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A Spectroscopic Study of Bonding and Structure in Dihalotetrakis(tolyl isocyanide)iron(II) Complexes

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Both cis and trans isomers of dihalotetrakis(tolyl isocyanide)iron(II) complexes were synthesized and characterized. Nuclear magnetic resonance spectroscopy was used primarily for identification and characterization. The infrared spectra were studied in the isocyanide stretching region and the number of and intensities of the observed bands were used to infer structural information, while the measured spectral shifts were used to discuss the changes in the π*-accepting abilities of the isocyanides and the correlation with the electronegativities of the halide ligands. The Mössbauer spectra of these complexes are also reported and the partial center shift and partial quadrupole splitting values of the ligands have been derived. The bonding characteristics of both the isocyanides and the halides are discussed in terms of* σ *and* π *contributions.*

The experimental Mössbauer data is correlated to the other spectroscopic data although it appears to be more informative, especially in the case of indicating the halide π*-donor capabilities.*

Introduction

Triply bonded octahedrally coordinating ligands such as carbonyls, cyanides and isocyanides have been extensively studied because of their exceptional σ and π bonding capabilities. Their infrared stretching frequencies have been used as a tool for interpreting donor–acceptor properties,[1] as well as for group theoretical structure determination.[2,3] It has been postulated that at least for singly coordinated carbon monoxide, the stretching frequency responds sensitively to any changes in the environment of the central metal atom.[4] More recently, isonitrile and carbonyl complexes have been studied both by N.M.R.[5,6] and by Mössbauer[6] techniques. Octahedral complexes of the type *cis* and *trans* FeL_4X_2, where L = an isocyanide and X = a halide, have now been studied by both infrared[2] and by Mössbauer[7,8] spectroscopy from the standpoint of bonding and structure determination.

Bancroft, Mays and Prater[8] applied Mössbauer spectrometry to compounds of the type FeL_4X_2 and summarized previous data on compounds of this type in order to test the suggested[9] correlation between partial center shift (p.c.s.) values and the spectrochemical rankings of ligands. They stated that *cis* or *trans* structures could be assigned to isonitrile compounds* on the basis of the predicted[7,10] –1:2 quadrupole splitting (Q.S.) ratio. However, for isocyanides and other ligands which exhibit both σ- and π-bonding effects, it was found that the p.c.s. values appear to change markedly. They assumed that the differences in center shift (C.S.) values were due to differences in π-bonding, and proposed that σ- and π-bonding effects could be separated by this means, although it was noted that more *cis-trans* pairs were needed to test this theory carefully. For the present work, *ortho*-(OTI) and *para*- (PTI) tolyl isocyanides were chosen since the N≡C group is directly attached to the aromatic ring, lending itself to conjugation. σ- and π-bonding effects might be separated[2] by choosing such an extensive π system.

Using these conventional methods of spectroscopy, dihalotetrakis(tolyl isocyanide)iron(II) complexes were characterized and correlated to their Mössbauer spectra, as described below.

Vibrational analysis of substituted metal carbonyls of the type $(M(CO)_{6-n}L_n)$ has been reported by Orgel.[3] In addition, isomers of the type *cis*- and *trans*-$[Fe(CNR)_4X_2]$ have been assigned[2] pseudo C_{2v} and pseudo D_{4h} symmetry, respectively, neglecting asym-

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* Methyl, Ethyl, Benzyl, and *p*-methoxyphenyl isocyanides were used by ref. 8.

metry due to possible[11] nonlinearity of the CNR bond. Thus the distribution of N≡C stretching absorptions should be similar to *cis* and *trans* $M(CO)_4L_2$ which gives rise to a weak $A_1^{(1)}$ mode, a B_1 mode, and $A_1^{(2)}$ and B_2 modes of comparable intensity for the *cis* isomer, and two IR active E_u modes of the same frequency (similar to the B_1 *cis* mode) for the *trans* isomer. The two A_1 modes can interact such that the $A_1^{(1)}$ borrows intensity from the $A_1^{(2)}$ mode.

In the case of the N.M.R. spectra of the *cis* isomers of these complexes, if the geometric difference carries over into the aromatic system of the ligands, then two different resonance signals of the methyl protons of these pairs might be observed. All methyl protons would yield equivalent resonance signals in the *trans* compounds, as for the uncomplexed isocyanide ligand.

Using the additivity model,[8] the Mössbauer spectra of these low spin Fe(II) complexes might provide C.S. and Q.S. data resolvable into p.c.s. and partial quadrupole splitting (p.q.s.) values characteristic of each ligand.

The Q.S. arising from the removal of some of the degeneracy of the 3/2 state of the ^{57}Fe Mössbauer nucleus by an electric field gradient attributable to valence electrons ($q_{valence}$) or to external charges ($q_{lattice}$) has been discussed in terms of a molecular orbital model[14] for an additive e.f.g. at the metal nucleus. In the case of π-acceptor ligands, symmetry considerations show[14,15] that there is no justification for writing a π-bonding contribution to the e.f.g. as a partial field gradient parameter which is completely independent of the stoichiometry and steriochemistry of the particular complex.

Here, the McClure MO[10] approach of Bancroft and co-workers[8,15] will be followed, with the two steriochemistries of consideration being given separate treatment. Additivity is assumed to hold for geometric type. The functional dependence of the observables (p.c.s. and p.q.s.) upon the bonding parameters (σ-donation and π-acceptance) is embodied in eqns. (1) and (2) postulated by Bancroft *et al.*[8,15]

$$\text{p.c.s.} = -k(\sigma+\pi) \quad (1)$$

$$\text{p.q.s.} = -q_{lattice} + C(\pi-\sigma) \quad (2)$$

Employing this scheme, some deductions concerning the bonding properties of ligands have already been demonstrated by Bancroft and co-workers.

Experimental

Materials

p-tolyl isocyanide (PTI) was prepared by the method of Appel;[16] o-tolyl isocyanide (OTI) was prepared by the method of Ugi.[17]

Ferrous chloride ($FeCl_2 \cdot 4H_2O$) was obtained in reagent grade purity from Merck and Co., Inc. Ferrous bromide ($FeBr_2 \cdot 6H_2O$) and ferrous iodide ($FeI_2 \cdot 4H_2O$) were obtained from Alfa Inorganics–Ventron. All were used as received.

Complex Preparation

All complexes were prepared according to modifications[18,24a] of the method of Malatesta.[19] The OTI complexes are new.

trans-$[Fe(CNR)_4X_2]$

Dry ice–acetone cooling was found to be a more suitable method for the isolation of the dibromo and diiodo complexes. Furthermore, once isolated and recrystallized, *trans*-$[Fe(CNR)_4I_2]$ complexes were found to be stable in chloroform for at least a week. The dichloro and dibromo complexes do isomerize within minutes at room temperature.

The ease with which the complexes are formed and isolated follows the order Cl > Br > I, and OTI > PTI. Once isolated, the stability of the complexes follows the order I > Br > Cl and OTI > PTI.

The *trans*-$[Fe(CNR)_4Cl_2]$ complexes are blue-violet, the *trans*-$[Fe(CNR)_4Br_2]$ complexes are blue and the *trans*-$[Fe(CNR)_4I_2]$ complexes are green.

cis-$[Fe(CNR)_4X_2]$

Caution is urged in heating, since complexes of this type[26] are prone to decompose upon heating. In some cases, the *cis* isomer has been known to precipitate from the mother liquor upon standing, without heating. Bonati and Minghetti[5] have cautioned against use of

TABLE I. Analytical Data. Analyses Found (Calcd.) (%)

Complex	C	H	N	Fe	X
trans-$Fe(PTI)_4Cl_2$	(64.56)	(4.74)	(9.41)	(9.38)	(11.91)
	64.31	4.85	9.56	9.24	11.75
cis-$Fe(OTI)_4Br_2$	(56.17)	(4.12)	(8.19)	(8.16)	(23.35)
	55.97	4.27	8.23	8.16	23.30
trans-$Fe(OTI)_4Br_2$	(56.17)	(4.12)	(8.19)	(8.16)	(23.35)
	56.17	4.21	8.32	8.26	23.23
cis-$Fe(PTI)_4Br_2$	(56.17)	(4.12)	(8.19)	(8.16)	(23.35)
	56.12	4.16	8.33	8.00	23.22
trans-$Fe(OTI)_4I_2$	(49.39)	(3.63)	(7.20)	(7.18)	(32.61)
	49.45	3.78	7.14	7.10	32.47

additional product which can be isolated from the mother liquor.

The dichloro complexes are orange, the dibromo complexes are orange-brown to brown, and the diiodo complexes are brown to red-brown.

Table I summarizes the analytical data for the complexes.[20]

Instrumentation

The infrared spectrum of each complex was recorded on a Perkin–Elmer Model 180 grating spectrophotometer. The *cis* moieties were run in chloroform solution in a 0.01 mm pathlength KBr cell, as were the *trans*-diiodo complexes, which showed no evidence of isomerization after over a week in solution. The *trans*-dibromo und dichloro moieties showed evidence of isomerization within minutes, and – as a result – were run only as KBr pellets. KBr appears to depress the frequencies on the order of 5 cm^{-1}.[21] The Perkin–Elmer 180 is quoted to have a resolution of 1.4 cm^{-1} and be accurate to ±0.36 cm^{-1} in this region.

The spectrum of *cis*-[Fe(PTI)$_4$Br$_2$] was run on a Beckman Instruments IR-20 infrared spectrophotometer after an analysis of the data indicated the presence of an impurity in the original sample.

The intensities of the observed bands were obtained by duplicating the spectrum with Gaussian lineshapes on a Dupont Instruments 310 Curve Resolver and 310 Curve Plotter, and then integrating the relative area of each peak.

Nuclear Magnetic Resonance spectra were recorded for all complexes in CDCl$_3$ with an internal tetramethylsilane (TMS) reference on a Varian Instruments Model T-60 spectrometer.

Mössbauer Spectrometer

The Mössbauer spectrometer used for obtaining the spectra consists of a laser interferometer calibrated loudspeaker drive system coupled to a Canberra 1024 channel multichannel analyzer interfaced to a PDP-11 digital computer. Computations were made to correct the baseline for experimental geometry and to fit the resonance absorptions with Lorentzian line shapes. The γ-ray source for the Mössbauer spectrum was ^{57}Co in palladium foil, and the center shifts are corrected[22,23] to sodium nitroprusside. Calibration of this instrument against natural iron foil indicates the accuracy of the velocity scale to be within 0.01 mm/second.

Results

The data from the N.M.R. spectra of the compounds studied are summarized in Table II. The table lists the chemical shifts, δ, in ppm for both the methyl and the aromatic protons. In the case of the aromatic protons, the splitting patterns were often too complex to completely resolve, and only the predominant resonances are listed.

TABLE II. Nuclear Magnetic Resonance Data.

Complex	δ_{Me}(ppm)	δ_{Ar}(ppm)
trans-[Fe(OTI)$_4$Cl$_2$]	2.67	7.33 (bs/sh)
cis-[Fe(OTI)$_4$Cl$_2$]	2.53, 2.67	7.27 (bs/sh)
trans-[Fe(OTI)$_4$Br$_2$]	2.63	7.28 (bs/sh)
cis-[Fe(OTI)$_4$Br$_2$]	2.53, 2.67	7.27, 7.32 (sd/wm)
trans-[Fe(OTI)$_4$I$_2$]	2.65	7.30 (ss/wm)
cis-[Fe(OTI)$_4$I$_2$]	2.57, 2.70	7.27, 7.30 (sd/wm)
trans-[Fe(PTI)$_4$Cl$_2$]	2.40	7.17, 7.30, 7.50, 7.65
cis-[Fe(PTI)$_4$Cl$_2$]	2.37	7.23[a]
trans-[Fe(PTI)$_4$Br$_2$]	2.40	7.13, 7.25, 7.43, 7.57
cis-[Fe(PTI)$_4$Br$_2$]	2.37	7.13, 7.25, 7.47, 7.60
trans-[Fe(PTI)$_4$I$_2$]	2.37	7.12, 7.25, 7.37, 7.52
cis-[Fe(PTI)$_4$I$_2$]	2.37	7.13, 7.26, 7.40, 7.56
Free OTI	2.23	7.10
Free PTI	2.33	7.13

Legend: Me, methyl protons; Ar, Aromatic protons; bs/sh, broad singlet with a shoulder; sd/wm, strong doublet with a weak multuplet; ss/wm, strong singlet with a weak multuplet

Estimated Error: 0.03 ppm

[a] This multuplet (or unresolved asymetric quartet) might also be evidence of the impurity indicated by the I.R.

Integration of each spectrum yielded a ratio approaching 4:3 for the aromatic protons versus the methyl protons for all complexes. In all cases involving PTI as the ligand, the *para* methyl protons did not show separate absorptions due to geometric non-equivalence in the *cis* isomer. *Cis* isomers with OTI as the ligand did show two absorptions of the methyl peak due to geometric nonequivalence, with integration over the methyl region yielding a ratio of 1:1. Both integrations are in agreement with predictions.

Table III summarizes the data collected for the N≡C stretching frequencies. The relative areas of the component peaks, obtained by integration of the spectra duplicated by Gaussian lineshapes on the Dupont curve resolver and plotter, are also included. Assignment, by group theory, of the four infrared active stretching modes present in the *cis* complexes has been made in accordance with Orgel[3] and Taylor.[2] It is interesting to note that the intensity of the $A_1^{(1)}$ band increases as the size of the halide increases. Ostensibly, this "almost forbidden" mode is becoming more allowed as the size of the halide distorts the complex further away from pure octahedral geometry.

Study of the B_1 mode for *cis*-[Fe(PTI)$_4$Cl$_2$], indicates[24] that cationic complexes of the type [Fe(PTI)$_5$X]$^+$ can also be isolated as by-products when using the

TABLE III. Infrared Data.

Complex	Assignment (cm^{-1})				Intensity (%)			
	B_2	B_1	$A_1^{(2)}$	$A_1^{(1)}$	B_2	B_1	$A_1^{(2)}$	$A_1^{(1)}$
cis-$Fe(OTI)_4Cl_2$	2124	2146	2155	2193	42	9.5	44	4.5
cis-$Fe(OTI)_4Br_2$	2122	2140(sh)	2149	2188	41	8	41	9
cis-$Fe(OTI)_4I_2$	2115	2129(sh)	2136	2178	36	5	50	9
cis-$Fe(PTI)_4Cl_2$	2131	2171[a]	2159	2195	35	15	46	4
cis-$Fe(PTI)_4Br_2$	2127	2141	2150	2188	43	8	40	9
cis-$Fe(PTI)_4I_2$	–[b]	–[b]	2138[b]	2179	–[b]	–[b]	48	12
		E_u				E_u		
trans-$Fe(OTI)_4Cl_2$		2130				100		
trans-$Fe(OTI)_4Br_2$		2129				100		
trans-$Fe(OTI)_4I_2$		2127				100		
trans-$Fe(PTI)_4Cl_2$		2141				100		
trans-$Fe(PTI)_4Br_2$		2138				100		
trans-$Fe(PTI)_4I_2$		2130				100		
Free OTI in $CHCl_3$		2128						
Free PTI in $CHCl_3$		2130						

[a] This band agrees with reference 5, but not with reference 2. A 25 : 1 scale expansion indicates a weaker band at 2149 (10%) in agreement with reference 2. [b] This extremely broad band has apparent shoulders around 2108 (29%) and 2125 (12%) but we feel that to make these assignments would be speculative.

method of Malatesta. This type of complex (pseudo C_{4v} symmetry) exhibits a very strong E mode (80%) at around 2165–2175 cm^{-1}. In as much as the appearance of the quadruply split $C\equiv N$ band differs for this complex (as opposed to the other 5 *cis* complexes) one can interpret as the true B_1 mode the weaker band at 2149 cm^{-1} (see note, Table III), while the band at 2171 cm^{-1} – as we observed, and was reported by Bonati[5] at 2172 cm^{-1} – is due to a minor amount of the $[Fe(PTI)_5Cl]^+$ species.[25] The band at 2159 cm^{-1} must be the $A_1^{(2)}$ mode, however, because of its strong intensity. The B_1 modes, which were reported to be strong by Taylor and Horrocks,[2] only give the appearance of being strong since they sit high on the shoulder of the $A_1^{(2)}$ band.*

Table IV summarizes the data collected for the M–C stretching frequencies. No attempt has been made at

TABLE IV. Infrared M–C Stretching Frequencies.

Complex	Frequencies (cm^{-1})	Solvent
trans-$[Fe(OTI)_4Cl_2]$	585, 565, 530	KBr
cis-$[Fe(OTI)_4Cl_2]$	590, 560	$CHCl_3$
trans-$[Fe(OTI)_4Br_2]$	585, 565, 530	KBr
cis-$[Fe(OTI)_4Br_2]$	590, 560	$CHCl_3$
trans-$[Fe(OTI)_4I_2]$	590, 560, 520	KBr
	585, 560, (535, 525)[a]	$CHCl_3$
cis-$[Fe(OTI)_4I_2]$	590, 560	$CHCl_3$
trans-$[Fe(PTI)_4Cl_2]$	548, 470	KBr
cis-$[Fe(PTI)_4Cl_2]$	(570, 555, 545)[a]	$CHCl_3$
trans-$[Fe(PTI)_4Br_2]$	555, 480	KBr
cis-$[Fe(PTI)_4Br_2]$	560	KBr
trans-$[Fe(PTI)_4I_2]$	560, 475	$CHCl_3$
cis-$[Fe(PTI)_4I_2]$	(545, 535, 530)[a]	$CHCl_3$

[a] Denotes multuplet.

TABLE V. Quadrupole Splitting and Center Shift Data.[a]

Complex	Quadrupole Splitting		Center Shift[b]	
	Obs.	Calc.	Obs.	Calc.
trans-$[Fe(OTI)_4Cl_2]$	1.505	1.492	0.382	0.382
cis-$[Fe(OTI)_4Cl_2]$	0.837	0.812	0.279	0.274
trans-$[Fe(OTI)_4Br_2]$	1.610	1.664	0.369	0.370
cis-$[Fe(OTI)_4Br_2]$	0.891	0.896	0.276	0.282
trans-$[Fe(OTI)_4I_2]$	1.769	1.716	0.351	0.353
cis-$[Fe(OTI)_4I_2]$	0.874	0.890	0.278	0.280
trans-$[Fe(PTI)_4Cl_2]$	1.569	1.568	0.372	0.378
cis-$[Fe(PTI)_4Cl_2]$	0.758	0.774	0.285	0.290
trans-$[Fe(PTI)_4Br_2]$	1.802	1.704	0.372	0.366
cis-$[Fe(PTI)_4Br_2]$	0.861	0.858	0.303	0.298
trans-$[Fe(PTI)_4I_2]$	1.736	1.792	0.351	0.349
cis-$[Fe(PTI)_4I_2]$	0.867	0.852	0.298	0.296

[a] In mm/sec. [b] Relative to sodium nitroprusside.[15]

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* As pointed out by the referee the compounds studied by reference 2 are sometimes very impure samples as indicated by their analyses.

TABLE VI. Calculated p.q.s. and p.c.s. Values.

	Trans		
	p.q.s.	p.c.s.[a]	
Cl^-	−0.300	0.100	(0.191)
Br^-	−0.257	0.094	(0.185)
I^-	−0.244	0.085	(0.176)
OTI	−0.673	0.000	(0.000)
PTI	−0.692	−0.001	(−0.001)
	Cis		
	p.q.s.	p.c.s.[a]	
Cl^-	−0.300	0.100	(0.191)
Br^-	−0.258	0.104	(0.195)
I^-	−0.261	0.103	(0.194)
OTI	−0.706	−0.027[b]	(−0.027)
PTI	−0.687	−0.023[b]	(−0.023)

[a] Derived relative to 310SS for comparison to references 8 and 15. Parenthetical values derived relative to the suggested standard sodium nitroprusside. [b] Average value for all four ligands.

present to assign the M–C frequencies to normal modes, since the 300 cm^{-1} cut-off of KBr limited the measurements, but they have been included for future reference.

The quadrupole splitting and center shifts for the complexes studied during the course of this work are listed in Table V. We have calculated p.q.s. and p.c.s. values for the halides as well as for the isocyanides. *Cis* and *trans* values have been calculated separately (see above). Table V also contains the Q.S. and C.S. values for the complexes, calculated from the derived p.q.s. and p.c.s. values by the method of Bancroft and co-workers.[8] Table VI contains the derived p.q.s. and p.c.s. values. Because the estimated error of the C.S. and Q.S. values is within 0.01 mm/sec, the error in the derived p.c.s. and p.q.s. values should be considerably less. Realistically, the derived values are only relative values but should suffice to demonstrate trends. The calculated Q.S. and C.S. values only serve as a check on self consistence, since additivity has been assumed. The p.q.s. and p.c.s. values of Cl^- were assumed[8] to be −0.300 and 0.100 mm/sec, respectively, relative to 310 SS.

Discussion

Nuclear Magnetic Resonance

Comparison of the N.M.R. spectra shows a downfield shift for all protons upon complexation. This shift is on the order of 0.2 ppm for the OTI aromatic protons, 0.1 ppm for the PTI methyl protons, and 0.4 ppm for the OTI methyl protons. The magnitude of the effect is difficult to assess for the PTI aromatic protons because of the complex splitting patterns which arise, but a net downfield shift is also apparent here. We attribute these effects to a net shift of electron density from the ligand to the metal.

For the *cis* moieties with OTI as the ligand, the non-equivalence of the two pairs of ligands is sufficiently large to show two resonance absorption peaks (note that in two of the cases, the predominant aromatic peak also shows splitting). For the *cis* moieties with PTI as the ligand, the non-equivalence is not observed. It has already been noted above that there is an increase in the chemical shift upon complexation. However, the two absorptions for the methyl proton of OTI indicate that, for the ligands *trans* to the halides, the magnitude of the downfield shift is not as large. That is, the shift of electron density from the ligand to the metal is being partially compensated for by increased back-donation from the metal to the ligand.

Infrared Spectroscopy

The B_2 mode of the *cis* isomer consists of the asymmetric stretching of the two ligands *trans* to halides, and the B_1 mode consists of the asymmetric stretching of the ligands *trans* to each other. For the *trans* isomer, the only active band (E_u) consists of the asymmetric stretching of *trans* ligands, comparable to the B_1 mode of the *cis* isomer. It might then be proposed that one compare the frequency of the B_2 mode to the frequencies of the B_1 and E_u modes to obtain a picture of the differences in bonding between ligands *trans* to halides and ligands *trans* to each other. Intercomparison of the B_1 and E_u modes would serve as a check on how the frequencies exhibited by *trans* ligands vary with structure. Orgel[3] has made a case for the comparison of symmetry related vibrations, at least along a series.

To better facilitate this qualitative comparison of the trends in frequency changes along a series and

TABLE VII. Adjusted[a,b] Ligand Asymmetric Stretching Frequencies.[c]

Stoichiometry	*Trans* to Halides	*Trans* to Each Other	
	B_2	B_1	E_u
$[Fe(OTI)_4Cl_2]$	2124	2146	2135[a]
$[Fe(OTI)_4Br_2]$	2122	2140	2134[a]
$[Fe(OTI)_4I_2]$	2115	2129	2127
$[Fe(PTI)_4Cl_2]$	2131	2149	2146[a]
$[Fe(PTI)_4Br_2]$	2127	2141	2143[a]
$[Fe(PTI)_4I_2]$	2108[b]	2125[b]	2130

[a] 5 cm^{-1} have been added[21] to the frequencies obtained in KBr pellets to compensate for the solvent effect. [b] The assignments which are speculative have been assumed for the purpose of this comparison. [c] An attempt to adjust data in this fashion seems a bad precedent. However, solvent broadening makes KBr unsuitable for resolving all four *cis* bands, and solution instability makes $CHCl_3$ unsuitable for the four corrected *trans* complexes.

between *cis* and *trans* pairs of ligands, Table VII summarizes the pertainent values from Table III. For these two qualitative comparisons, the B_2 modes are found to be on the order of 17 cm^{-1} lower in frequency than the B_1 modes, while the E_u modes average only 2 cm^{-1} lower than the B_1 modes. All modes decrease in frequency along the series Cl>Br>I.

Thus, the ligands which are *trans* to halides have lower vibrational frequencies, indicating lower bond order through greater back-donation into antibonding π-orbitals, and the decrease in frequency along the series Cl>Br>I is easily attributable to an electronegativity effect.

Mössbauer Spectrometry

The center shift can be expressed as the sum of the isomer shift, the second-order Doppler shift,[27] and the zero-point motion shift. The isomer shift is the dominant contribution to the center shift and arises from the interaction between the nuclear charge distribution and the extranuclear electrons, principally those in s states.[28] In the first approximation, the close similarity of the vibrational spectra and, presumably, a close similarity of the lattices suggest that the zeropoint motion shift and the temperature dependent second-order Doppler shift are nearly constant for the compounds studied here, as suggested by Bancroft and co-workers[8] for a much wider range of ligands. It is thus assumed that any measurable change in the center shift from compound to compound is a result of changes in the isomer shift.

It has been suggested,[8] that for good σ-donors, one would expect the p.c.s. values to be sensitive to the bonding properties of the other ligands in the complex, especially to those of the *trans* ligand. While it does appear obvious that the p.c.s. values be sensitive to the bonding properties of the other ligands present, the argument citing the spherical symmetry of the s wavefunctions (as requiring that bonding interactions reflect a scalar average) precludes a geometric dependence of the p.c.s. values. The *trans* ligand should not have overly significant importance inasmuch as the MO model for the sigma *trans* effect[29] indicates that the common unique orbital involved in bonding *trans* ligands is the p orbital, to which the Mössbauer effect is much less sensitive.[28] Bancroft[8] makes note that the effect does appear to be small since there is good agreement in the experimental data (for pure σ-bonding ligands).

For strong π-acceptors such as isocyanides, the p.c.s. values appear to change markedly for *cis* and *trans* dichloro isomers, an effect which is attributed[8, 15] to an increase in the π-accepting ability of the isocyanide groups *trans* to the chlorides. Perhaps the most striking feature of Table V is the fact that, in all cases, the C.S. of the *cis* isomer is notably more negative than the C.S. of the *trans* isomer, lending support to the postulated increase in π-accepting ability of the two isocyanide groups *trans* to the halides. On one pair of isomers, the average p.c.s. of *p*-methoxyphenyl isocyanide had been noted[8] to decrease on the order of 0.02 mm/sec. For the six new isomers reported here, there is an average decrease on the order of 0.03 mm/sec for *o*-tolyl isocyanide and of 0.02 mm/sec for *p*-tolyl isocyanide. If one is to now consider the p.q.s. values of the isocyanides, the assumption that the $q_{lattice}$ term will be significant only for relatively ionic ligands can be made.[15] The slight positive increase in the p.q.s. for PTI reinforces the postulated increase in π-accepting ability as indicated by the change in the p.c.s. values. The larger decrease in the p.q.s. for OTI, on going from *trans* to *cis*, unfortunately does not reinforce this trend and can only be rationalized if the greater magnitude of the change in the p.c.s. values for OTI is also partially due to σ-bonding inequalities (Eqns. 1 and 2) which play the dominant role in determining the p.q.s.

The data for the halides appears to be even more interesting. The p.c.s. values for the *trans* case decrease along the series $Cl^- > Br^- > I^-$. This trend disagrees with the order of the halides in the p.c.s. series postulated by Bancroft, and with the order of the halides in the spectrochemical series, both of which have been termed[8] "anomalous". The anomalous behavior has been rationalized by citing the reversal in the p.c.s. series which would occur (Eqn. 1) if one is to consider the π-donor capabilities of the halogens. This may be true for the spectrochemical series (which is primarily sensitive to d electron interactions), but the rationalization can not be used for the p.c.s. series, being opposed to the fact that the C.S. is more sensitive to σ-donation into the s orbitals of the d^2sp^3 hybrid than to shielding by donation into the T_{2g} orbitals, especially in the case of *trans* halides which one considers to have relatively little π-interaction compared to σ bonding. The series should follow as indicated above if one considers the σ-donor capabilities of the halides. For the *cis* case, the previously indicated reversal is seen (although not as large), which one may now attribute to the increased π-donor capabilities of the halides which is more consistent with the postulated increase in the π-acceptor properties of the isocyanides which are now *trans* to the halides.

The p.q.s. values of the halides are more difficult to interpret in terms of bonding information because of $q_{lattice}$ effects. For both cases, the increase in p.q.s. values down the series indicates that the $q_{lattice}$ term dominates the values. The near constancy of the p.q.s. values are going from *trans* to *cis* is a further indication that the values are not as sensitive to bonding interactions. Although the slight change in the I^- value might be taken as further evidence of the postulated increased π-donor capabilities, distortion from idealized geometry is probably a more likely hypothesis.

Conclusion

Two analogous series of complexes have been synthesized and characterized with respect to their structure and bonding. Nuclear magnetic resonance studies indicated that structure determinations are only possible for specific circumstances and bonding informations is both tenuous and limited to having a suitable isotope in a sensitive position being rather insensitive to the other ligands present in the complex. Both infrared and Mössbauer spectroscopy appear to be better than adequate (although not unequivocal) methods of confirming the structure of complexes. One is able to conclude from both of these methods that π-bonding ligands *trans* to halides show an enhanced π-accepting ability, and that the donor properties of the halides follow the order $Cl < Br < I$, as would be predicted by their electronegativities. Mössbauer spectrometry has further indicated itself to be quite adept in the area of bonding interactions, not only allowing one to separate σ and π effects, but also showing measurable sensitivity to the changes in π-bonding with structure.

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