Sigma-Bond-to-Ligand Charge Transfer Transitions and Excited States of d6 Metal-Diimine Complexes.

van Slageren, J.

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CHAPTER

Influence of the Metal–Ligand Interaction and the Character of the Electronic Transitions on the Resonance Raman Spectra of $d^6$ Metal–Diimine Complexes

Chapter 8. Influences on the Resonance Raman Spectra of \(d^6\) Metal-Diimine Complexes

8.1 Abstract

This chapter presents the results of a resonance Raman (rR) study of \(d^6\) transition metal α-diimine complexes. The α-diimine ligand employed is \(N,N'\)-diisopropyl-1,4-diaza-1,3-butadiene (iPr-DAB) which has a relatively simple structure and hence few vibrations. This makes assignment of the vibrational spectra of complexes of this ligand easier. It is shown that with the help of DFT calculations the bands observed in the rR spectra, obtained by irradiation into the lowest-energy absorption band, can be assigned unambiguously. Comparison of the spectra show how factors such as metal–ligand interaction and electronic transition character affect the rR spectra and enables one to assess how rR spectra can be used to characterize electronic transitions.

8.2 Introduction

Most of the early experimental data on molecular vibrations were provided by Raman spectroscopy, but the development and use of this technique stagnated when commercial infrared spectrometers became available in the 1940s. The discovery of the laser as a powerful monochromatic light source and the development of sensitive detectors in the 1960s initiated the renaissance of Raman spectroscopy. In addition, contrary to the light sources used earlier, lasers and dye-lasers made the recording of so-called resonance Raman (rR) spectra viable.\(^1\)\(^\text{-6}\) Such rR spectra show enhancement of intensity of some Raman bands when the frequency of the exciting light approaches that of a strongly allowed electronic transition. If, as is usually the case, the ground state is totally symmetric, only bands due to totally symmetric vibrations are resonantly enhanced. Additionally, the intensity of a rR band belonging to a certain vibration depends on the relative displacement of the potential energy curve of the excited state with respect to that of the ground state along the normal coordinate of that vibration. In other words, the intensities are highest for those vibrations, which are most strongly coupled to that particular electronic transition. Although absorption bands of molecules contain information about all the displaced normal modes, they normally show up as an unresolved envelope in condensed media when many modes are displaced. In contrast, rR 'excitation profiles' (EP), which represent the rR intensity of a specific vibration as a function of the
Chapter 8. Influences on the Resonance Raman Spectra of d^6 Metal–Diimine Complexes

The wavelength of excitation, provide instead information about the displacement of individual modes. EPs of many inorganic complexes were successfully analysed by Zink and others in terms of excited state distortions with the time-dependent theory of Lee, Tannor and Heller. Thus, rR spectra do not only provide the vibrational frequencies of a molecule in its ground state but also characterize its allowed electronic transitions by giving valuable information about the involvement of individual vibrations in these transitions.

For many years we have applied the rR technique to assign and characterize the low-energy electronic transitions of low-valent transition metal α-diimine complexes. The main aim of these studies was to determine the changes in structure caused by the electronic transitions and to relate these changes to the photochemical and photophysical behaviour of the complexes. However, most rR bands could only be assigned qualitatively, since a complete vibrational analysis of the complexes was too complicated at the time. Partly due to increasing computer processor speeds, quantum chemical calculations have recently improved to such an extent that they can now provide unambiguous assignments of vibrational spectra even for complicated systems.

In view of this development and in order to obtain comparative rR data of a series of d^6 metal α-diimine complexes differing in their ground- and/or excited state bonding properties, we recorded the rR spectra of these complexes under the same conditions. All complexes under study (Figure 8.1) contain the same α-diimine ligand iPr–DAB (N,N-diisopropyl-1,4-diaza-1,3-butadiene). This ligand was chosen since due to its simple structure it has relatively few vibrations. At the same time, DFT B3LYP calculations were performed on the free ligand and several (model) complexes.

This chapter shows that by thorough comparison of the rR spectra of these complexes in combination with the results of the DFT calculations, most rR bands can be assigned.
Furthermore, the influences of electronic transition character, and metal–ligand interaction on the rR spectra can be separated and understood.

8.3 Experimental Section

Materials. Triphenylphosphine (PPh₃, Aldrich), [W(CO)₆] (Strem), neutral alumina (Fluka) and AgNO₃ (Aldrich) were used as received. Solvents purchased from Acros (dichloromethane, pentane, tetrahydrofuran, toluene), were dried on and distilled from the appropriate drying agent.

Syntheses. All syntheses were performed under a nitrogen atmosphere using standard Schlenk techniques. N,N’-diisopropyl-1,4-diaza-1,3-butadiene (iPr-DAB),[17] [Ru(Cl)(R)(CO)₂(iPr-DAB)],[13,15,18] [Ru(R)(SnPh₃)(CO)₂(iPr-DAB)],[19] [Pt(R)₄(iPr-DAB)] (R = CH₃, CD₃)[20,21] [M(SnPh₃)₂(CO)(iPr-DAB)] (M = Ru, Os)[19,22] [Pt(SnPh₃)₂(CH₃)₂(iPr-DAB)][21] [Ru(RuCp(CO)₂)₂(CO)(iPr-DAB)] were synthesized according to published procedures.

[Re(PPh₃)(CO)₅(iPr–DAB)](NO₃) was prepared by stirring [Re(Br)(CO)₅(iPr–DAB)] with one equivalent of AgNO₃ and an excess of PPh₃ in CH₂Cl₂. Filtration, evaporation of the solvent and washing with pentane afforded the pure product in near quantitative yield. IR (THF); ν(CO): 2027, 1927, 1908 cm⁻¹. ¹H NMR (CDCl₃); δ: 1.50 (d, J = 6.6 Hz, 12H, CH(C₃H₃)₂), 4.22, (septet, J = 6.6 Hz, 2H, CH(C₃H₃)₂), 8.61 (s, 2H, imine H) ppm.

[W(CO)₆(iPr–DAB)] was prepared by refluxing [W(CO)₆] and 1.1 equivalent of iPr-DAB overnight in toluene. Flash column chromatography over neutral alumina yielded a mixture of product and starting compound, the latter of which was removed by sublimation (30 °C) in vacuo. IR (CH₂Cl₂); ν(CO): 2013, 1909, 1843 cm⁻¹. ¹H NMR (CDCl₃); δ: 1.56 (d, J = 6.6 Hz, 12H, CH(CH₃)₂), 4.29, (septet, J = 6.6 Hz, 2H, CH(CH₃)₂), 8.59 (s, 2H, imine H) ppm.

Spectroscopic Measurements. Resonance Raman spectra of the complexes dispersed in KNO₃ pellets were recorded on a Dilor XY spectrometer equipped with a Wright Instruments CCD detector, using Spectra Physics 2040E Ar⁺ laser in combination with Coherent CR490 and CR590 dye lasers (with Coumarin 6 and Rhodamine 6G dyes) as excitation sources under a 180° backscattering geometry. The pellet was spun in order to minimize thermal and photochemical decomposition. Data acquisition was controlled by Dilor Labspec 2.08 software. The spectra were calibrated using the Raman bands due to the symmetrical stretching and in plane bending vibrations of NO₃⁻ (at 1051 and 716 cm⁻¹, respectively) and corrected for baseline deviations using Grams software.

Computational Details. The ground state electronic structures were calculated by density functional theory (DFT) methods using the ADF1999[25,26] and Gaussian 98[27] program packages. Gaussian 98[27] was used for the calculations of the vibrations.
Within Gaussian 98, Dunning's polarized valence double $\zeta$ basis sets were used for C, N, O, Cl and H atoms and the quasirelativistic effective core pseudopotentials and corresponding optimized set of basis functions for W, Ru, Os, Pt and Sn. In these calculations, the hybrid Becke's three parameter functional with the Lee, Yang and Parr correlation functional (B3LYP) were used.

Within the ADF program, Slater type orbital (STO) basis sets of triple $\zeta$ quality with 3d polarization functions for C and additional p functions for metals were employed. The inner shells were represented by a frozen core approximation, viz. 1s for C, N, O, 1s–2p for Cl, 1s–3d for Ru, 1s–4d for Os, 1s–4f for Pt and 1s–4p for Sn were kept frozen. The following density functionals were used within ADF: a local density approximation (LDA) with VWN parametrization of electron gas data or a functional including Becke's gradient correction to the local exchange expression in conjunction with Perdew's gradient correction to the LDA expression (BP). The scalar relativistic (SR) zero order regular approximation (ZORA) was used within this study.

The calculations on iPr-DAB, [W(CO)$_4$(Me-DAB)], [Pt(CH$_3$)$_4$(Me-DAB)], [Pt(CD$_3$)$_4$(Me-DAB)], [Pt(SnH$_3$)$_2$(CH$_3$)$_2$(Me-DAB)], [Ru(SnH$_3$)$_2$(CO)$_2$(iPr-DAB)], [Ru(SnH$_3$)$_2$(CO)$_2$(Me-DAB)] and [Os(SnH$_3$)$_2$(CO)$_2$(Me-DAB)] were performed in constrained $C_2v$ symmetry, with the z-axis coincident with the $C_2$ symmetry axis. The R-DAB ligand and the C atoms of the equatorial CO/CH$_3$/CD$_3$-groups are located in the yz-plane and the SnH$_3$/CH$_3$/CD$_3$-axial ligands lie on the x-axis. Calculations on [Ru(Cl)(CH$_3$/CD$_3$/CO)$_2$(Me-DAB)] and [Ru(CH$_3$)(SnMe$_3$)(CO)$_2$(Me-DAB)] were performed in constrained $C_4$ symmetry, with the z-axis bisecting the DAB ligand as above.

8.4 Results and Discussion

In this section the Raman spectrum of the free iPr-DAB ligand and the rR spectra of several of its complexes are presented, assigned and discussed. The assignments of the rR bands are based on comparisons with literature data, and on the results of DFT calculations. Firstly, the Raman spectrum of free iPr-DAB is presented and assigned. The complexes to be discussed thereafter were selected as follows: [Re(PPh$_3$)(CO)$_3$(iPr-DAB)]$^+$ and [W(CO)$_4$(iPr-DAB)] are both characterized by MLCT transitions in the visible region, but the metal–$\alpha$-diimine interaction is stronger for the W(0) than the Re(I) complex. The effect of this difference in interaction on the rR spectra is the subject of the second part of this section. The third part is concerned with the complexes [Re(CH$_3$)(CO)$_3$(iPr-DAB)], [Ru(Cl)(R)(CO)$_2$(iPr-DAB)], [Ru(R)(SnPh$_3$)(CO)$_2$(iPr-DAB)] and [Pt(R)$_4$(iPr-DAB)] (R = CH$_3$, CD$_3$) and deals with the influence of the introduction of methyl co-ligands on the rR spectra and character of
the CT transition. Finally, the fourth part of this section contains the rR spectra of the di- and trinuclear metal–metal bonded complexes [Ru(Cl)(SnPh₃)(CO)₂(iPr-DAB)], [Re{Re(CO)₅}(CO)iPr–DAB)], [Pt(SnPh₃)₂(CH₃)₂(iPr–DAB)], [M(SnPh₃)₂(CO)iPr–DAB)] (M = Ru, Os) and [Ru{RuCp(CO)₂}₂(CO)iPr–DAB)]. In the subsequent conclusions section, the principal factors (π-backbonding, orbital delocalization and electronic transition character) that influence the rR spectra are discussed. Table 8.1 lists the main resonance enhanced rR bands of all complexes under study.

![Figure 8.2](image)

**Figure 8.2** The Raman spectrum of iPr-DAB in CH₂Cl₂, \( \lambda_{exc} = 514.5 \text{ nm} \). Asterisks denote solvent bands.

(1) **The ligand N,N'-diisopropyl-1,4-diaza-1,3-butadiene (iPr–DAB).**

The Raman spectrum of iPr–DAB was obtained by excitation at 514.5 nm of the freshly sublimed free ligand in CH₂Cl₂ solution, rather than dispersed in a KNO₃ pellet, in order to prevent sublimation by the laser beam. Figure 8.2 displays the resulting Raman spectrum, with solvent bands denoted with asterisks (*). To assist the assignment, the vibrations of this ligand were calculated in constrained s-cis geometry. The main band is observed at 1636 cm⁻¹ and is attributed to the symmetrical stretching vibration of the CN bonds, \( \nu_s(CN) \). It is calculated about 3% too high (1693 cm⁻¹), but such a difference between calculated and observed frequencies is quite normal for DFT calculations with B3LYP functionals and double \( \xi \) basis sets.³³ A number of weaker bands are found, but these are not readily assigned with the help of the calculations.
### Table 8.1 Main bands in the rR spectra of several iPr-DAB complexes. Assignments include major contributions only, for details see text. Calculated values\(^a\) are between brackets.

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<th>Compound</th>
<th>(v_v(CO))</th>
<th>(v_v(CN))</th>
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<th>(\delta(Me))</th>
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<th>(\delta(MCO))</th>
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<td>(1176)</td>
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<td>(830)</td>
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<td>(427)</td>
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<td>(641)</td>
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<td>(480)</td>
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<td>958</td>
<td>832</td>
<td>606</td>
<td>405</td>
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</table>

\(^a\) iPr-DAB was simplified to Me-DAB, and SnPh\(_3\) was replaced by SnH\(_3\); \(^b\)[W(CO)\(_4\)(iPr-DAB)]; \(^c\)[Ru(SnH\(_3\))\(_2\)(CO\(_2\))(iPr-DAB)]
(2) The influence of metal–ligand interaction

The iPr–DAB ligand has a low-lying π* orbital, while low-valent transition metal atoms have relatively high-lying filled metal d orbitals. Because of this, the complexes formed between such a metal and a chelating iPr–DAB ligand possess low-energy Metal-to-Ligand Charge Transfer (MLCT) transitions. Such an MLCT transition affects the bonds and vibrations of iPr–DAB and to a lesser extent those of the co-ligands. Which vibrations are influenced by an MLCT transition depends on the strength of the metal–ligand interaction as will be shown by the rR spectra of two representative complexes.

![Graph showing RR spectra](image)

**Figure 8.3** RR spectra of [Re(PPh₃)(CO)₃(iPr–DAB)]⁺ (top, λₑₓc = 457.9 nm) and [W(CO)₄(iPr–DAB)]⁻ (bottom, λₑₓc = 514.5 nm) in KNO₃. Asterisks denote NO₃⁻ bands.

[Re(PPh₃)(CO)₃(iPr–DAB)]⁺. As the first example of a complex with a lowest MLCT transition [Re(PPh₃)(CO)₃(iPr–DAB)]⁺ was selected rather than the well known complex [Re(Cl)(CO)₃(iPr–DAB)]. In the latter complex the chloride ligand orbitals participate in the highest filled orbitals, causing a deviation of the lowest-energy electronic transition from pure MLCT character. This is evidenced by the observation of ν(Re–Cl) in the rR spectrum of this complex.¹² ³ The rR spectrum of [Re(PPh₃)(CO)₃(iPr–DAB)]⁺, obtained by excitation into its lowest-energy absorption band, only shows two resonantly enhanced Raman bands (Figure
8.3). The stronger one of these is found at 1557 cm\(^{-1}\) and is attributed to \(v_4(CN)\). It is ca. 80 cm\(^{-1}\) lower in frequency than observed for the free ligand, due to \(d_g(Re)\rightarrow\pi^*\text{(iPr-DAB)}\) \(\pi\)-backbonding. This \(\pi^*\) orbital is antibonding with respect to the CN bonds, which explains the lowering of frequency of \(v_4(CN)\) in the ground state of the complex compared to the free ligand. The MLCT transition increases the electron density in the \(\pi^*\text{(iPr-DAB)}\) orbital even more. Hence, this transition affects the CN stretching vibration, leading to resonance enhancement of the Raman intensity for this vibration in the \(rR\) spectrum. The other resonantl \(y\) enhanced band at 2025 cm\(^{-1}\) belongs to the in-phase symmetric vibration \(v_5(CO)\) of the three carbonyls.\(^{35}\) During the electronic transition the metal atom is oxidized, which decreases the metal–CO \(\pi\)-backbonding and leads to resonance enhancement of the CO stretching vibration.

\(\text{[W(CO)}_4\text{(iPr-DAB)}\)]. Going from Re(I) to W(0) the metal d orbital energy is raised, causing an increase of the metal\(\rightarrow\text{Me}\) iPr–DAB \(\pi\)-backbonding. In the \(rR\) spectrum (Figure 8.3) this is manifested by a lowering of frequency for \(v_4(CN)\) from 1557 to 1499 cm\(^{-1}\). The calculated value is 1531 cm\(^{-1}\) for \(\text{[W(CO)}_4\text{(iPr-DAB)}\]). Since the metal atom is oxidized during the electronic transition, the in-phase symmetric mode of the carbonyls,\(^{36}\) \(v_4(CO)\), is again resonantly enhanced and observed at 2017 cm\(^{-1}\) (calculated at 2089 cm\(^{-1}\)). However, a number of extra Raman bands are observed for \(\text{[W(CO)}_4\text{(iPr-DAB)}\]) (at 1147, 931, 847, 624, 480, 432 and 222 cm\(^{-1}\)), which are not present in the spectrum of the Re complex. With the aid of the DFT vibrational calculations these can be assigned. The band at 1147 cm\(^{-1}\) was observed at 1150 cm\(^{-1}\) for \(\text{[Mo(CO)}_4\text{(iPr-DAB)}\]),\(^{37}\) and found to shift on \(^{15}\text{N}\) isotope substitution.\(^{38}\) It is assigned to a vibration which has combined \(\delta_4(CH)\) and \(v_4(CN)\) character. The former component is an in-plane symmetric motion of the two imine hydrogen atoms. The frequency of this vibration is very sensitive to the nature of the substituent on the N atoms of the diazabutadiene backbone, which was proven by vibrational calculations on \(\text{[W(CO)}_4\text{(R-DAB)}\]) (R = Me, iPr) (\textit{vide infra}). For R = Me, \(\delta_4(CH)\) is calculated at 1409 cm\(^{-1}\), while the calculated value for R = iPr (1176 cm\(^{-1}\)) is much closer to the observed one (1147 cm\(^{-1}\)). The bands found at 931 and 847 cm\(^{-1}\) (calculated at 960 cm\(^{-1}\) and 830 cm\(^{-1}\) for \(\text{[W(CO)}_4\text{(iPr-DAB)}\])) are assigned to in-plane deformation modes of the ligand. For \(\text{[W(CO)}_4\text{(Me-DAB)}\]) these deformation vibrations are not correctly calculated. Similar results were obtained for the calculations for other Me–DAB model complexes. The band found at 623 cm\(^{-1}\) (calculated at 616 cm\(^{-1}\)) is due to a \(\delta_4(WCO)\) mode, while the ones observed at 480 and 431 cm\(^{-1}\) (calculated at 449 and 427 cm\(^{-1}\), respectively) belong to combined \(v_5(WC)\) and
\(v_7(\text{WN})\) modes. Additionally, the band at 222 cm\(^{-1}\) has been attributed to \(v_7(\text{WN})\) on the basis of isotope labelling studies,\(^{38}\) and is calculated at 227 cm\(^{-1}\). The occurrence of these extra rR bands is caused by the increase of interaction between the metal d\(_{n}\) and ligand \(\pi^*\) orbitals in both the HOMO and LUMO going from the Re to the W complex, leading to delocalization of these orbitals. As a result the electronic transition has less charge transfer character and obtains partial metal–ligand bonding to anti-bonding character. As such a transition causes a weakening of the metal–nitrogen bonds and distortion of the iPr–DAB ligand, it invokes rR effects for deformation modes of iPr–DAB and for \(v_8(\text{W–N})\).\(^{37}\) This \(d_x\pi^*\) interaction can be further enhanced by increasing the metal d-orbital energy (e.g. in \([\text{Ni(CO)}_2(\text{tBu–DAB})]\)),\(^{39}\) or by decreasing the \(\pi^*(\alpha\text{-diimine})\) orbital energy (e.g. in \([\text{W(CO)}_4(\text{R–DAB})]\) (R = pTol, Mes)).\(^{37}\) The rR spectra of these complexes show much higher intensities for the ligand deformation modes below 1000 cm\(^{-1}\) while at the same time both \(v_7(\text{CO})\) and \(v_8(\text{CN})\) have become much weaker. In extreme cases, \(v_7(\text{CO})\) and \(v_8(\text{CN})\) virtually disappear.

So far, the co-ligands were not directly involved in the HOMO→LUMO transition. However, this situation changes if a co-ligand is introduced with high-lying filled orbitals which contribute to the HOMO. For instance, in the case of the halide (X) complexes \([\text{Re(X)(CO)}_3(\alpha\text{-diimine})]\) a \(\pi_n(X)\) orbital contributes to the HOMO, causing a change of character of the low-energy transition from Metal-to-Ligand Charge Transfer into Halide-to-Ligand Charge Transfer going from \(X = \text{Cl}^-\) to \(X = \Gamma\).\(^{12}\) Another ligand with a high-lying orbital is the methyl ligand. The influence of the introduction of this ligand in d\(^6\) metal–diimine complexes on the rR spectra is discussed in the next section.

(3) The influence of methyl ligands

\([\text{Re(CH}_3\text{)(CO)}_3(\text{iPr–DAB})]\).\(^{40}\) Due to the electron donating character of the methyl group, the lowest-energy MLCT transition is shifted to longer wavelength with respect to that of \([\text{Re(PPh}_3\text{)(CO)}_3(\text{iPr–DAB})]\).\(^1\). Although, UV-photoelectron spectroscopic studies showed that the \(\sigma(\text{Re–CH}_3)\) orbital itself lies at only slightly lower energy than the metal d-orbitals,\(^{40}\) the rR spectra show only a small influence of the \(\text{CH}_3\) group. Thus, similarly to \([\text{Re(PPh}_3\text{(CO)}_3(\text{iPr–DAB})]\), \(v_7(\text{CO})\) (at 1988 cm\(^{-1}\)) and \(v_8(\text{CN})\) (at 1511 cm\(^{-1}\)) are observed. The shifts of these vibrations to lower frequency compared to the PPh\(_3\) complex are again in correspondence with the higher electron density on the metal, leading to an increase of both metal→CO and metal→diimine \(\pi\)-backbonding. A weak band at 1156 cm\(^{-1}\) is the first evidence that the \(\text{CH}_3\) ligand participates in the electronic transition. Since for the
corresponding complexes $\text{[Re}(R)(\text{CO})_3(\text{dmb})] \ (R = \text{CH}_3, \ \text{CD}_3; \ \text{dmb} = 4,4'$-dimethyl-2,2'$-bipyridine$)$ this vibration was found to shift from 1166 to 898 cm$^{-1}$ going from the CH$_3$ to the CD$_3$ complex$^{16}$ it is assigned to the symmetrical CH$_3$ deformation vibration, $\delta$(CH$_3$). A similar vibration was found for $\text{[Re}(\text{CH}_3)(\text{CO})_3]$$^{41}$ The weak band at 732 cm$^{-1}$ is assigned to the corresponding rocking mode of the CH$_3$ group, $\rho$(CH$_3$). Further bands are observed at 503, 488 and 451 cm$^{-1}$, all of which are very weak and belong to metal–ligand stretching and deformation modes, probably similar to the ones found for $\text{[W}(\text{CO})_4(i\text{Pr-DAB})]$. In conclusion, the rR spectra of $\text{[Re}(\text{CH}_3)(\text{CO})_3(i\text{Pr-DAB})]$ are very similar to those of $\text{[Re}(\text{PPh}_3)(\text{CO})_3(i\text{Pr-DAB})]^+$, and the methyl ligand of the former complex is only weakly involved in the charge transfer transition.

![Figure 8.4](image.png)

**Figure 8.4** Raman spectra of (A) $\text{[Ru}(\text{Cl})(\text{CH}_3)(\text{CO})_2(i\text{Pr-DAB})] \ (\lambda_{\text{exc}} = 457.9 \ \text{nm})$, (B) $\text{[Ru}(\text{CH}_3)(\text{SnPh}_3)(\text{CO})_2(i\text{Pr-DAB})] \ (\lambda_{\text{exc}} = 488.0 \ \text{nm})$, (C) $\text{[Pt}(\text{CH}_3)_4(i\text{Pr-DAB})] \ (\lambda_{\text{exc}} = 591.0 \ \text{nm})$ and (D) $\text{[Pt}(\text{CD}_3)_4(i\text{Pr-DAB})] \ (\lambda_{\text{exc}} = 545.0 \ \text{nm})$ in KNO$_3$. Asterisks denote NO$_3^-$ bands.

$\text{[Ru}(\text{Cl})(\text{R})(\text{CO})_2(i\text{Pr-DAB})] \ (R = \text{CH}_3, \ \text{CD}_3)$.$^{13}$ Raman spectra were recorded for the complexes $\text{[Ru}(\text{Cl})(\text{R})(\text{CO})_2(i\text{Pr-DAB})] \ (R = \text{CH}_3, \ \text{CD}_3)$ (Figure 8.4) and DFT vibrational calculations were performed on the model complexes $\text{[Ru}(\text{Cl})(\text{R})(\text{CO})_2(\text{Me-DAB})] \ (R = \text{CH}_3, \ \text{CD}_3)$. The rR spectra of $\text{[Ru}(\text{Cl})(\text{R})(\text{CO})_2(i\text{Pr-DAB})] \ (R = \text{CH}_3, \ \text{CD}_3)$ are very similar to
those of the Re–methyl complex discussed above. Thus, \( \nu_s(\text{CO}) \) is observed at 2016 cm\(^{-1} \) (calculated at 2110 cm\(^{-1} \) for the model complex). Furthermore, \( \nu_s(\text{CN}) \) is observed at 1573 cm\(^{-1} \) (calculated at 1626 cm\(^{-1} \)). In addition, a weak band is observed at 1209 cm\(^{-1} \) (calculated at 1269 cm\(^{-1} \)) which shifts to 924 cm\(^{-1} \) (calculated at 962 cm\(^{-1} \)) on deuteration of the methyl group. Again this band is attributed to \( \delta(\text{CH}_3/\text{CD}_3) \). A strongly enhanced band is observed at ca. 490 cm\(^{-1} \) for both the \( \text{CH}_3 \) and \( \text{CD}_3 \) complex. For the \([\text{Ru}(\text{I})(\text{R})(\text{CO})_2(i\text{Pr-DAB})]\) complexes, this band was assigned to \( \nu_s(\text{Ru–CO}) \) and not to \( \nu(\text{Ru–CH}_3) \), in view of the lack of shift on deuteration.\(^{15} \) The present calculations show that this normal mode (calculated at 500 cm\(^{-1} \), observed at 492 cm\(^{-1} \)) has \( \nu_s(\text{Ru–N}) \) and \( \nu_s(\text{Ru–CO}) \) character with a \( \nu(\text{Ru–CH}_3) \) contribution for the \( \text{CH}_3 \) complex. According to the calculations, \( \nu(\text{Ru–CD}_3) \) does not contribute to this normal mode (calculated at 496 cm\(^{-1} \), observed at 490 cm\(^{-1} \)) in the \( \text{CD}_3 \) complex.

\([\text{Ru(SnPh}_3)(\text{R})(\text{CO})_2(i\text{Pr-DAB})]\) (\( \text{R} = \text{CH}_3, \text{CD}_3 \)).\(^{19} \) Replacement of Cl\(^- \) by an SnPh\(_3\) ligand drastically changes the electronic structure of these complexes. The methyl and SnPh\(_3\) ligands are in axial positions and the HOMO consists of the antisymmetric combination of their lone pairs with a small contribution of a \( \pi(\text{Ru}) \) orbital.\(^{14} \) This \( \sigma(\text{Sn–Ru–Me}) \) orbital has the same symmetry as the \( \pi^*(i\text{Pr-DAB}) \) orbital. The main difference with the preceding complexes is that instead of \( d_\pi(\text{Ru}) \), \( \sigma(\text{Sn–Ru–Me}) \) is responsible for the \( \pi \)-backbonding to \( i\text{Pr–DAB} \) in the HOMO and that the charge transfer transition to this ligand originates from this orbital. This transition is called a \( \sigma \rightarrow \pi^* \) or Sigma-Bond-to-Ligand Charge Transfer (SBLCT) transition. As is shown hereinafter, the rR spectra of these and other metal–methyl complexes with a lowest SBLCT state are different from those discussed before. For the assignment of the rR bands of this complex (Figure 8.4), the DFT calculated vibrations of the model complex \([\text{Ru(\text{CH}_3)(SnMe}_3)(\text{CO})_2(\text{Me-DAB})]\) are used.

The first striking observation is the absence of an rR effect for \( \nu(\text{CO}) \), which implies that the electron density on the central metal atom is hardly affected by the SBLCT transition. This may be due to the fact that the central metal atom is hardly involved in this transition, or because the transition has little charge transfer character due to a strong \( \sigma \rightarrow \pi^* \) interaction, comparable with the \( d_\pi \rightarrow \pi^* \) interaction in the complexes \([\text{Ni(CO)}_2(t\text{Bu-DAB})]\) and \([\text{W(CO)}_4(\text{R–DAB})]\) (\( \text{R} = \text{pTol, Mes} \)) (\text{vide supra}). Probably, both effects are of importance here. The DFT calculations show that the \( \pi(\text{Ru}) \) orbital contributes merely ca. 12% to the HOMO and LUMO of the model complex \([\text{Ru(SnH}_3)(\text{CH}_3)(\text{CO})_2(\text{H–DAB})]\).\(^{14} \) On the other hand, the small solvatochromic shift of the SBLCT transition\(^{19} \) points to a strong \( \sigma \rightarrow \pi^* \)
interaction in ground and excited states. The low frequency of $v_s$(CN) (observed at 1491 cm$^{-1}$, calculated at 1543 cm$^{-1}$) is due to a strong $\pi$-backbonding to iPr-DAB. At 1156 cm$^{-1}$, $\delta$(CH$_3$) is found, shifting to 884 cm$^{-1}$ on deuteration. This vibration is strongly resonance enhanced for this complex since the SBLCT transition lowers the electron density in the $\sigma$(SnPh$_3$–Ru–CH$_3$) orbital, causing a change of the methyl bonds and angles and accordingly a rR effect for $\delta$(CH$_3$). In the case of [Ru(Cl)(CH$_3$)(CO)$_2$(iPr–DAB)] the rR effect of $\delta$(CH$_3$) is weaker, since the methyl ligand of this complex has only a minor contribution to the HOMO and the lowest MLCT transition. The low frequency of $v_s$(CN) and the appearance of $\delta$(DAB) deformation vibrations at 950 and 836 cm$^{-1}$ point again to a strong delocalization of HOMO and LUMO, just as in the case of [W(CO)$_4$(iPr–DAB)] (vide supra). In addition, however, a new (weak) band shows up at 1296 cm$^{-1}$. According to the calculations, it mainly consists of a symmetric in-plane movement of the imine hydrogen atoms, coupled to a symmetric CN stretching vibration, and is therefore denoted as $\delta$(CH), like in the case of [W(CO)$_4$(iPr–DAB)].

![Figure 8.5 Pictorial representation of the $\delta$(CH) vibration.](image)

Figure 8.5 shows a pictorial representation of this vibration. It was shown in the case of [W(CO)$_4$(iPr–DAB)] (vide supra) that the large difference between the observed (1296 cm$^{-1}$) and the calculated value (1407 cm$^{-1}$) is due to the sensitivity of the frequency of this vibration to the nature of R in the R–DAB ligand. Further bands are observed at 610 and 241 cm$^{-1}$ (calculated 618 and 239 cm$^{-1}$) belonging to $\delta$(RuCO) and $v_a$(RuN), respectively, according to the calculations.
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$[Pt(R)_4(iPr-DAB)]$ ($R = CH_3, CD_3$).\(^{21,42}\) The two axial methyl groups of this complex contribute to two $\sigma(CH_3-M-CH_3)$ orbitals. One of these is the HOMO which consists of the antisymmetric combination of the axial methyl sp$^3$ orbitals, of $\pi^*(iPr-DAB)$ and a minor contribution from a $p(Pt)$ orbital. The rR spectra, obtained by excitation into the SBLCT transition of $[Pt(R)_4(iPr-DAB)]$ ($R = CH_3, CD_3$) (Figure 8.4) are interpreted with the help of DFT calculations on the $[Pt(R)_4(Me-DAB)]$ ($R = CH_3, CD_3$) model complexes.

Two major bands are found in the rR spectra. First of all, $v_s(CN)$ is observed at ca. 1565 cm$^{-1}$ (calc. at ca. 1595 cm$^{-1}$) for both the CH$_3$ and CD$_3$ complexes (Table 8.1). However, the most intense rR band is found at 1175 cm$^{-1}$ for the CH$_3$ complex and at 894 cm$^{-1}$ for the CD$_3$ complex. This band is again assigned to the symmetrical deformation of the methyl groups, $\delta(CH_3/CD_3)$, on the basis of the shift on deuteration and the calculated frequencies of 1213 and 923 cm$^{-1}$ for the CH$_3$ and CD$_3$ model complexes, respectively. The rR intensity of $\delta(CH_3/CD_3)$ is much higher for these complexes than for $[Re(CH_3)(CO)_3(iPr-DAB)]$ and $[Ru(Cl)(R)(CO)_2(iPr-DAB)]$ ($R = CH_3, CD_3$) and even higher than for $[Ru(CH_3)(SnPh_3)(CO)_2(iPr-DAB)]$. This agrees with the results from DFT calculations that in the $[Pt(R)_4(iPr-DAB)]$ ($R = CH_3, CD_3$) complexes the $\sigma(CH_3)$ orbitals are the main contributors to the HOMO from which the SBLCT transition originates. For $[Pt(CH_3)_4(iPr-DAB)]$, $v_s(PtC)_{eq}$ and $v_s(PtC)_{as}$ are found as very weak bands at 517 and 469 cm$^{-1}$, respectively. Although especially the latter vibration can be expected to be vibronically coupled to the SBLCT electronic transition, the absence of strong resonance enhancement contradicts this expectation.

(4) The influence of metal–metal bonds

Just as the methyl ligand, a metal fragment bonded to the central metal atom can affect the rR spectra in various ways, depending on the involvement of the metal–metal bonding orbital in the excited electronic transition. If in the complex $[Ru(Cl)(Me)(CO)_2(iPr-DAB)]$ the methyl ligand is replaced by SnPh$_3$, the rR spectrum of the resulting complex $[Ru(Cl)(SnPh_3)(CO)_2(iPr-DAB)]$ is even simpler than that of $[Ru(Cl)(Me)(CO)_2(iPr-DAB)]$. In this case only the Raman band belonging to $v_s(CN)$ is resonance enhanced. It has shifted from 1576 to 1543 cm$^{-1}$, pointing to an increase of $\pi$-backbonding on going to $[Ru(Cl)(SnPh_3)(CO)_2(iPr-DAB)]$.\(^{14,19}\) The rR band belonging to $v_s(CO)$ has disappeared. This could imply a loss of charge transfer character, but the relatively high frequency of $v_s(CN)$ (1543 cm$^{-1}$) points to a weak metal–diimine $\pi$-backbonding and an appreciable transfer of
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charge during the transition. Hence, the disappearance of \(\nu_s(\text{CO})\) is probably at least in part due to the fact that the transition has partly XLCT \((X = \text{Cl})\) character, in line with similar observations when Cl\(^-\) is replaced by I\(^-\) in \([\text{Ru(Cl(CH}_3)_3\text{)(CO)}_2\text{(iPr-DAB)})\].\(^{13}\) In addition, only very weak bands are observed at 605, 478 and 244 cm\(^{-1}\), due to \(\delta(\text{RuCO}), \nu_s(\text{Ru–C})\) and \(\nu_s(\text{Ru–N})\) respectively, in accordance with the assignments of bands at similar frequencies for e.g. \([\text{W(CO)}_4\text{(iPr–DAB)}]\) (\textit{vide supra}).

The influence of replacing a methyl group by a metal fragment is much larger when the methyl ligand in \([\text{Re(CH}_3\text{(CO)}_3\text{(iPr–DAB)})\] is substituted by a Re(CO)\(_5\) fragment. The HOMO of \([\text{Re(Re(CO)}_3\text{(CO)}_2\text{(iPr–DAB)})\] was shown to be the \(\sigma(\text{Re–Re})\) orbital,\(^{43}\) but the lowest-energy allowed transition has \(d_\alpha(\text{Re})\rightarrow\pi^*(\text{iPr–DAB})\) (MLCT) character.\(^{11}\) Again, the absence of any \(\nu(\text{CO})\) band in the rR spectrum obtained by excitation into this MLCT transition, shows the small degree of charge transfer character, due to the fact that both HOMO and LUMO are delocalized over the Re–DAB metallacycle. In this case the delocalization is so extensive that even \(\nu_s(\text{CN})\) (observed at 1467 cm\(^{-1}\)) has become weak. In fact the strongest bands in the rR spectrum are now the \(\delta(\text{DAB})\) bands at 957 and 838 cm\(^{-1}\). The band observed at 1289 cm\(^{-1}\) is attributed to the same \(\delta(\text{CH})\) vibration that is observed for \([\text{Ru(R)(SnPh}_3\text{(CO)}_2\text{(iPr–DAB)})\] (\(\text{R = CH}_3, \text{CD}_3\)) (\textit{vide supra}).

The last part of this section is devoted to trinuclear metal–metal bonded complexes. In these complexes the metal fragments participate in the HOMO and in the lowest-energy transition, which therefore has SBLCT character, just as in the case of \([\text{Pt(CH}_3]_4\text{(iPr–DAB)})\] (\textit{vide supra}).

\([\text{Pt(SnPh}_3\text{)}_2\text{(CH}_3\text{)}_2\text{(iPr–DAB)})\].\(^{21}\) In this complex, \(\pi\)-backbonding lowers the frequency of \(\nu_s(\text{CN})\) to the very low value of 1474 cm\(^{-1}\). This is accompanied by an intensity increase of \(\delta(\text{CH})\) at 1292 cm\(^{-1}\) (Figure 8.6) Apparently, a frequency lowering of \(\nu_s(\text{CN})\) causes a coupling of this vibration to \(\delta(\text{CH})\), which coupling results in resonance enhancement of the latter vibration. This change in enhancement of \(\delta(\text{CH})\) appears to be rather sudden, since this vibration is only weak for \([\text{Ru(CH}_3\text{(SnPh}_3\text{(CO)}_2\text{(iPr–DAB)})\] (\(\nu_s(\text{CN})\) at 1492 cm\(^{-1}\)), but strongly enhanced for \([\text{Pt(SnPh}_3\text{)}_2\text{(CH}_3\text{)}_2\text{(iPr–DAB)})\] (\(\nu_s(\text{CN})\) at 1474 cm\(^{-1}\)). However, the \(\delta(\text{DAB})\) vibrations (observed at 949 and 834 cm\(^{-1}\)) are only very weakly enhanced. This means that in spite of the strong \(\pi\)-backbonding in this complex, its SBLCT transition does not cause a distortion of the Pt–iPr–DAB metallacycle, which indicates that the delocalization of HOMO and LUMO is rather weak and SBLCT transition
in this complex has appreciable charge transfer character. With decreasing charge transfer character, the DAB deformation modes become enhanced (vide infra).

![Figure 8.6](image)

**Figure 8.6** RR spectra of (a) \([\text{Pt}(\text{SnPh}_3)_2(\text{CH}_3)_2(i\text{Pr}-\text{DAB})]\) \((\lambda_{\text{exc}} = 595.6 \text{ nm, recorded at 90 K})\), (b) \([\text{Ru}(\text{SnPh}_3)_2(\text{CO})_2(i\text{Pr}-\text{DAB})]\) \((\lambda_{\text{exc}} = 457.9 \text{ nm})\) and (c) \([\text{Ru}(\text{Cp})(\text{CO})_2(\text{iPr}-\text{DAB})]\) \((\lambda_{\text{exc}} = 590.0 \text{ nm})\) in KNO₃. Asterisks denote NO₃⁻ bands.

\([\text{M}(\text{SnPh}_3)_2(\text{CO})_2(i\text{Pr}-\text{DAB})]\) \((\text{M} = \text{Ru, Os})\). In order to investigate the influence of the central metal atom on the electronic structure and SBLCT transition, the rR spectra of both the Ru and Os complexes were studied. The spectrum of \([\text{Ru}(\text{SnPh}_3)_2(\text{CO})_2(i\text{Pr}-\text{DAB})]\) is shown in Figure 8.6. In addition, DFT calculations were performed on the model complexes \([\text{Ru}(\text{SnH}_3)_2(\text{CO})_2(i\text{Pr}-\text{DAB})]\), \([\text{Ru}(\text{SnH}_3)_2(\text{CO})_2(\text{Me}-\text{DAB})]\) and \([\text{Os}(\text{SnH}_3)_2(\text{CO})_2(\text{Me}-\text{DAB})]\) in order to deduce the influence of both the central metal atom and the substituents R of R–DAB on the vibrational frequencies.

The observed \(v_5(\text{CN})\) and \(\delta_6(\text{CH})\) bands in the rR spectra, obtained by excitation into the SBLCT transition of the \([\text{M}(\text{SnPh}_3)_2(\text{CO})_2(i\text{Pr}-\text{DAB})]\) \((\text{M} = \text{Ru, Os})\) complexes, are hardly shifted compared to those of \([\text{Pt}(\text{SnPh}_3)_2(\text{CH}_3)_2(i\text{Pr}-\text{DAB})]\). Thus, \(v_5(\text{CN})\) is observed at ca. 1473 \text{ cm}^{-1} and \(\delta_6(\text{CH})\) at 1292 and 1278 \text{ cm}^{-1} for \(\text{M} = \text{Ru and Os, respectively. The}\)
DFT calculations show that the frequency of $\delta_i$(CH) is very sensitive to the substituent R of the R–DAB ligand, since the calculated frequency of $\delta_i$(CH) of $[\text{Ru(SnH}_3)_2(\text{CO})_2(\text{R–DAB})]$ (R = Me, iPr) shifts from 1405 cm$^{-1}$ to 1326 cm$^{-1}$ going from R = Me to R = iPr. As expected, the latter value is a few percent too high, compared to the observed frequency (1292 cm$^{-1}$). The lowest-energy absorption bands of $[\text{M(SnPh}_3)_2(\text{CO})_2(\text{iPr–DAB})]$ (M = Ru, Os) are less solvatochromic ($\Delta = \nu(\text{MeCN}) - \nu(\text{toluene}) = 500 - 600$ cm$^{-1}$) than that of $[\text{Pt(SnPh}_3)_2(\text{CH}_3)_2(\text{iPr–DAB})]$ ($\Delta = 900$ cm$^{-1}$). This explains the high intensity of the $\delta_i$(DAB) vibrations in the rR spectra of $[\text{M(SnPh}_3)_2(\text{CO})_2(\text{iPr–DAB})]$ (M = Ru, Os) and their absence in the spectrum of $[\text{Pt(SnPh}_3)_2(\text{CH}_3)_2(\text{iPr–DAB})]$ (vide supra), since these vibrations become enhanced whenever the HOMO and LUMO orbitals become strongly delocalized. Interestingly, the observed frequencies of all bands hardly shift going from the Ru to the Os complex, which supports the results of our DFT calculations that Ru and Os orbitals are only minor contributors to the HOMO and LUMO. It also implies that the $\pi$-backbonding to iPr-DAB, reflected in a low frequency of $\nu_i$(CN), can only be caused by a strong $\sigma$–$\pi^*$ interaction between the SnPh$_3$ ligands and iPr-DAB. The strong $\sigma$–$\pi^*$ interaction is also evident from a large $J_{\text{Sn–H}}$ coupling constant for the imine protons of iPr-DAB.$^{19,22}$ Furthermore, the crystal structure of this complex shows a significantly elongated CN bond.$^{44}$

Similar low-frequency bands are observed for these complexes as for other complexes with a delocalized electronic system. Thus $\delta_i$(MCO) is observed at 610 cm$^{-1}$, $\nu_i$(MC) at 419 cm$^{-1}$ and $\nu_i$(MN) at ca. 249 cm$^{-1}$. Although the intensities of these bands are lower than those of the other ones, the distortion along these normal modes is significant in view of their low frequencies.

$[\text{Ru[RuCp(\text{CO})_2](\text{CO})_2(\text{iPr–DAB})]}]$.$^{23}$ This complex is an example of an extremely delocalized electronic system, shown by e.g. the solvatochromism of its first absorption band, which is negligible. Just as in the case of $[\text{Re[Re(\text{CO})_5](\text{CO})_3(\text{iPr–DAB})]}$ this leads to a complete disappearance of $\nu_i$(CN) and $\delta_i$(CH), while the $\delta_i$(DAB) bands and the metal–ligand and metal–metal stretching modes are the strongest in the rR spectrum (Figure 8.6). This implies that the SBLCT transition of this complex has metal–ligand and metal–metal bonding to antibonding character, which is accompanied by a distortion of the iPr-DAB ligand.
8.5 Conclusions

The preceding section gave an overview of the rR spectra of a number d⁶ metal-diimine complexes, with special attention paid to three factors that influence the appearance of these spectra. These three factors are: (1) the π-backbonding to the iPr-DAB ligand, (2) the delocalization of the frontier orbitals determining the degree of charge transfer character of the excited transition and (3) the character of that transition.

Whenever a strong π-backbonding is present in the ground state of the complex, whether by δπ−π* or σ−π* interaction, the symmetric CN stretching vibration is lowered in frequency. If νₛ(CN) is shifted to a frequency lower than ca. 1490 cm⁻¹, a concomitant resonance enhancement of δ(CH) (Figure 8.5) is observed. Apparently, this is due to δ(CH) obtaining some νₛ(CN) character, thus being vibrationally coupled to the electronic transition.

Delocalization of the orbitals between which the electronic transition occurs, results in the loss of charge transfer character. As a consequence, stretching vibrations, such as νₛ(CO) and in extreme cases also νₛ(CN) disappear from the rR spectrum, while δₛ(DAB) vibrations gain intensity. Since δₛ(CH) is coupled to νₛ(CN), the bands due to both vibrations decrease simultaneously in intensity when delocalization increases.

In the case of methyl complexes, the change in character of the electronic transition from MLCT to SBLCT gives rise to strong resonance enhancement of intensity for the symmetric methyl group deformation vibration. Remarkably the metal–carbon stretching vibration is not resonantly enhanced. Hence, the metal–methyl ligand stretching vibration is generally not a good indicator of electronic transition character, in contrast to δₛ(CH₃).

One of the remarkable results of this study is that, while the rR spectra of e.g. [Ru(Cl)(CH₃)(CO)₂(iPr–DAB)] and [Ru(SnPh₃)₂(CO)₂(iPr–DAB)] are very different in appearance, most of these differences can be rationalized in terms of π-backbonding and orbital delocalization rather than attributed to a change in the character of the electronic transition.

A large part of the assignments of the vibrations were based on DFT-calculations. As such they have proven very useful. However, it was also shown that structural simplifications in the calculated complex (e.g. iPr–DAB to Me–DAB) may have profound influence on the frequency and character of certain calculated vibrations.
8.6 References

Chapter 8. Influences on the Resonance Raman Spectra of $d^6$ Metal–Diimine Complexes
