220 | −2330[b] | −2360 | |
| | 4-H | +208 (0.023) | +221 (0.025) | +315 (0.035)[d] | |
| 4-vinyl-py[c] | 2-H | −8800 | −9000 | −9107 | 11b |
| | 3-H | −2127 | −2219 | −2303 | |
| | a-H | +114 (0.013) | +145 (0.016) | +187 (0.021) | |
| | b-H | +107 (0.012) | +128 (0.014) | +170 (0.019) | |
| | c-H | +52 | −6 | −48 | |
| $4\text{-}CH_3\text{-py}$ | 2-H | −8928 | −9068 | −9183 | 10, 11c |
| | 3-H | −2157 | −2240 | −2325 | |
| | $CH_3$ | −121 (0.014) | −234 (0.026) | −377 (0.041) | |
| $3\text{-}CH_3\text{-py}$ | 2-H | −9175 | −9240 | −9385 | 10, 11c |
| | 3-H | −2338 | −2411 | −2504 | |
| | 4-H | +271 (0.029) | +277 (0.030) | +362 (0.039) | |
| | $CH_3$ | −129 | −128 | −76 | |
| $3,4\text{-}(CH_3)_2\text{-py}$ | 2-H | −9201 | −9356 | −9416 | 11c |
| | 3-H | −2371 | −2347 | −2512 | |
| | $4\text{-}CH_3$ | −162 (0.018) | −289 (0.031) | −425 (0.045) | |
| | $3\text{-}CH_3$ | −161 | −154 | −102 | |
| $3\text{-}C_2H_5\text{-py}$ | 2-H | −9243 | −9398 | −9393 | 11c |
| | 3-H | −2353 | −2402 | −2477 | |
| | 4-H | +276 (0.030) | +290 (0.031) | +365 (0.039) | |
| | $CH_2$ | −170 | −170 | −134 | |
| | $CH_3$ | −55 | −62 | −67 | |
| $3,5\text{-}(CH_3)_2\text{-py}$ | 2-H | −9448 | −9585 | −9580 | 11c |
| | 4-H | +302 (0.032) | +312 (0.032) | +391 (0.041) | |
| | $CH_3$ | −126 | −123 | −73 | |

[a] Shifts in cps at 60 Mcps, in deuteriochloroform (~0.1 *M*), at 29°, referenced to diamagnetic ligand. Uncertainty for 2-H is 40 cps, for 3-H is 20 cps, and for all others is 3 cps. [b] Taken from ref 6, though the 2-H peak for the Br complex had not been reported. [c] Protons a and b are *gem* protons, with b-H *trans* to c-H. The multiplet structure for the I complex was clearly resolved, making assignment possible. [d] In parentheses are given the ratios (absolute) of the 4-H or $4\text{-}CH_3$ to the 2-H shifts, which is an index of the relative $\pi$ to $\sigma$ spin delocalization.

assumption of identical structures becomes very precarious, and the observed covalency trends could just as well reflect structural effects, such as slight metal–ligand bond length or angle variations. Moreover, the covalency trends on which the MO model was based[6] comprised only the $(py)_2CoX_2$ and $((phen)_3P)_2NiX_2$ complexes. For the $((p\text{-tolyl})_3P)_2NiX_2$ series, the apparent covalency order is Br > I > Cl, while for the $((m\text{-tolyl})_3P)_2NiX_2$ and $((phen)_3P)_2CoX_2$ compounds it is Br > I.[1] Even for the $((phen)_3P)_2NiX_2$ series, the shifts for the Br and I complexes are equal within experimental error.[1] Thus the experimental data support this MO model[6] in only a few cases.

The data to be presented here, however, give strong evidence that the steric repulsion of the ligands is significant[7-9] and that the resultant structural variations manifest themselves in the pmr contact shifts in a manner very similar to that expected from the anion ligand field strength argument.[6] Previous work with $L_2NiI_2$ complexes, where L = py or $CH_3$-py,[5] has indicated that the shift magnitudes and, hence, the apparent covalency also depend on the ligand substituent, increasing in the order py ~ $4\text{-}CH_3$-py < $3\text{-}CH_3$-py. Since the methyl substituents do not alter the ligand field strength,[10] structural variations seem likely,[7-9] probably reflecting steric effects, since the 3 position is quite close to the metal. To test this steric effect hypothesis, the $L_2CoX_2$ complexes were prepared,[11,12] with X = Cl, Br, or I, and L = py, $3\text{-}CH_3$-py, $4\text{-}CH_3$-py, $3\text{-}C_2H_5$-py, 4-vinyl-py, $3,4\text{-}(CH_3)_2$-py, $3,5\text{-}(CH_3)_2$-py, and their pmr spectra were recorded.[13] The observed contact shifts are given in Table I, clearly showing that the shift does increase in the order Cl < Br < I for any ligand, as predicted by the MO model.[1] However, varying the neutral ligand for fixed halide ion reveals that the shifts also depend on the ligand substituent, with increasing covalency in the order py ~ 4-vinyl-py ~ $4\text{-}CH_3$-py < $3\text{-}CH_3$-py < $3,4\text{-}(CH_3)_2$-py < $3\text{-}C_2H_5$-py < $3,5\text{-}(CH_3)_2$-py for each halide ion.[14] It appears safe to attribute the shift differences for various sub-

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(11) (a) All complexes were prepared *via* the method of H. C. King, E. Körös, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963), though it was found more advantageous to use 1-butanol as solvent in some cases. Only C and H analyses were obtained, which were satisfactory in every case, as these complexes are members of a well-characterized series of tetrahedral monomers. (b) N. H. Agnew and L. F. Larkworthy, *ibid.*, 4669 (1965). (c) J. deO. Cabral, H. C. King, S. M. Nelson, T. Shepherd, and E. Körös, *ibid.*, 1348 (1966).

(12) The $2\text{-}CH_3$-py complexes were also prepared, but the $CDCl_3$ solutions turned immediately cloudy, yielding white precipitates within 1 hr. Their pmr spectra were characterized by broad, concentration-dependent peaks, indicating decomposition.

(13) Spectra were obtained on a Varian DP-60 spectrometer, using deuteriochloroform as solvent and tetramethylsilane as internal reference. The probe temperature was 29°, and the sample concentrations were ~0.1 *M*.

(14) The covalency increase caused by the halogens, taking the 2-H shift as an index, is 1.0:1.015:1.025 for Cl:Br:I, which holds quite well for each pyridine ligand. For the covalency variation with pyridine substituent, the general trend is given by 1.00:1.00:1.01:1.03:1.04:1.05:1.06 for the ligands in descending order in Table I. Thus the pyridine substituents are more effective than the halogens in altering the pyridine–cobalt covalency.

stituted pyridine ligands to changes in covalency. The substituent could affect the ligand $\sigma$ MO such as to alter the MO coefficients for the contributing carbons. However, the substituent effect would be expected to be localized, such that in the unsymmetrically substituted pyridines the MO coefficient and, hence, the contact shift for the two inequivalent *ortho* protons should be different if the substituent indeed significantly affects the $\sigma$ MO. However, for $(3\text{-}C_2H_5\text{-py})_2CoX_2$, only one *ortho* resonance was found, with essentially identical line width as for $(py)_2CoX_2$, except some 300–400 cps further downfield, such that the changes in the $\sigma$ MO appear negligible. It would be surprising if the 3 substituent would affect MO coefficients for the two *ortho* protons identically. The 4 substituents apparently do not affect ligand repulsions or structure, as might be anticipated. However, for the 3 position the shifts increase as both the size and the number of substituents increase. Molecular models indicate that 3 substituents could interfere with neighboring ligands, such that small but finite structural changes are sterically forced upon the complex. Such changes might well be small increases in the L–Co–L angles.[7] For the halogens, steric repulsions should increase $Cl < Br < I$, such that one mechanism can consistently explain both the anion and the substituent effects on covalency.

To test further the validity of this steric effect, it is instructive to inspect the shift distributions for the complexes more closely. Since the 4-H experiences upfield shifts, while the $4\text{-}CH_3$ displays downfield shifts, both $\sigma$ and $\pi$ delocalization mechanisms are operative,[5,6] with the former dominant for the 2 and 3 positions, while the latter predominates for the 4 position. The dipolar shift is ignored, since the shift distributions here closely resemble those observed for pyridine in magnetically isotropic octahedral nickel complexes.[15] As the halogen is varied, the relative $\pi$ to $\sigma$ delocalization increases as $Cl < Br < I$, as evidenced by increasing ratio of shifts for the 4 position to the 2-H (shown in parentheses in Table I), again true for each substituent. As the pyridine substituent is varied, a similar increase in $\pi$ to $\sigma$ delocalization is observed, also increasing with increasing contact shift or covalency. Thus all characteristics of the shifts produced by varying the halide ion can also be produced by alkyl substitution on the pyridine. The evidence thus supports the contention that structural changes are primarily responsible for the observed covalency trends, though anion ligand field strength may have a secondary influence.[6] For these pyridine-type complexes, steric effects seem to account for the structural changes. Lack of X-ray data precludes a more detailed analysis of the steric effect on the covalency at this time. The ability of the substituents to simulate all of the effects of the halogens strongly suggests that the previously proposed simple MO model relating the ligand field strength to covalency is insufficient.

For the $((aryl)_3P)_2MX_2$ complexes, structural changes, ligand field strength of the anions, and sizable dipolar shifts complicate any detailed analysis.[1,3,6] For the $(HMPA)_2CoX_2$ complexes, structural variations can also account for the observed shift trends, since they resemble those of the pyridine complexes. Moreover, it is really not justified to neglect the dipolar shift as the source of the very small shifts as well as the trends. This was done[6] on the basis that HMPA is very similar to the halogens in ligand field strength. However, this appears to be an oversimplification, since if steric effects alter the tetrahedral angles, magnetic anisotropy in the order $Cl < Br < I$ can be expected.[1] In addition, separation of the observed shifts into contact and dipolar contributions for the $((aryl)_3P)_2MX_2$ complexes has indicated[1,16] that the magnetic anisotropy arises primarily from the $D_{2h}$ distortion, which reflects the compression of the tetrahedron due to presumably steric effects, rather than the $C_{2v}$ distortion, which reflects the difference in ligand field strength between phosphine and halogen. It is thus virtually impossible to ascertain the orgin of the small HMPA shifts with any confidence, much less the origin of their halide dependence.

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## Recalculation of Force Constants in Carbon and Silicon Cobalt Tetracarbonyls[1,2]

*Sir:*

In a recent publication[3] we have reported values of $(k_e - k_a)$ where $k_e$ and $k_a$ are the force constants for the equatorial and axial carbonyl groups, respectively, in compounds of the type $RCo(CO)_4$ (R = organic or silicon-containing groups). It has been brought to our attention[4] that eq 3 in this paper,[3] $\lambda_E = (k_e - 2k_i)/\mu$, should be $\lambda_E = (k_e - k_i)/\mu$.[5,6] This equation together with eq 1[3] gives the relationship

$$k_e = \mu(\lambda_{A_1{}^e} + 2\lambda_E)/3$$

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[1] This report is based on portions of a thesis to be submitted by A. P. Hagen to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This research was sponsored by AFOSR(SRC)-OAR, USAF Contract No. AF 49(638)1519.

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[4] The authors are greatly indebted to Professor F. G. A. Stone, Bristol University, England, who kindly brought this fact to their attention.

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