Effect of Changing Oxidation State on the Metal–Ligand Vibrations of $[Cr(2,2'\text{-bipyridyl})_3]^{n+}$ Type Complexes

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Summary In the series of tris-(2,2′-bipyridyl) complexes of chromium, the Cr–N stretching frequencies change very little by changing the oxidation state of chromium from III to 0, this unexpected result indicating that the strength of the Cr–N bond does not change appreciably over a wide change in the oxidation state of chromium.

PREVIOUS investigations on the change in metal–ligand stretching frequencies with changing oxidation state of the metal have been limited to a few cases. Clark[1] compared the metal–halogen stretching frequencies of several halogeno-complexes and noted that the frequency decreases markedly as the oxidation number is reduced by one.

In the case of tris-(2,2′-bipyridyl), tris(bipy), complexes of chromium, it is possible to prepare a series of complexes where the formal oxidation state of chromium is III, II, I, or

0.[2] No i.r. studies have yet been made on the effect of changing the oxidation state over such a wide range using a series of complexes of the same symmetry (D_3). It was, therefore, of interest to carry out a detailed i.r. study on this series.

We have prepared [Cr(bipy)$_3$](ClO$_4$)$_3$, [Cr(bipy)$_3$](ClO$_4$)$_2$, [Cr(bipy)$_3$](ClO$_4$), and Cr(bipy)$_3$ according to the methods described by Herzog and his co-workers,[2] and their i.r. spectra have been compared in the far-i.r. region where the Cr–N stretching vibrations appear. In order to assign the Cr–N stretching modes, we have prepared ^{50}Cr(bipy)$_3$ and ^{53}Cr(bipy)$_3$ on a milligram scale,[3] and observed the isotopic shifts shown in Table 1. From these results, it is reasonable to assign two isotope-sensitive bands at 385·0 and 312·0 cm^{-1} of the ^{50}Cr complex to the Cr^0–N stretching modes.

TABLE 1. *Far-i.r. spectra and isotopic shifts of* ^{50}Cr(bipy)$_3$ *and* ^{53}Cr(bipy)$_3$ *(cm^{-1})*

ν (^{50}Cr)	$\tilde{\nu}$ (^{53}Cr)	$\tilde{\nu}$ (^{50}Cr) − $\tilde{\nu}$ (^{53}Cr)
616·5w	616·8	−0·3
597·0s	597·3	−0·3
477·0s	476·5	0·5
411·6m	411·8	−0·2
385·0m	381·5	3·5
357vw	357	0
312·0s	306·5	5·5

A similar experiment has also been carried out on a pair of [^{50}Cr(bipy)$_3$](ClO$_4$)$_2$ and its $^{\mathrm{NA}}$Cr analogue [$^{\mathrm{NA}}$Cr(natural abundance) contains *ca.* 84% of ^{52}Cr and small amounts of ^{53}Cr, ^{50}Cr, and ^{54}Cr]. In this case, two bands at 355·0 and 347·0 cm^{-1} of [^{50}Cr(bipy)$_3$](ClO$_4$)$_2$ were shifted to lower frequencies by *ca.* 4 cm^{-1} when ^{50}Cr was substituted by $^{\mathrm{NA}}$Cr. Therefore, these two bands must be assigned to the Cr$^{\mathrm{II}}$–N stretching modes. Since the spectra of the Cr$^{\mathrm{III}}$ and Cr$^{\mathrm{I}}$ complexes are similar to that of the Cr^0 complex, the Cr–N stretching bands of these complexes can be assigned without metal isotope data. Table 2 lists the Cr–N stretching frequencies of all the complexes studied in this work. Tris(bipy) complexes of other metals exhibit a ligand vibration near 355 cm^{-1}.[4] In view of these results, our previous assignments on Cr(bipy)$_3$ must be revised.[5]

According to the present results, the Cr–N stretching frequencies of all four tris(bipy) complexes are at 385—350 and 350—308 cm^{-1} regardless of the formal oxidation state of the central metal. Since the symmetry of the complex is the same for the whole series, this result indicates that the strength of the Cr–N bond does not change appreciably in this series. In general, the ligand–metal σ-bonding becomes weaker and the metal–ligand π-bonding (back bonding) becomes stronger as the oxidation state of the metal becomes lower. It is, therefore, not unreasonable to expect that the total contribution from both types is similar in the whole oxidation state series. This suggests that an increasing amount of electron density would reside on ligand orbitals in the Cr^0 and Cr$^{\mathrm{I}}$ complexes. If that is the case, the electron density around the chromium atom is similar throughout the series, and the use of formal oxidation states is unrealistic and misleading in these cases.

TABLE 2. *Far-i.r. spectra of the* [Cr(bipy)$_3$]$^{n+}$ *series in the* 400—300 cm^{-1} *region (cm^{-1})*

[Cr(bipy)$_3$]$^{3+}$	[Cr(bipy)$_3$]$^{2+}$	[Cr(bipy)$_3$]$^{+}$	[Cr(bipy)$_3$]^{0}	Assignment
385s	351s	371s	383m	Cr–N stretch
(hidden)	359s	352w	357w	ligand vib.
349s	343s	343s	308s	Cr–N stretch

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