Inorganic Chemistry, Vol. 14, No. 10, 1975 **2389**

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Spectroscopic Substituent Constants for Ligands

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Received January 16, 1975

AIC50043I

The possible existence of spectroscopic substituent constants for ligands, X (mainly uninegative ligands), applicable to a variety of metal compounds was explored. Linear relationships were found which correlated a variety of spectroscopic properties of compounds in the first, second, and third transition metal series (as well as for mercury(II)) with the substituent constants, α values. These were based, initially, on PMR spectroscopic properties of cobalt(III) complexes. It was found that a PMR spectrochemical series exists and this series is given. The principal characteristic which determines the α value of X is the ligating atom. After consideration of several alternatives, it was found that an approximate calculation of the electrostatic force on one of the lone pair of electrons in uncoordinated X gave a reasonable correlation with the α value of X. A simple procedure for approximating these forces is given.

Introduction

An enormous effort to understand the effect of ligands on the properties of coordination and organometallic complexes has been expended over the years.[2] Success comparable to that enjoyed by organic chemists in the application of substituent constants has thus far eluded inorganic and organometallic chemists. Such comparisons to organic chemistry are perhaps inappropriate. The wide-ranging success of substituent constants in organic chemistry is due in part to the relatively small changes that are made in the series being investigated. Rather more drastic changes are made by inorganic chemists including changes in the atom (the metal center) to which the substituent, X (the ligand), is attached. When comparably small changes are made in series of metallic compounds, good correlations are often found.

In this report, we investigate in some detail the effect of ligand substituents, X, on the PMR spectra of cobalt(III) complexes and report evidence that a PMR spectrochemical series exists. Spectroscopic substituent constants, PMR α values, are given. The application of these PMR α values to spectral changes in other metal systems is analyzed. This analysis leads to more general α values. A major objective of this work was to delineate which groups, X, would be most fruitful for study in systematic investigations. These substituent constants cannot be easily understood on the basis of current bonding theory. After a search in the literature for some basic quantities which might correlate with these spectroscopic constants proved fruitless, it was noted that the approximate electrostatic force, which holds one of the lone pair of electrons to the ligand, correlates well with the substituent constant. Such forces may not be the ultimate explanation for these substituent constants nor are they advanced as such. Rather they are offered at a possible starting point for more sophisticated attempts to explain the spectroscopic substituent constants.

Results

Cobaloxime Complexes. New proton magnetic resonance spectral data for complexes of the type $LCo(DH)_2X$, where L = 4-*tert*-butylpyridine (*t*-Bupy) or tri-*n*-butylphosphine (Bu_3P) and DH = monoanion of dimethylglyoxime, $HONC(CH_3)C(CH_3)NO^-$, are given in Table I.[3] The complexes were prepared and characterized for a mechanistic investigation and details will be reported elsewhere.

The data extend and support our previous study[4] on (*t*-Bupy)$Co(DH)_2X$ in several important ways. First, in our previous study we showed that a good linear relationship existed between the chemical shifts of the α_H resonance and the oxime methyl resonance. This linear relationship is maintained with the new complexes, Figure 1. Based on McConnell's equation[5] for an axially symmetric anisotropic group (cobalt), a shielding and deshielding region will exist, centered at cobalt, Figure 2. The value for X = C_6H_5 of α_H = τ 1.50 and oxime methyl value τ 8.00 considerably extend the series. Furthermore, the resonance position of the α_H of uncoordinated *t*-Bupy (τ 1.53) is upfield of this resonance in the phenyl complex. Second, several complexes with α_H resonances τ <1.79 (the value for X = CN) have been prepared. In our previous study,[4] we had few complexes with resonances in this range.

Table II. Linear Correlation Coefficients (LCC) for Plots of α_H Resonance[4] in *t*-$BupyCo(DH)_2X$ vs. Resonances in Other Compounds

Common X	Type of resonances correlated	LCC
CN, NO_2, Cl, Br[a]	Trans NH_3 in $XCo(NH_3)_5$[b]	0.987
CN, NO_2, Cl, Br, NO_3	Cis NH_3 in $XCo(NH_3)_5$[b]	0.988
Cl, Br, NO_2, NCS, CN	Trans NH_3 in $XCo(NH_3)_5$[c]	0.856
Cl, Br, NO_2, NCS, CN	Cis NH_3 in $XCo(NH_3)_5$[c]	0.879
Cl, Br, NO_2, NCS, N_3	Prox NH_2 in $X_2Co(en)_2$[d]	0.985
Cl, Br, NO_2, NCS, N_3	Prox NH_2 in $X_2Co(en)_2$[e]	0.983

[a] Not reported for NO_3. [b] Reference 6, DMSO. [c] Reference 7, H_2SO_4. [d] Reference 8, dimethylformamide (DMF). [e] Reference 8, dimethylacetamide (DMA).

Pentaammine Complexes. Recently, the PMR spectra of $[Co(NH_3)_5X]^{n+}$ complexes in dimethyl sulfoxide (DMSO) solution were reported.[6] The authors, however, failed to see that a linear relationship existed between the chemical shifts of the cis and trans amine hydrogen resonances (Figure 3). The lack of a good linear relationship when a similar plot is made using data obtained for H_2SO_4 solutions[7] probably arises from specific solvation or ion-pairing effects which influence the cis and trans amine groups differently.

The variation in chemical shift for the limited $Co(NH_3)_5X^{n+}$ series is roughly 3 times that found for the α_H in the related *t*-$BupyCo(DH)_2X$ complexes. The slope of the line in Figure 3 is close to 1, whereas we calculate a slope of ca. 0.5 with McConnell's equation.[5] The amine hydrogens are much closer to the cobalt center than are any of the hydrogens in *t*-$BupyCo(DH)_2X$. This proximity explains the greater range of shifts and suggests a reason why the point-dipolar model may no longer be applicable. There is a linear correlation between the shifts of the resonances in $[Co^{III}(NH_3)_5X]^{n+}$ and the α_H resonances in *t*-$BupyCo(DH)_2X$ (Figure 4).[3] It is clear that, if we assume that the near-neighbor paramagnetic effect dominates in both cases, the effect of X on the paramagnetic anisotropy of cobalt is not modified (or is linearly modified) by the other ligands about cobalt.

A PMR Spectrochemical Series. The good linear correlation cited above between chemical shifts of cobaloxime and pentaammine complexes leads us to believe that a PMR spectrochemical series exists. Some linear correlation coefficients (LCC) for a variety of Co(III) complexes are listed in Table II. In general, the agreement is fairly good, con-

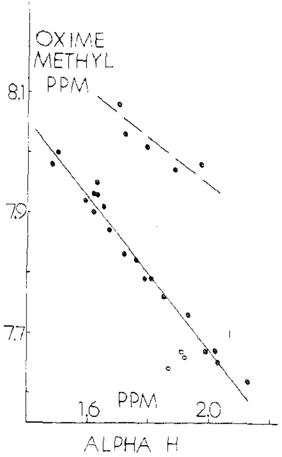

Figure 1. Plot of the chemical shifts (τ) of the oxime methyl resonance vs. the α_H of *t*-Bupy in (*t*-Bupy)Co(DH)$_2$X (CH_2Cl_2 solvent). Solid points near solid line, top to bottom, are for X = C_6H_5, 4-BrC_6H_4 and 4-$CH_3OC_6H_4$(identical), Sn(*n*-C_4H_9)$_3$, CH_3, C_2H_5 (touching CH_3), *i*-C_3H_7, $CH_2Si(CH_3)_3$, P(O)(OCH_3)$_2$, CH_2Br, CCl_3, $CHBr_2$, CN (left), S-*t*-C_4H_9(touching line), S_2CO(*i*-C_3H_7), NO_2, Cl (left), Br, NCS, and NO_3. Open points are for the linear triatomic ligands. The axis of these ligands is not coincident with the molecular axis and influences the oxime methyl shift.[4] Top to bottom, X = SCN, N_3, SeCN. Points about dashed lines are for ligands which have anisotropic aromatic groups which are not perpendicular to the dioxime plane; left to right, X = $CH_2C_6H_5$, $CH_2C_6H_4$-4-CN, SC_6H_5, $SO_2C_6H_4$-4-CH_3, SC(C_6H_5)$_3$. The I represents the point for iodide. This ligand and also Sn(*n*-C_4H_9)$_3$ probably fall off the solid line as a consequence of the "bulky atom effect" on chemical shifts (see W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 324 (1974).

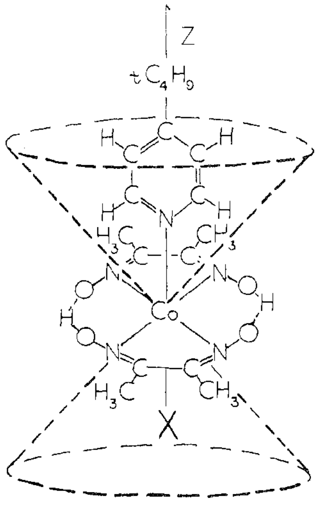

Figure 2. The magnetic anisotropy of cobalt has a shielding and deshielding region separated by a cone-shaped region of zero shielding. This cone is depicted for the (*t*-Bupy)Co(DH)$_2$X complexes and it can be seen that the axial ligands will experience different shielding to the dioxime ligands.

sidering the differences in solvents used in such studies.

Furthermore, the literature contains several examples of series consistent with the cobaloximes but which have too few overlapping ligands for meaningful comparisons to be made. We note, particularly, that the large effect of the phenyl group on anisotropy is apparent also in data reported for some Schiff base complexes.[9] These Schiff base complexes usually exhibit chemical and spectroscopic properties rather different from those exhibited by the cobaloximes.[10] Some trends[11] in cobalamin (corrin $C_{10}H$) also parallel these α_H values. We have used the measured values of α_H and overlapping X complexes in other series to establish a quantitative PMR spectrochemical series, Table III. This series appears to be essentially independent of the nonvaried ligands in the complexes.

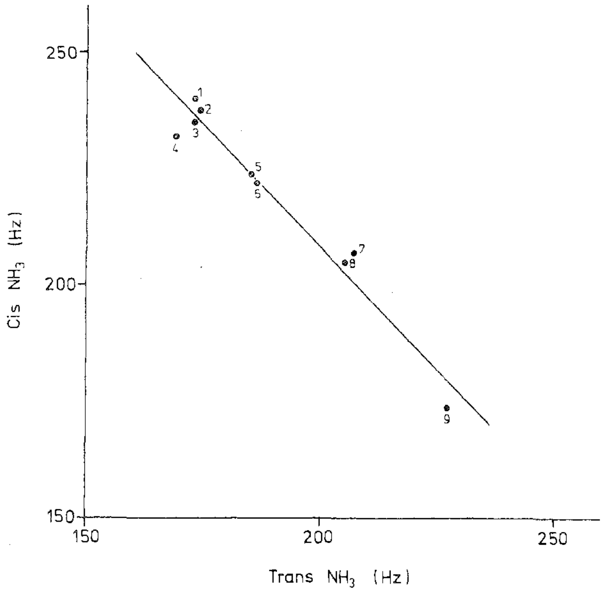

Figure 3. Plot of chemical shift (in hertz using DSS as a standard) of cis vs. trans amine protons in [Co(NH_3)$_5$X]$^{n+}$, DMSO solvent: 1, H_2O; 2, CCl_3CO_2; 3, $CHCl_2CO_2$; 4, CH_2ClCO_2; 5, Br; 6, Cl; 7, NH_3; 8, NO_2; 9, CN.

Table III. PMR Spectrochemical Series

Ligand	α_H (τ)	Ligand	α_H (τ)
F	2.24^{a,d}	$SO_2C_6H_4CH_3$	1.88^c
H_2O	2.14^{a,d}	SeCN	1.87^b
HSO_4	2.14^{a,e}	*i*-PrXan	1.85^b
NO_3	2.13^b	S-*t*-Bu	1.81^b
CCl_3CO_2	2.10^{a,d}	SC_6H_5	1.80^b
(NH_2)CO	2.09^{a,f}	CN	1.79^b
OH	2.08^{a,d}	$CHBr_2$	1.76^b
I	2.06^b	CCl_3	1.72^b
HCO_2	2.05^{a,d}	$CH_2C_6H_4$-4-CN	1.71^b
CH_3CO_2	2.04^{a,d}	$CH_2C_6H_5$	1.70^b
NCS	2.03^b	P(O)(OCH_3)$_2$	1.68^{b,g}
Br	2.02^b	BrH_2C	1.67^b
NCO	1.99^{a,f}	$CH_2Si(CH_3)_3$	1.65^b
Cl	1.99^b	Sn(*n*-Bu)$_3$	1.63^b
SC(C_6H_5)$_3$	1.97^b	CH_3	1.62^b
NO_2	1.93^b	Et	1.62^b
NH_3	1.92^{a,d}	*i*-Pr	1.59^b
N_3	1.92^b	C_6H_5	1.50^b
SCN	1.91^b	C_6H_4OMe	1.48^b
SO_2CH_3	1.89^c	C_6H_4Br	1.48^b

[a] Estimated from literature data. [b] Reference 4 or this work, measured values. [c] Bound through S; value for $CH_3C_6H_4SO_2$ measured by adding *t*-Bupy to $CH_3C_6H_4SO_2$Co(DH)$_2H_2O$ (supplied by J. Palmer and E. Deutsch) and value for CH_3SO_2 estimated from PMR measurements of Palmer and Deutsch. [d] Estimated from pentaammine complexes (DMSO solvent, ref 6) by linear correlations with α_H for common X. The F complex was prepared by a literature procedure. [e] Estimated from data in ref 7. [f] Estimated from data of R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 9, 1567 (1970). [g] Incorrectly given as 1.62 in ref 4.

A comparison between the PMR spectrochemical series and the visible–uv spectrochemical series[12] is instructive. For this comparison we will consider ligands with *small* α values to be *high* in the PMR spectrochemical series. Present thinking, which has remained relatively unchanged for over a decade,[12] is that the halides are π donors, CN and NO_2 are π acceptors, and H_2O, NH_3, and CH_3 are primarily σ donors. Thus, the halides are lower and CN and NO_2 are higher in the uv–visible spectrochemical series than would be predicted on the basis of σ donation. In the PMR spectrochemical series, these

Table IV. Summary of Correlations

System	Spectroscopic property	Compd	No. correlated	LCC	Ref
1	$\nu(Pt\text{-}H)$	*trans*-$Pt^{II}HXL_2$	10	0.963	2, p 366
2	$\nu(Pt\text{-}CH_3)$	*trans*-$Pt^{II}CH_3XL_2$	7	0.936	13
3	$J(Pt\text{-}C\text{-}H)$	*trans*-$Pt^{II}CH_3XL_2$	9	0.975	2, p 383
4	$J(Hg\text{-}C\text{-}H)$	CH_3HgX	8	0.989	14
5	$J(Pt\text{-}C\text{-}H)^a$	$Pt^{IV}(CH_3)_3X(bpy)$	12	0.994	15
6	$\nu(Pt\text{-}C)$	$Pt^{IV}(CH_3)_3X(bpy)$	9	0.973	15
7	$J(Pt\text{-}P)$	*trans*-$Pt^{II}[(RO)_2PO]XL_2$	10	0.958	16
8	$\nu(Ru\text{-}H)$	*trans*-$Ru^{II}HX[C_2H_4(PR_2)_2]^b$	5	0.986	17
9	$\nu(Ru\text{-}H)$	*trans*-$Ru^{II}HX[C_2H_4(PR_2)_2]^c$	6	0.984	17
10	$J(Pt\text{-}C\text{-}F)$	*trans*-$Pt^{II}CF_3XL_2$	9	0.967	18
11	$\sigma(\alpha_H)$	*trans*-*t*$BupyCo(DH)_2X^d$	16	0.981	4, this work
12	$J(P\text{-}H)^e$	*trans*-$Bu_3PCo(DH)_2X$	11	0.983	4, this work

[a] Group trans to X. [b] $R = C_2H_5$. [c] $R = CH_3$. [d] Values calculated also included. [e] Oxime methyl hydrogen.

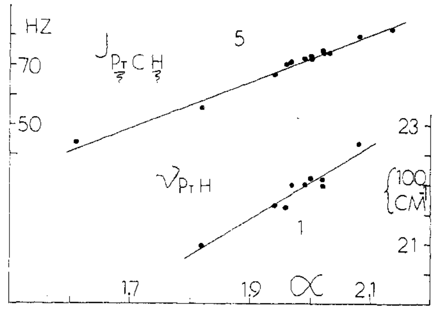

Figure 5. Plots of spectroscopic measurements vs. average α values for series in Table IV: series 5, left to right, X = CH_3, CN, NO_2, SCN, NH_3, NCO, NCS (top), I (bottom), Cl (top), Br (bottom), CH_3CO_2, NO_3, H_2O; series 1, left to right, X = CN, NO_2, SCN, NH_3 and N_3 (identical), NCO, NCS, Cl (top), Br, NO_3.

π-bonding effects are apparently small or absent.

Other Metals. The approximate correlations between PMR data on cobaloxime and various trends in platinum(II) chemistry have been noted.[4] The correlations for different Co(III) systems noted above prompted us to seek quantitative relationships between the trends in cobalt(III) chemistry with those for other metal systems. Several systems for which good correlations with our α values were found are given in Table IV. The correlations were obtained in the following fashion. First, least-squares fits of the α values in Table III vs. the spectroscopic parameters for the series in Table IV were used to calculate a spectroscopic α value (to 0.01) for each ligand in each series. All the spectroscopic α values for a particular ligand were averaged and these average α values (rounded to 0.01) were used in a new series of least-squares analyses which now included the experimental PMR α values. This latter process was repeated until the average spectroscopic α values remained essentially constant (±0.01). Although in some cases there are reasons for discarding some spectroscopic values (for example, when vibrational coupling is likely in stretching frequency measurements), we, nevertheless, chose to include all values. Our reasoning was that small errors are inherent in all the measurements and when large numbers of correlations are possible, one might hope that these errors are random and might cancel. Such an approach combined with the variation in α values in steps of 0.01 will lead to larger standard deviations and lower LCC than might otherwise be obtained. For the types of comparison being made between widely different spectroscopic parameters and with the likelihood that other properties of the ligands such as steric or anisotropic effects will influence these parameters, the LCC observed are remarkably good. The LCC are sufficiently high to leave no doubt that the series are linearly related and, in most cases, there is only a 0.1% probability that a linear relationship does not exist. Some correlations are plotted in Figures 5 and 6.

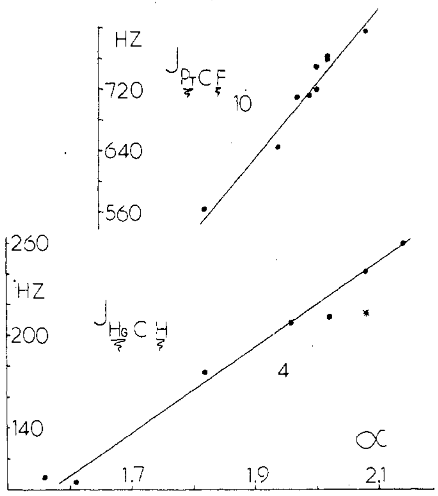

Figure 6. Plots of spectroscopic measurements vs. average α values for series in Table IV: series 4, left to right, X = C_6H_5, CH_3, CN, SCN, Br, star "OH", NO_3, H_2O (methylmercury hydroxide does not exist as such and probably is $(CH_3Hg)_3O^+$; this point *was* included in the correlation for the reasons stated in the text); series 10, left to right, X = CN, NO_2, N_3, NCO, NCS (bottom), I (top), Cl (bottom), Br (top), NO_3.

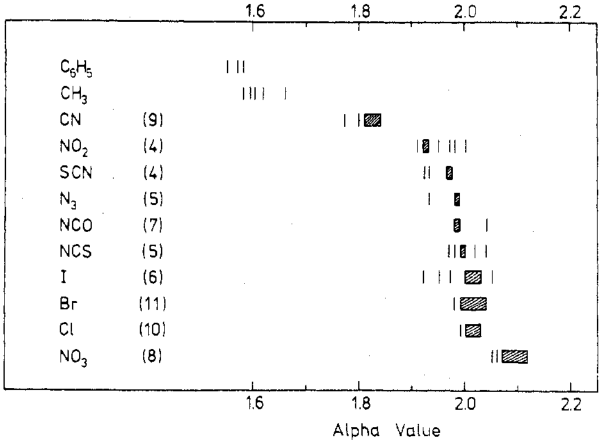

Figure 7. Schematic representative summary of the α values obtained for the 12 series. A complete listing of α values will appear in the microfilm edition.[3] The numbers in parentheses reflect the number of points in the bars.

A compilation of the individual α values for frequently occurring ligands is plotted schematically in Figure 7. This figure is quite revealing; it is clear that many of the ligands which are most commonly studied, Cl, Br, I, NCS, SCN, NCO, and NO_2, overlap considerably in their effects on the spectroscopic properties of metallic compounds. The reversal in trends often cited for the halides[2] may sometimes be more a consequence of scatter than of any fundamental change in bonding property. Clearly (at least for the correlations we have chosen), NO_3, CN, and CH_3 (which do not overlap with each other, the halides, or the pseudohalides) are probably good ligands to have in a series. Also, little scatter is observed for Cl and (except for one series) NCO, whereas I and NO_2 are probably capable of inducing the largest spurious effects. It is extremely unfortunate that some series in the literature include only halides and/or pseudohalides. The effort devoted to preparing halide and pseudohalide complexes has not been particularly fruitful. We suggest that, in the future, more effort should be devoted to preparing complexes with CH_3, CN, and NO_3, as well as Cl or NCO. Furthermore, thiolate ligands should be investigated in more detail.

Correlations with several other series were attempted. A good correlation was evident for ν(Os–H) in some Os hydride complexes,[17] but the series was too short for meaningful quantitative comparisons. Two rather extensive series involving carbonyl stretching frequencies in Rh and Ir complexes[19] gave poorer correlations.

Discussion

Our objective was to probe the question of whether spectroscopic substituent constants were feasible. The parameter being measured (coupling constant, chemical shift, stretching frequency, etc.) must be a sensitive function solely of the electronic properties of the metal complex. Extraneous factors (particularly solvent and steric effects) should be small or absent. Obviously, it is unlikely that these conditions will be met completely. Therefore, inherent errors will exist in the spectroscopic constants.

Appleton, Clark, and Manzer[2] have suggested that an attempt at an exact explanation of such phenomena is not warranted by the current state of quantum theory. We agree with the assessment that theory is not adequate for a complete treatment. However, our observation that transferable spectroscopic constants are possible convinced us that some success might be gained by concentrating our initial investigation on the isolated ligand, X. Many of the smaller ligands have been treated by rigorous theoretical calculations. It seemed reasonable to seek a property which is indicative of the availability of the ligand's lone-pair electrons for interaction with an acceptor. The donor power of the ligand should be closely related to its effect upon the metal ion.

We accordingly investigated a number of properties which would seem to be related to the availability of the ligand lone pair. These included the orbital electronegativities and ionization potentials of the ligating atoms, the calculated (ab initio SCF) molecular orbital energies of the ligands, their Taft substituent constants, and others. None of these quantities appeared promising.

We decided, therefore, to try to make a direct estimate of the electrostatic force of attraction exerted by the rest of the ligand upon one of its lone-pair electrons. We assumed that this force can be approximated by the formula

$$\mathfrak{F} = \frac{Z_{\mathrm{eff}}}{\langle r\rangle^2} + \sum_{\mathrm{A}} \frac{Q_{\mathrm{A}}}{R_{\mathrm{A}}{}^2} \qquad (1)$$

Z_{eff} represents the effective nuclear charge seen by the lone-pair electron on the atom to which the lone pair "belongs" (i.e., the bonding atom). It was calculated using the rules presented by Clementi and Raimondi.[20] These rules take into account the screening effect of the other electrons on the atom. $\langle r\rangle$ is the average radial distance from the nucleus of the lone-pair orbital, ψ, on the bonding atom and is defined as $\langle r\rangle_\psi = \int \psi^* r \psi \, d\tau$. The values of $\langle r\rangle$ were obtained from free-atom Hartree–Fock wave functions,[21] hybridization being taken into account as shown below.

Table V. Comparison of α Values and Estimated Forces

Ligand	Av α^k or PMR α	Force, au	Ref to Molecular wave function
C_6H_5	1.56 ± 0.02		
CH_3	1.61 ± 0.03	0.97	*a*
CN	1.82 ± 0.02	1.04	*b*
CO		1.14	*c*
NO_2	1.94 ± 0.03	1.84	*d*
SCN	1.96 ± 0.02	1.45	*c*
N_3	1.97 ± 0.02	1.80	*e*
NH_3	1.97 ± 0.04	1.86	*f*
NCO	1.99 ± 0.02	1.86	*c*
NCS	2.00 ± 0.02	1.88	*c*
I	2.00 ± 0.04		
Cl	2.02 ± 0.02	1.70	
Br	2.02 ± 0.02	1.97	
CH_3CO_2	2.03 ± 0.02		
HCO_2	2.05	2.99	*g*
NO_3	2.08 ± 0.02	3.01	*h*
OH	2.08 ± 0.06	2.95	*i*
H_2O	2.14 ± 0.03	2.96	*j*
F	2.24	4.04	

[a] R. E. Kari and I. G. Csizmadia, *J. Chem. Phys.*, **56**, 4337 (1972). [b] P. E. Cade, private communication. [c] A. D. McLean and M. Yoshimine, "Tables of Linear Molecule Wave Functions", IBM Corp., San Jose, Calif., 1967. [d] R. Bonaccorsi, C. Petrongolo, E. Scrocco, and J. Tomasi, *J. Chem. Phys.*, **48**, 1497 (1968). [e] S. D. Peyerimhoff and R. J. Buenker, *ibid.*, **47**, 1953 (1967). [f] P. Rajagopal, *Z. Naturforsch, Teil A*, **20**, 1557 (1965). [g] S. D. Peyerimhoff, *J. Chem. Phys.*, **47**, 349 (1967). [h] L. E. Harris, *ibid.*, **58**, 5615 (1973). [i] P. E. Cade, *ibid.*, **47**, 2390 (1967). [j] J. W. Moskowitz and M. C. Harrison, *ibid.*, **43**, 3550 (1965). [k] Error limits are one standard deviation.

The other terms in eq 1, $\sum_{\mathrm{A}}(Q_{\mathrm{A}}/R_{\mathrm{A}}{}^2)$, represent the forces due to the other atoms in the ligand. Since these are farther away from the electron being considered, it is assumed that they can be treated as point charges, Q_{A}. The magnitudes of all atomic charges were computed by a recently proposed method which is based on the electronic density function of a molecule.[22,23] The distances, R_{A}, from each atom, A, to the supposed average position of the lone-pair electrons were calculated using the value of $\langle r\rangle$ and the known geometry of the ligand.[24]

In determining Z_{eff}, an attempt was made to take into account both the charge and the hybridization of the bonding atom. The procedure used can best be explained by means of an example, such as the ligand NO_2^-. The ligating atom, nitrogen, is taken to be in a state of sp^2 hybridization; accordingly, we write[25]

$$Z_{\mathrm{eff}} = {}^1/_3 Z_{\mathrm{eff,2s}} + {}^2/_3 Z_{\mathrm{eff,2p}} \qquad (2)$$

$Z_{\mathrm{eff,2s}}$ and $Z_{\mathrm{eff,2p}}$ are the effective nuclear charges that a 2s or 2p electron on the nitrogen would see. In calculating these with Clementi and Raimondi's rules, the charge on the nitrogen was included. This charge was computed to be 0.23+; we therefore treated the nitrogen as having 2.77 2p electrons rather than 3.00. The value used for $\langle r\rangle$ also was designed to reflect the effect of hybridization; for NO_2^-

$$\langle r\rangle = {}^1/_3 \langle r\rangle_{2s} + {}^2/_3 \langle r\rangle_{2p} \qquad (3)$$

For some of the ligands included in this study, the atomic charges have already been calculated, using near-Hartree–Fock molecular wave functions.[22] A few previously unpublished charges were computed in the course of this work, using the approach presented in ref 22c.

Table V (and Figure 8[3]) compares average α values with the results obtained by evaluating eq 1 for all those ligands for which appropriate wave functions could be found and the atomic charges estimated. The $\mathfrak{F}$ quantities are proposed as rough estimates of the attractive force exerted upon one of the lone-pair electrons in each case. Several points merit further discussion.

(1) The main contribution to $\mathcal{F}$ comes, in each instance, from the $Z_{\rm eff}/\langle r\rangle^2$ term. The contributions of the Q_A/R_A^2 terms are generally very small, usually less than 4% of $Z_{\rm eff}/\langle r\rangle^2$, and they are sometimes relatively insignificant.

(2) The calculation predicts that Cl and Br will have properties most similar to the N-donor ligands, as is generally found.

(3) Two regions of greatly differing sensitivity of α to $\mathcal{F}$ exist. For forces <1.4 au, the α value is very sensitive to small changes in force; for force values ~ 1.8 au and higher, the α parameter becomes very much less sensitive. It may be that a change is occurring in the degree of electron sharing in the M–X bond. Perhaps when the lone pair is very tightly held (NO_3 and F), the metal is no longer competing effectively for these electrons. In this regard, it is somewhat unfortunate that so few series include fluoride.

Sufficient information exists for us to calculate an approximate force for CO. The value 1.14 au (Table V) is quite close to that for CN and this result implies that CO should have an α value close to that for CN. Limited experimental spectroscopic data on platinum complexes[26,27] do place CO close to CN. Such a conclusion, although interesting, must be considered tentative because of the present approximate method of obtaining the forces and the rather limited relevant experimental data.

A major impetus for the investigation of metal complex series has been the attempted correlation of spectroscopic effects with thermodynamic and kinetic trans effects. Hill has speculated about such a relationship for cobaloximes.[28] We have noted the relationship between PMR spectra and kinetic properties of cobaloximes.[29] Deutsch[30] has reached a similar conclusion and, furthermore, has concluded that the α_H resonance in $pyCo(DH)_2X$ complexes is the best available parameter (among several) with which to compare the trans effect of X. Studies comparing these spectroscopic constants for X and the trans effect of X are in progress.[31]

Only five series in Table IV (two of which are cobaloximes) have ligands which span the series from methyl to nitrate. It is clear at this time that many more such extensive series should be investigated. It would be of particular interest to determine whether organometallic compounds and coordination compounds can be further interrelated. Also, it remains to be seen whether such correlations may serve as a useful aid in complex characterization and in the understanding of ligand effects on metal centers.

Acknowledgment. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We wish to thank Drs. Joan Palmer and Edward Deutsch for some of the sulfinatocobaloxime complexes and for communication of their results prior to publication.

Supplementary Material Available. Table I, containing PMR data on cobaloximes, Table VI, giving all the α values for systems 1–12, Figure 4, comparing the relationship between α_H and cis and trans amine proton shifts, and Figure 8, comparing α to $\mathcal{F}$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50043I-10-75.

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