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Trends in the Nitrogen–Oxygen Stretching Frequency of 4-Substituted Pyridine N-Oxide Coordination Compounds

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Trends in the nitrogen–oxygen stretching frequency, ν_{NO}, for twenty-four series of 4-substituted pyridine N-oxide complexes have been investigated and compared. It was found that the complexes fall into several general categories based on the correlation of ν_{NO} and $\Delta\nu_{NO}$ (the decrease in ν_{NO} of the ligands upon coordination) with σ_{PyO} substituent constants. The data suggest that the trends depend significantly on the effective charge of the central metal ion but that stereochemistry, steric effects, and the previously proposed π-bonding effects also contribute.

Introduction

The donor properties of aromatic amine N-oxides have created sufficient interest in recent years to merit three review articles.[1–3] These N-oxides are somewhat unique in the sense that there are few Lewis base systems with such versatility as to allow marked changes in basicity without a change in steric hindrance, and vice versa. For example, in the series of 4-substituted pyridine N-oxides with substituents CH_3O, CH_3, H, Cl, and NO_2, the steric environment near the donor site is not affected by the change in the *para*-substituent but there is a rather marked range in basicity as reflected by the pK_a values of 2.05, 1.29, 0.79, 0.36, and –1.7, respectively.[4] Correlations of various physical properties of this series with basicity have been made, and a set of substituent constants (σ_{PyO}) based on pyridine N-oxides have been developed for use in these linear free energy correlations.[4]

A number of correlations have been made with the nitrogen–oxygen stretching frequency ν_{NO} and σ_{PyO} values.[1,3,4] Nearly all explanations of the observed trends have been based on metal–ligand π-bonding effects however there are several series of complexes where these arguments do not seem to hold. Furthermore, most explanations have been derived from rather limited amounts of data. For these reasons the existing infrared data for various 4-substituted pyridine N-oxide (4-ZPyO) coordination complexes have been collected and summarized, and new data have been taken to fill in the void areas so that a total picture can be realized. Plausible explanations for the observed trends are given based on this total picture.

Experimental

Synthesis

The manganese, zinc, silver, lanthanum, and thorium perchlorate complexes were prepared for this work using methods similar to those previously described[5–7] with ligand-to-metal salt mole ratios of 7:1, 7:1, 2:1, 9:1, and 9:1, respectively. The hydrochloride salts were prepared by bubbling HCl gas through about 10 ml of a saturated ethanolic solution of the N-oxide for 20 to 30 minutes. Nitrogen gas was then used to flush the reaction flask of excess HCl. The solution was transferred to a Schlenk tube and a stream of nitrogen was vigorously bubbled through the solution. Anhydrous ether was then added to induce precipitation. The white product was filtered in a Schlenk frit apparatus,[8] washed with ether, and dried by passing nitrogen through the frit tube. The salts are quite hygroscopic.

Infrared Spectra

Infrared spectra for this work were obtained as Nujol mulls between NaCl plates on a Beckman IR-5A recording spectrophotometer. These spectra were calibrated using polystyrene reference bands. Infrared spectral data obtained from the cited literature references were also from solid state spectra. The ν_{NO} values for compounds reported by different authors varied by 0 to 10 cm^{-1}, the agreement being about 3 cm^{-1} in most cases. Bands for a few complexes appeared as closely spaced doublets and these values were averaged. The slopes of the $\Delta\nu_{NO}$ versus σ_{PyO} plots were obtained from least squares calculations.

Results and Discussion

The ν_{NO} values listed in Table I are averages of the many but reasonably consistent values reported in the literature. Figure 1 shows ν_{NO} of the free ligands and of the zinc complexes plotted versus σ_{PyO}. The graph for the free ligands, a linear relationship where 4-NO_2-PyO exhibits the highest ν_{NO} and 4-CH_3OPyO the lowest, is as expected. Pyridine N-oxide can be represented by several contributing resonance forms, of which some have double and some have single nitrogen–oxygen bonds.[1,3] The NO_2-group, the strongest electron withdrawing group of the series, enhances the nitrogen–oxygen double bond character while the CH_3O-group, the strongest donating group of the series, enhances the nitrogen–oxygen single bond character. A linear trend of ν_{NO} with σ_{PyO} is also present for the zinc complexes but the ν_{NO} values have decreased from those exhibited by the free ligands. This decrease is expected due to a lowering of the nitrogen-oxygen bond order upon coordination and a mass effect. One can see from Table I that there is a decrease in ν_{NO} for all the metal ion complexes relative to the corresponding free ligands. The trend observed for the zinc(II) complexes also exists for the manganese(II), cobalt(II), and nickel(II) complexes, with the range of ν_{NO} values being around 30 cm^{-1} for each. On the other hand, the range in ν_{NO} for the iron(III), chromium(III), and vanadium(III) complexes is only about 7 cm^{-1}. This latter trend is also seen in the ν_{NO} values for the quadravalent vanadium and titanium complexes $VF_4 \cdot 2(4\text{-ZPyO})$, $VCl_4 \cdot 2(4\text{-ZPyO})$, and $TiCl_4 \cdot 2(4\text{-ZPyO})$, where the range is about 5 cm^{-1} each.

TABLE I. Nitrogen–Oxygen Stretching Frequencies (cm^{-1}) of 4-Substituted Pyridine N-Oxide Complexes.

Complex	Ligand Substituent					Range in ν_{NO}	Slope of $\Delta\nu_{NO}$ vs. σ_{PyO}	Refs.[a]
	CH_3O	CH_3	H	Cl	NO_2			
Uncomplexed Ligands (L)	1212	1232	1243	1246	1273	61	–	5, 9–15
Metal Perchlorate Complexes								
$NiL_6(ClO_4)_2$	1201	1210	1218	1218	1231	30	16	5, 9, 12, 16, 17
$CoL_6(ClO_4)_2$	1201	1212	1218	1220	1228	27	18	5, 12, 16, 17
$ZnL_6(ClO_4)_2$	1208	1213	1224	1228	1238	30	15	1, 12, 17, tw
$MnL_6(ClO_4)_2$	1207	1208	1220	1235	1228	28	19	1, 16, 17, tw
$FeL_6(ClO_4)_3$	1206	1207	1210	1210	1208	4	31	5, 12, 13, 16, 17
$CrL_6(ClO_4)_3$	1198	1200	1202	1199	1206	8	28	1, 5, 16, 17
$VL_6(ClO_4)_3$	1200	(1203)[b]	(1202)[b]	1201	(1209)[b]	9	28	18
$AgL_2(ClO_4)$	1199	1203	1214	1225	1230	31	14	1, tw
$CuL_4(ClO_4)_2$	1200	1210	1208	1210	1220	20	22	5, 12, 16, 17
$LaL_8(ClO_4)_3$	1221	1230	1226	1233	1238	17	23	6, tw
$ThL_8(ClO_4)_4$	1220	1227	1223	1228	1238	18	23	7, tw
Metal Halide Diadducts								
$VF_4 \cdot 2L$	1199	1200	1197	–	1203	6	30	19
$VCl_4 \cdot 2L$	–	1197	1200	1200	1195	(5)	30	10
$TiCl_4 \cdot 2L$	–	1217	1214	1216	1215	(3)	28	10
$TiF_4 \cdot 2L$	1210	1213	1219	1222	1230	20	21	11
$ZrF_4 \cdot 2L$	1212	1213	1220	1219	1229	17	22	20
$SnCl_4 \cdot 2L$	–	1199	1201	1199	1205	(6)	24	10
$SnF_4 \cdot 2L$	1197	1200	1197	1199	1200	3	30	21
Other Complexes								
$Sn(CH_3)_2Cl_2 \cdot 2L$	1197	1201	1204	1205	–	(8)	(33)	22
$Sn(CH_3)_3Br \cdot L$	1200	1208	1214	1216	–	(16)	(23)	22
$Pb(CH_3)_3Cl \cdot L$	1197	1211	1220	1224	–	(27)	(9)	22
$VOCl_2 \cdot H_2O \cdot 4L$	1200	1208	1211	–	–	(11)	–	23
$VOCl_2 \cdot H_2O \cdot 2L$	–	–	1195	1201	1212	(17)	–	23
LH^+Cl^-	1217	1208	1258 1200	1252	1255	50	–	tw
	(2262)[c]	(2257)[c]	(2160)[c]	(2137)[c]	(2030)[c]			

[a] tw = this work. [b] Impure compounds. [c] ν_{OH} for hydrochloride salts.

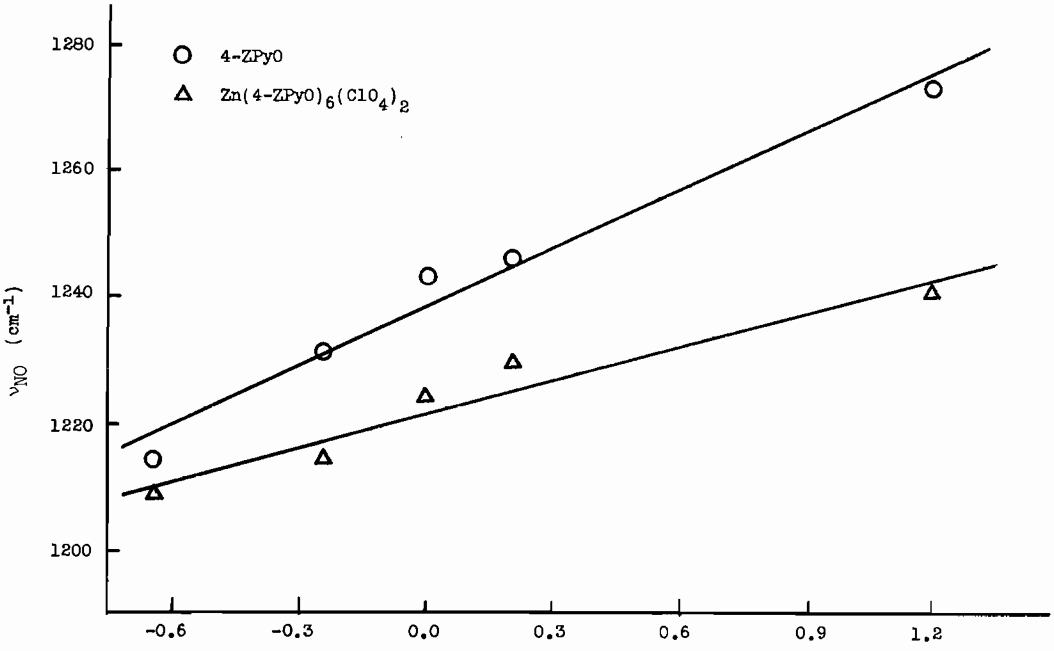

Figure 1. ν_{NO} for 4-ZPyO Ligands and $Zn(4\text{-}ZPyO)_6(ClO_4)_2$ Complexes *versus* σ_{PyO}.

The relatively large range of ν_{NO} values for the divalent cobalt, nickel, and zinc series have been previously explained on the basis of metal-to-ligand π-bonding[1,3,9,10] since these metal ions have essentially filled t_{2g} orbitals as a result of their d^7, d^8, and d^{10} electronic configurations, respectively. These results and explanations can be contrasted with those for the low d-electron cases such as chromium(III), vanadium(III), vanadium(IV), and titanium(IV) which have d^3, d^2, d^1, and d^0 electronic configurations, respectively. A ligand-to-metal π-bonding argument has been previously offered to account for these data due to the availability of essentially empty d-orbitals.[1,10,19,23] However, a comparison of the ν_{NO} range for the two high spin d^5 series shows a large range for manganese(II) and a compressed one for iron(III). It does not seem reasonable to invoke metal-to-ligand π-bonding for the manganese complexes and ligand-to-metal π-bonding for the iron complexes. This would clearly suggest the charge on the metal ion has a significant effect on the trends. It has also been suggested[10] that the various πbonding contributions have a strong influence on how much the *para*-substituent can affect the nature of the nitrogen–oxygen bond and several authors have commented on the "insensitive" substituent effect in the low d-electron cases.[10,19,23] However, it is important to note that just because the ν_{NO} values for a given series of complexes are nearly the same, it does not necessarily mean that the frequency is insensitive to the substituent. Each complex in a given series should not only be compared with the unsubstituted PyO complex, but also with the corresponding ligands since the ligands themselves show a marked substituent effect. Therefore, in contrast to the approach taken by other authors, it is suggested here that the decrease in ν_{NO} upon coordination, that is $\Delta\nu_{NO}$, be plotted *versus* the σ_{PyO} substituent constants such as shown in Figure 2 for the chromium(III) and nickel(II) complexes. While the $\Delta\nu_{NO}$ values are about the same for both CH_3O-derivatives, the values for the NO_2-derivatives are quite different, illustrating that from this point of view the nitrogen–oxygen frequency is more sensitive to substituent in the case of chromium than in the nickel case.

In order to obtain a measure of the sensitivity of ν_{NO} for the various complexes, a $\Delta\nu_{NO}$ versus σ_{PyO} plot was made for each series. The calculated slopes are reported in Table I. The divalent manganese, cobalt, nickel, and zinc complexes all have slopes of about 17 while the trivalent vanadium, chromium, and iron complexes exhibit slopes of about 30. Since the trivalent ions are generally strong Lewis acids due to their greater charge and smaller size, the larger slopes associated with the trivalent ions is not surprising. Since the nitrogen–oxygen bond in $4\text{-}CH_3OPyO$ has significant single bond character, its ν_{NO} value may be only slightly above an apparent lower limit of 1195–1200 cm^{-1} (see Table I) and therefore does not decrease much upon coordination. On the other hand, $4\text{-}NO_2PyO$ has predominately a nitrogen–oxygen double bond and the extent to which it decreases upon coordination should be much more dependent on the

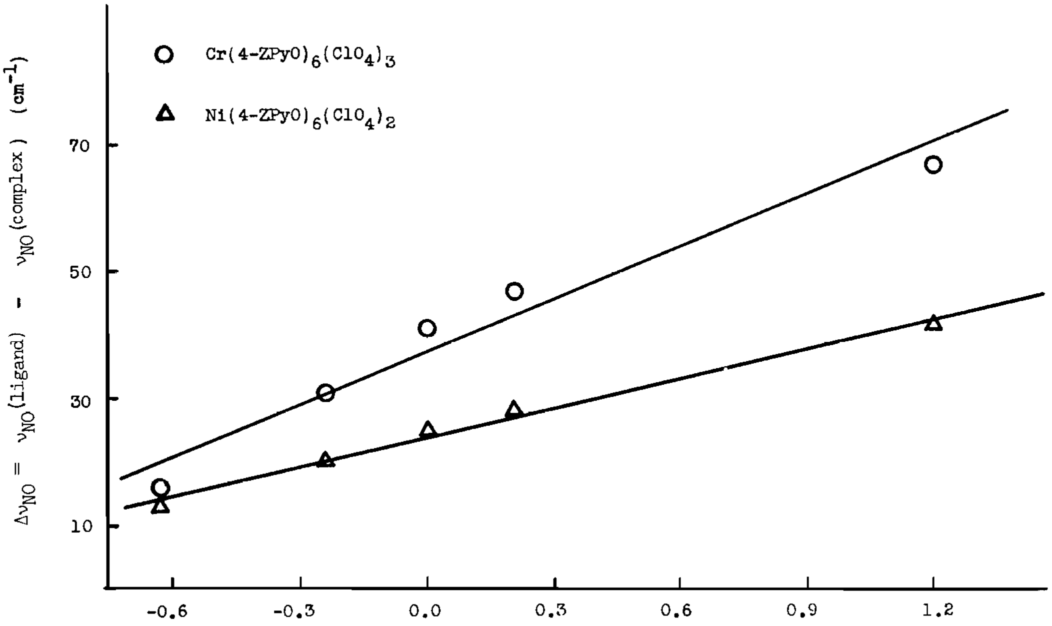

Figure 2. $\Delta\nu_{NO}$ *versus* σ_{PyO} for $Cr(4\text{-}ZPyO)_6(ClO_4)_3$ and $Ni(4\text{-}ZPyO)_6(ClO_4)_2$ Complexes.

strength of the Lewis acid to which it is coordinated. The difference in slopes again suggests the importance of the charge on the metal ion.

In an effort to further investigate the charge effects several other comparisons were made between ions of different valence but similar electronic configuration. One finds the data for the silver(I) complexes nearly identical with that of the zinc(II) complexes (both d^{10} ions) while the data for the lanthanum(III) and thorium(IV) complexes (both d^0 ions) are identical with one another but intermediate between those of the first row divalent and trivalent metal ions. The ν_{NO} for the lanthanum and thorium CH_3O-derivatives actually increases slightly upon coordination. In choosing these particular metal ions the variable of coordination number has been introduced. The first row metal ion complexes of PyO are six-coordinate,[1] those for lanthanum and thorium are eight-coordinate,[1, 24] and the silver is two-coordinate.[1] The fact that the lanthanum(III) data is intermediate relative to the other di- and trivalent ions suggests a reduced metal–ligand interaction that may be a result of a steric effect associated with eight-coordination. If so, the increased charge on the thorium is apparently not sufficient to overcome the effect of this steric interaction. The anticipated decrease in metal–ligand interaction due to the lower charge on the silver may be somewhat offset by the decreased steric hindrance of two-coordination. Data for the series of four-coordinate $Cu(4\text{-}ZPyO)_4(ClO_4)_2$ complexes show a slightly smaller ν_{NO} range and a slightly higher $\Delta\nu_{NO}$–σ_{PyO} slope than the other divalent first row ions. Furthermore both $\Delta\nu_{NO}$ and $\nu_{Cu\text{–}O}$ are larger for $Cu(PyO)_4^{2+}$ than for $Cu(PyO)_6^{2+}$ (35 cm^{-1} and 417, 385 cm^{-1} doublet versus 24 cm^{-1} and 366 cm^{-1}, respectively).[5] These data suggest a stronger metal–ligand interaction in the four-coordinate case. Although not all available data are consistent, it has been observed[12] that ν_{NO} for (unsubstituted) PyO complexes generally fall into two groups: around 1220 cm^{-1} for complexes where PyO is the only ligand in the first coordination sphere, and around 1205 cm^{-1} where PyO and another ligand (such as water, halide, nitrate) are in the first coordination sphere, again demonstrating a stereochemical dependence on ν_{NO}.

It is also of interest to compare the various $MX_4 \cdot 2L$ type complexes. Whereas the data for the SnF_4, $SnCl_4$, VF_4, VCl_4, and $TiCl_4$ adducts are all similar, data for the TiF_4 and ZrF_4 complexes are quite different. It is clear that the previously proposed ligand-to-metal π-bonding argument is not supported by the TiF_4 and ZrF_4 data, nor can the previously proposed metal-to-ligand π-bonding argument account for the SnF_4 and $SnCl_4$ data. These data, however, continue to demonstrate the importance of the effective charge on the central metal ion. It is likely that two opposing effects are operative in these complexes – the inductive effect of the halogens and the tendency of the halogen (especially fluorine) to participate in $p \rightarrow d$ π-bonding with the central metal ion. The former would tend to increase the effective charge on the central metal ion while the latter would decrease it. One would expect the positive charge on the central metal in TiF_4 and ZrF_4 to be decreased due to fluorine-to-metal π-bonding which in turn would decrease the metal–ligand interaction, giving a larger ν_{NO} range and a smaller $\Delta\nu_{NO}$–σ_{PyO} slope. Since tin(IV) is a d^{10} case, fluorine-to-tin π-bonding is unlikely due to the filled d-shell. Therefore SnF_4 should be more like $SnCl_4$ in Lewis acid strength and indeed the ν_{NO} ranges and the $\Delta\nu_{NO}$–σ_{PyO} slopes are comparable. Available data for the organo-tin(IV) and lead(IV) complexes are fairly consistent (see Table I) in that the ν_{NO} range tends to increase as the inductively withdrawing halogens are replaced by methyl groups. The $\Delta\nu_{NO}$–σ_{PyO} slopes are less meaningful since data are not available for the NO_2-derivatives for which the σ_{PyO} of 1.19 is much different that those for the other substituents (–0.603 to 0.206). The apparent inconsistency of the VF_4 data suggests that the presence of the lone d-electron of vanadium(IV) may be sufficient to reduce the tendency of fluorine to π-bond enough that the inductive effect beomes equally important. It is interesting that ν_{NO} data for all 4-ZPyO series of vanadium(IV) complexes are very much alike regardless of stoichiometry, stereochemistry, or anion.[10,19,23] The only consistent feature among these complexes is the oxidation state.

The hydrochloride salts of the 4-ZPyO ligands were prepared in order to study substituent effects on ν_{NO} and ν_{OH}. The broad ν_{OH} bands, found at considerably lower energy than typical O–H stretching frequencies, show a trend corresponding to a basicity effect. As thc strength of the base increases the O–H bond becomes stronger, giving a higher ν_{OH} frequency. No systematic trend is observed in the ν_{NO} or $\Delta\nu_{NO}$ values, making these salts one of the few series of 4-ZPyO compounds which do not show a correlation with σ_{PyO}.

Previous explanations for the ν_{NO} trends for 4-ZPyO complexes have centered on metal-to-ligand and ligand-to-metal π-bonding arguments, but have generally been based on data for only a few series of complexes. Although the π-bonding effects cannot be ruled out, it is believed that the more complete collection of data presented here and the approach of examining the changes that occur upon coordination clearly demonstrate that the effective charge of the central metal ion contributes significantly to the observed trends. It is difficult to separate the contributions of charge, stereochemistry, steric effects, and π-bonding since the ability of a given metal ion to participate in various types of π-bonding will certainly be related to its effective charge as well as its electronic configuration and hybridization, and on the closeness of approach of the ligands as governed by steric effects.

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