Ligand Field Analysis of the Electronic Spectra of
[M(H$_2$O)$_6$]$^{3+}$, [M(NH$_3$)$_6$]$^{3+}$, [M(en)$_3$]$^{3+}$, [M(chxn)$_3$]$^{3+}$
and [M(tacn)$_2$]$^{3+}$ Complexes (M = Co$^{III}$, Rh$^{III}$, Ir$^{III}$).
Spectrochemical Strength and Nephelauxetic Effect of
Ammine and Amine Ligands

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Gaussian analyses of the electronic spectra of homoleptic aqua, ammine, ethan-1,2-diamine (en), trans-cyclohexane-1,2-diamine (chxn) and 1,4,7-triazacyclononane (tacn) complexes of cobalt(III), rhodium(III) and iridium(III) have provided transition energies that are not distorted by the overlap of absorption bands. This has uncovered the true $^{1}A_{1g}$→$^{1}T_{2g}$ ligand field transition of [Ir(NH$_3$)$_6$]$^{3+}$ and [Ir(en)$_3$]$^{3+}$. Apart from an interchange observed for cobalt(III), the spectrochemical series was found to be H$_2$O < NH$_3$ < chxn < en < tacn for all three metal ions. The spectrochemical order thus follows the order of am(m)ine ligand gas-phase basicities. The anomaly of [Co(chxn)$_3$]$^{3+}$ has been explained in terms of steric crowding around the metal centre. For all three metal ions the nephelauxetic series was found to be H$_2$O < am(m)ine, with the am(m)ine ligands all giving rise to quite similar degrees of nephelauxetism.

The very extensive and similar coordination chemistries of the robust metal ions cobalt(III), rhodium(III) and iridium(III) provide a unique possibility, not encountered anywhere else in the Periodic Table, to study the variation of the ligand field spectra of analogous complexes over all three transition periods. Electronic spectra of octahedral low-spin d$^3$ complexes usually contain two spin-allowed absorption bands, which are assigned to the d→d transitions $^{1}A_{1g}$→$^{1}T_{1g}$ and $^{1}A_{1g}$→$^{1}T_{2g}$. By means of ligand field energy matrices, the transition energies may be translated into values for the spectrochemical parameter $\Delta$, measuring the one-electron $d$ orbital splitting $E(e_2)$ $-$ $E(t_{2g})$, and the Racah interelectronic repulsion parameter $B$, measuring the repulsion between the electrons in the partly filled $d$ shell. We present a comparative ligand field analysis based on Gaussian resolution of electronic absorption spectra of [M(H$_2$O)$_6$]$^{3+}$, [M(NH$_3$)$_6$]$^{3+}$, [M(en)$_3$]$^{3+}$, [M(chxn)$_3$]$^{3+}$ and [M(tacn)$_2$]$^{3+}$ complexes (M = Co$^{III}$, Rh$^{III}$, Ir$^{III}$).

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Experimental

Most of the complexes of Rh$^{III}$ and Ir$^{III}$ studied have previously been synthesised and characterised by us; otherwise, they were prepared as described in the footnotes to Table 1. The UV–vis absorption spectra were measured or re-measured at room temperature in aqueous solution (acidic for the hexaaqua complexes) by using a Perkin-Elmer Lambda 17 spectrophotometer. Each digital spectrum, consisting of absorbance values at regularly spaced ($\Delta \lambda = 1$ nm) wavelength values, was represented as a sum of symmetric Gaussian curves which had wavelength as their independent variable. The least-squares fit of Gaussian functions was made over a wavelength interval wide enough to include the main parts of the two ligand field bands of interest, but narrow enough to exclude bands not of interest such as the spin-forbidden bands of Ir$^{III}$ complexes. In the cases where the rise in
absorbance in the UV region overlapped with the spectral region of interest, the charge transfer “foot” was represented by a Gaussian function. Ligand field calculations and parameter fitting were made using the PC program LIGFIELD (version 0.78). For all complexes, regular octahedral coordination geometry was assumed.

Results and discussion

From the energies of the two absorption band maxima in the electronic spectrum of [Ir(NH₃)₂Cl]³⁺, the value

\[ B = 0.0470 \, \text{µm}^{-1} \]

may be calculated. However, this value for B is higher than those found for [Rh(H₂O)₃]³⁺ and [Ir(H₂O)₃Cl]³⁺, and is thus in disagreement with the nephelauxetic series both for metal ions and for ligands. Recently it was suggested that the spectrum of [Ir(NH₃)₃]³⁺ (Fig. 1) had been missassigned, that the absorption band at 213 nm was not due to the second spin-allowed ligand field transition \( ^1A_{1g} \rightarrow ^1T_{2g} \) and that the \( ^1A_{1g} \rightarrow ^1T_{2g} \) band was concealed between the two bands observed. The spectrum of [Ir(en)₃]³⁺ is similar to that of [Ir(NH₃)₃]³⁺, but the recently prepared [Ir(tacn)₃]³⁺ (Fig. 1) shows a \( ^1A_{1g} \rightarrow ^1T_{2g} \) band roughly in the position where a concealed band is suggested in the [Ir(NH₃)₃]³⁺ and [Ir(en)₃]³⁺ spectra. By resolution of the spectra into Gaussian components, the positions of the concealed bands in the [Ir(NH₃)₃]³⁺ (cf. Fig. 1) and [Ir(en)₃]³⁺ spectra have now been located. From these positions much more reasonable values for B were obtained (Table 1).

A d⁰ model calculation was based on the Δ and B values obtained for [Ir(NH₃)₃]³⁺ (Table 1) showed that the lowest-energy ligand field term above the \( ^3T_{2g} \) is the \( ^3T_{2g} \) at 7.2 µm⁻¹ (140 nm). The 213 nm band of [Ir(NH₃)₃]³⁺ is thus most likely to originate from a charge-transfer transition. However, the reason why this transition appears in some [Ir(H₂O)₃]³⁺ spectra ([Ir(NH₃)₃]³⁺ (Ref. 5), [Ir(en)₃]³⁺ (Ref. 6), [Ir(NH₃)₃(H₂O)]³⁻ (Ref. 5) and [Ir(tacn)(H₂O)]³⁺ (Ref. 7)) but not in others (leq and ob₂-[Ir(chxn)₃]³⁺ (Ref. 8) and [Ir(tacn)₃]³⁺ (ref. 7)) is unknown.

Representation of the spectra as sums of Gaussian curves removes the general problem of obtaining \( ^1A_{1g} \rightarrow ^1T_{1g} \) and \( ^1A_{1g} \rightarrow ^1T_{2g} \) transition energies for Rh³⁺ and Ir³⁺ complexes that are not distorted by the substantial overlap of the two band envelopes. This overlap causes the maxima of the unresolved spectral curve to be closer together than the maxima of the Gaussian component curves (cf. Table 1). Since the value of B is primarily determined by the energy difference between the two transitions, Gaussian analysis is essential for obtaining a reliable B value (cf. [Ir(tacn)₃]³⁺ in Fig. 1). Spectral and parametric data obtained in this way are given in

Table 1. Wavelengths for the d⁰ ligand field transitions \( ^1A_{1g} \rightarrow ^1T_{1g} \) (λ₁, max) and \( ^1A_{1g} \rightarrow ^1T_{2g} \) (λ₂, max) of [M(H₂O)₃]³⁺ and [M(N₂)₃]³⁺ complexes obtained by Gaussian analyses of the aqueous solution electronic spectra and the corresponding calculated d⁰ model parameter values (C=4B).¹

<table>
<thead>
<tr>
<th></th>
<th>λ₁, max/ nm</th>
<th>λ₂, max/ nm</th>
<th>Δλ/ µm⁻¹ b</th>
<th>B/ µm⁻¹ b</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(H₂O)₆]³⁺</td>
<td>1</td>
<td>(606.1)</td>
<td>(401.6)</td>
<td>1.816</td>
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<tr>
<td>[Co(NH₃)₆]³⁺</td>
<td>1</td>
<td>(471.1)</td>
<td>(338.4)</td>
<td>2.287</td>
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<tr>
<td>leq,[Co(chxn)₃]³⁺</td>
<td>9</td>
<td>(472)</td>
<td>(342)</td>
<td>2.280</td>
</tr>
<tr>
<td>obox,[Co(chxn)₃]³⁺</td>
<td>9</td>
<td>(473)</td>
<td>(343)</td>
<td>2.275</td>
</tr>
<tr>
<td>[Co(en)₃]³⁺</td>
<td>1</td>
<td>(464.0)</td>
<td>(337.8)</td>
<td>2.317</td>
</tr>
<tr>
<td>[Co(tacn)₃]³⁺</td>
<td>10</td>
<td>(458)</td>
<td>(333)</td>
<td>2.348</td>
</tr>
<tr>
<td>[Rh(H₂O)₃]³⁺</td>
<td>13</td>
<td>398 (397)</td>
<td>310 (312)</td>
<td>2.661</td>
</tr>
<tr>
<td>[Rh(NH₃)₃]³⁺</td>
<td>d</td>
<td>305 (305)</td>
<td>253 (255)</td>
<td>3.420</td>
</tr>
<tr>
<td>leq,[Rh(chxn)₃]³⁺</td>
<td>15</td>
<td>302 (302)</td>
<td>253 (255)</td>
<td>3.449</td>
</tr>
<tr>
<td>obox,[Rh(chxn)₃]³⁺</td>
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<td>254 (256)</td>
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<tr>
<td>[Rh(en)₃]³⁺</td>
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<td>301 (301)</td>
<td>253 (255)</td>
<td>3.460</td>
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<tr>
<td>[Rh(tacn)₃]³⁺</td>
<td>18</td>
<td>295 (295)</td>
<td>248 (249)</td>
<td>3.529</td>
</tr>
<tr>
<td>[Ir(H₂O)₃]³⁺</td>
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<td>317 (314)</td>
<td>265 (271)</td>
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<tr>
<td>[Ir(NH₃)₃]³⁺</td>
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<td>leq,[Ir(chxn)₃]³⁺</td>
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<td>248 (248)</td>
<td>219 (—)</td>
<td>4.152</td>
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<tr>
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<td>7</td>
<td>243 (242)</td>
<td>214 (222)</td>
<td>4.243</td>
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¹ Wavelengths in parentheses are the directly observed maxima. The well separated absorption bands for Co³⁺ made Gaussian analyses unnecessary and literature data were used. \( 1 \, \text{µm}^{-1} = 10000 \, \text{cm}^{-1} \). c \[ \text{[Rh(H₂O)₃]Cl} \] was isolated as the amine \text{[C₃H₇][Rh(H₂O)₃]Cl} and \[ \text{[Rh(NH₃)₃]Cl} \] was isolated from a solution of \[ \text{[Rh(NH₃)₃]Cl} \] in \[ \text{[NH₃]Cl} \] and 14 M \[ \text{HCl} \] by an autoclave synthesis at 110 °C, 96 h analogous to that used for \[ \text{[Ir(NH₃)₃]Cl} \] and [Ir(tacn)₃][Br₂]. \[ \text{[Ir(tacn)Cl}₂\text{H₂O} \] was prepared from [Ir(tacn)Cl] and tacn·3HCl (Galsbel, F., Petersen, C.H. and Simonsen, K., Acta. Chem. Scand. Submitted, i.e. differently from the original synthesis. \( ^7 \) For \[ \text{[Ir(NH₃)₃]Cl} \] the global minimum for the fit of Gaussian functions was quite flat; a fit with an only 50% higher \( \chi^2 \) gave \( B \approx 0.0360 \, \text{µm}^{-1} \), which is more in line with what one would expect based on the Co³⁺ and Rh³⁺ data. 290
Fig. 1. Electronic spectra of \([\text{Ir(NH}_3\text{)}_6]^{3+}\) and \([\text{Ir(tacn)}_2]^{3+}\) and their Gaussian decompositions. The wavelength intervals where Gaussian functions were fitted are indicated by the spectral curves being drawn in solid rather than dashed lines. In the spectrum of \([\text{Ir(NH}_3\text{)}_6]^{3+}\) a concealed band assigned as the ligand field transition \(1^3\text{A}_2 \rightarrow 1^3\text{T}_2\) is found at 225 nm. For \([\text{Ir(tacn)}_2]^{3+}\), the substantial overlap of the envelopes of the two transitions \(1^3\text{A}_2 \rightarrow 1^3\text{T}_2\) and \(1^3\text{A}_2 \rightarrow 1^3\text{T}_2\) causes spectral maxima to occur at wavelengths quite different from the maxima of the Gaussian functions. Thus the value of the Racah interelectronic repulsion parameter \(B = 0.0360 \text{ \mu m}^{-1}\) calculated from the maxima of the Gaussian functions is very different from the value \(B = 0.0240 \text{ \mu m}^{-1}\) calculated from the maxima of the unresolved spectral curve.

Table 1. Figures 2 and 3 show spectra of Rh\text{III} complexes; some of these have not been published before, and some have been obtained by us in an improved quality, i.e. from samples of higher purity.

Following the spectrochemical series, \(\Delta\) is seen to be larger for am(m)ine complexes than for aqua complexes. The variation with the metal ion of \(\Delta\) for each \(N_x\) coordination sphere is illustrated in Fig. 4. Apart from \([\text{Co(chxn)}_3]^{3+}\), \(\Delta\) is seen to increase for all three metal ions as \(\text{NH}_3 < \text{chxn} < \text{en} < \text{tacn}\), thus following the gas phase basicities of the am(m)ine ligands: \(\text{NH}_3 < \text{primary amine} < \text{secondary amine}\). This general variation of \(\Delta\) with the am(m)ine ligand has been discussed by Hancock and is, for example, demonstrated by the series \([\text{Ni(NH}_3\text{)}_6]^{2+}\) \((\Delta = 1.075 \text{ \mu m}^{-1})\), \([\text{Ni(en)}_3]^{2+}\) \((\Delta = 1.150 \text{ \mu m}^{-1})\) and \([\text{Ni(tacn)}_3]^{2+}\) \((\Delta = 1.235 \text{ \mu m}^{-1})\). The same variation is found for Cr\text{III} complexes: \([\text{Cr(NH}_3\text{)}_6]^{3+}\) \((\Delta = 2.155 \text{ \mu m}^{-1})\), \([\text{Cr(en)}_3]^{3+}\) \((\Delta = 2.169\) and \(2.183 \text{ \mu m}^{-1})\), \([\text{Cr(chxn)}_3]^{3+}\) \((\Delta = 2.185 \text{ \mu m}^{-1})\) and \([\text{Cr(tacn)}_3]^{3+}\) \((\Delta = 2.278 \text{ \mu m}^{-1})\).

The occurrence of steric crowding around the metal ion may lead to elongation of the metal–nitrogen bonds. This means that even though the inherent donor strengths of the am(m)ine ligands follow the series \(\text{NH}_3 < \text{primary amine} < \text{secondary amine}\), an increased inherent donor strength need not be fully reflected in the \(\Delta\) value. Therefore, the size of the small metal ions and the bulkiness of the chxn ligand, steric crowding is expected to be very pronounced for \([\text{Co(chxn)}_3]^{3+}\). It prevents the nitrogen donor atoms from achieving the optimum orbital overlap with the metal atom. The effective donor strength of chxn
Fig. 3. Electronic spectrum of [Rh(H₂O)₆]³⁺ obtained by dissolution of the alun Co[Rh(H₂O)₆][SO₄]₂·6H₂O in 1 M H₂SO₄. Spectral extrema, (λ/μm, ε/1 mol⁻¹ cm⁻¹), are: (397,56), (352,32), (312,56), and (268,19). Gaussian functions were fitted in the wavelength interval 239-439 nm.

Fig. 4. Empirical values for the spectrochemical parameter of [M(NH₃)₃]³⁺ (M = Co, Rh, Ir) complexes. To ease comparison, the Δ values have, for each metal ion, been normalised relative to the value for [M(NH₃)₃]³⁺. The relative donor strengths of the ligands follow their gas phase basicities: NH₃ < primary amine < secondary amine. The generally observed increase in Δ/Δ(NH₃) along the series Co, Rh, Ir may be explained in terms of reduced steric crowding that facilitates metal-nitrogen orbital overlap.

in [Co(chxn)₃]³⁺, expressed in the value of Δ, is therefore smaller than that of NH₃ in [Co(NH₃)₃]³⁺, despite the inherent donor strength of the two ligands being the reverse. X-Ray crystallographic data show²² that the metal-nitrogen bond lengths in a [M(chxn)₃]³⁺ (M = Co, Rh, Ir) complex are typically 0.01 Å longer than in the corresponding [M(en)₃]³⁺ complex.

For the trivalent metal ions Co, Rh, Ir, and Cr, tacn yields a yield which is only 3–6% stronger than that of NH₃. In contrast, for Ni, tacn yields a field which is 15% stronger than that of NH₃, and for Co (Refs. 23 and 24) and Cu (Refs. 25 and 26) the situation is similar. An explanation for this different behavior of trivalent and divalent metal ions may, at least in part, be found in their sizes. Generally the ionic radii²⁷ of the trivalent ions \( R(CO³⁺) = 0.55 \AA, R(Rh³⁺) = 0.67 \AA, R(Ir³⁺) = 0.68 \AA, R(Cr³⁺) = 0.62 \AA \) are smaller than those of the divalent ions \( R(Ni²⁺) = 0.69 \AA, R(Co²⁺) = 0.70 \AA, R(Cu²⁺) = 0.73 \AA \). Complexes of the relatively bulky tacn ligand tend to be more sterically crowded when the metal ion is trivalent than when it is divalent. The tacn ligand is accordingly less likely to be able to exercise its full donor strength when it binds to a trivalent metal ion. The d orbital diffuseness varies, like the ionic size, strongly with the metal ion charge, and may play an additional role in determining the relative Δ values for different ligand systems.

Jorgensen has proposed⁴ a factorisation model in which Δ is expressed as a product of a parameter g characteristic for the metal ion and a parameter f characteristic for the ligand sphere. This model implies that within a set of ligands the relative spectrochemical strengths are independent of the metal ion to which they coordinate. From the data mentioned in the previous paragraph and from the variation of Δ/Δ(NH₃) seen in Fig. 4 it is clear that this is not strictly true.

When discussing the results (Table 1) for the interelectronic repulsion parameter B, it should be noted that its value may be quite sensitive towards small changes in the band energies from which it is calculated. A 1 nm red-shift in the \( ^1A_2g\rightarrow ^1T_2g \) transition thus decreases B with 1.3%, 2.6%, and 4.1%, respectively, for the \([M(en)]_3^3+ (M = Co, Rh, Ir) complexes. One nanometre is approximately the experimental error and the uncertainty of the model by which the Gaussian functions are defined. Values for B should be compared with this in mind. For Co, Rh, and Ir we find the nephelauxetic series to be \( NH₃ < tacn \approx chxn \approx en \). In accordance with this order, the amine complexes of Ir are found to show mutually quite similar degrees of nephelauxetism. The B value obtained for \([Ir(NH₃)₃]^{3+} \) is anomalous, the reason probably being that it is an approximation to represent real spectral components by Gaussian functions (cf. footnote f to Table 1).

References


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