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The Excited States of Bipyridyl and Phenanthroline Complexes of Fe(III), Ru(II) and Ru(III): A Molecular Orbital Study

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The semiempirical zero-differential-overlap molecular orbital model which was shown in earlier papers in this series to give a good account of the charge transfer and π–π^* spectra of Fe(II) complexes with conjugated ligands such as 2,2′-bipyridyl and 1,10-phenanthroline is extended to complexes having open-shell ground states, such as those of Fe(III), and to complexes of Ru(II) and Ru(III). The results are used to assign the observed charge transfer and intra-ligand absorption bands to specific orbital transitions. Observed and calculated intensities are in good agreement: reasons are advanced for the much lower intensity of the charge transfer bands in Ru(III) compared to Ru(II) complexes.

Key words: Bipyridyl Fe(III), Ru(II), Ru(III) complexes – Phenanthroline Fe(III), Ru(II), Ru(III) complexes

1. Introduction

The dipyridyl (dipy) and phenanthroline (phen) complexes of ruthenium have excited states whose unusual properties have attracted a great deal of attention in the last few years. Most people agree that the lowest energy excited states in these complexes are of charge transfer type, as in the corresponding iron complexes, metal-to-ligand in the 2+ examples and ligand-to-metal in the 3+. However, they have rather different properties from their iron analogues. For example, they belong to the very small group of inorganic compounds with charge transfer states which luminesce [1]; furthermore, the emitting state of Ru(dipy)$_3^{2+}$ combines the properties of a very strong reducing agent with those of a moderately strong oxidizing agent. Its photoredox properties have therefore come under close scrutiny [2]. More spectacularly, in terms of current preoccupations with energy

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problems, the ability of the lowest charge transfer state of $Ru(dipy)_3^{2+}$ to act as an electron donor in redox reactions, combined with the ability to $Ru(dipy)_3^{3+}$ to oxidize H_2O and OH^- [3], have made it attractive as the basis of possible solar energy conversion systems [4, 5]. For all these reasons it is important to obtain a better understanding of the excited states in these unusual molecules. *Ab initio* calculations on molecules of such complexity are not likely to be very illuminating even if they were feasible, and the ability of the scattered-wave $X\alpha$ model to deal with this kind of excited state has not been demonstrated. In fact, this is an area in which semiempirical models can still give useful insight.

Some years ago we developed a self-consistent-field molecular orbital (SCF-MO) model, at the "intermediate neglect of differential overlap" (INDO) level of approximation, which was designed specifically to calculate the energies, dipole strengths and both linear and circular polarizations of charge transfer excited states in metal complexes with conjugated ligands [6]. With it, we were able to account in detail for the properties of the visible absorption bands in $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$, due to metal-to-ligand charge transfer, including band shifts brought about by ligand substitution [7]. For this purpose the model considered only π electrons, that is, the ligand π and π^* orbitals together with $3d(xy)$, (xz) and (yz) on the metal. The single freely chosen parameter is the core charge of the metal atom, the metal-nitrogen resonance integral being determined by the Linderberg criterion [8] and the valence state ionization potentials from the tabulation of Pilcher and Skinner [9]. An SCF basis is employed, with extensive configuration interaction (CI). Full details are given in our earlier papers [6, 7]. The original form of the programme was designed to deal only with closed shell molecules. In the present paper we report its extension to open-shell examples, in particular Fe(III) complexes, and also to the $4d$ Ru(II) and Ru(III) systems mentioned above.

2. Methodology

Our point of departure is Roothaan's open-shell SCF theory [10], approximated and parametrized at the INDO level. To construct the excited state wavefunctions CI matrix elements must be derived for the particular spin configuration of the system considered. In the present case we are only interested in a single spin-free electron (or hole, as in low-spin t_{2g}^5).

As described by Roothaan, the open-shell SCF method applies to systems in which the total wavefunction is a sum of several antisymmetrized products, each of which contains a closed-shell core, ψ_c, and a partially occupied open-shell, ψ_o, the different antisymmetrized products containing different subsets of ψ_o:

$$\psi = (\psi_c, \psi_o). \tag{1}$$

Individual orbitals are assumed orthonormal and in referring to the MO's the indices k,l are used for closed-shell orbitals, m,n for open-shell orbitals. The expectation value of the energy is given by

$$\begin{aligned} E=2\sum_{k} H_k+\sum_{k,l}(2J_{kl}-K_{kl})\\ +f\left[2\sum_{m} H_m+f\sum_{m,n}(2aJ_{mn}-bK_{mn})+2\sum_{k,m}(2J_{km}-K_{km})\right], \end{aligned} \tag{2}$$

where a, b and f are numerical constants depending on the particular system considered while f is the fractional occupancy of the open shell. The first two terms of (2) represent the closed-shell energy, the next two terms the open-shell energy, and the last term the interaction energy of the closed and open shells. Defining Coulomb and exchange coupling operators as:

$$\begin{aligned} L_i\phi=(\phi_i|J_o|\phi)\phi_i+(\phi_i|\phi)J_o\phi_i,\\ M_i\phi=(\phi_i|K_o|\phi)\phi_i+(\phi_i|\phi)K_o\phi_i; \end{aligned} \tag{3}$$

and the corresponding closed, open and total coupling operators as

$$\begin{aligned} L_c=\sum_{k} L_k,\ L_o=\sum_{m} L_m,\ L_\tau=L_c+L_o,\\ M_c=\sum_{k} M_k,\ M_o=\sum_{m} M_m,\ M_\tau=M_c+M_o. \end{aligned} \tag{4}$$

the orbitals can now be shown to obey the equations:

$$F_c\psi_c=\psi_c\eta_c,\ F_o\psi_o=\psi_o\eta_o, \tag{5}$$

where

$$\begin{aligned} &F_c=H+2J_c-K_c+2J_o-K_o+2\alpha L_o-\beta M_o;\\ &F_o=H+2J_c-K_c+2aJ_o-bK_o+2\alpha L_c-\beta M_c;\quad \text{and}\\ &\alpha=(1-a)/(1-f),\ \beta=(1-b)/(1-f) \end{aligned} \tag{6}$$

On solution of (5) the closed-shell MO's are usually the p lowest energy eigenfunctions of F_c, and the open-shell MO's are the $(p+1)$'th Eigenfunction and up of F_o. Note that when $f=\frac{1}{2}$ the two parameters α and β of Eq. (6) need only satisfy the equality $(2a-b)=0$. Thus choices such as $\alpha=0$, $\beta=-2$ should give identical results to, for example, $\alpha=-2$, $\beta=-6$. This point is taken up again below.

In the LCAO form of the Fock equations, $\boldsymbol{F}\boldsymbol{C}_i=\varepsilon_i\boldsymbol{C}_i$, the Fock matrix takes the form:

$$\boldsymbol{F}=\boldsymbol{H}+\boldsymbol{P}-\boldsymbol{Q}+\boldsymbol{R}, \tag{7}$$

where

$$\begin{aligned}
&\boldsymbol{P}=2\boldsymbol{J}_\tau-\boldsymbol{K}_\tau,\\
&\boldsymbol{Q}=2\alpha\boldsymbol{J}_o-\beta\boldsymbol{K}_o,\\
&\boldsymbol{R}=2\alpha\boldsymbol{L}_\tau-\beta\boldsymbol{M}_\tau,\\
&J_{\tau,rs}=\tfrac{1}{2}\sum_t\sum_u P^\tau_{tu}(tu\mid rs),\\
&J_{c,rs}=\tfrac{1}{2}\sum_t\sum_u P^c_{tu}(tu\mid rs), &&(8)\\
&J_{o,rs}=\tfrac{1}{2}\sum_t\sum_u P^o_{tu}(tu\mid rs),\\
&K_{\tau,rs}=\tfrac{1}{2}\sum_t\sum_u P^\tau_{tu}(tu\mid rs),\\
&K_{c,rs}=\tfrac{1}{2}\sum_t\sum_u P^c_{tu}(tu\mid rs),\\
&K_{o,rs}=\tfrac{1}{2}\sum_t\sum_u P^o_{tu}(tu\mid rs),\\
&L_{\tau,rs}=2\alpha\sum_t\sum_u\sum_v\sum_w [\tfrac{1}{2}P^o_{tu}(tu\mid vs)P^\tau_{vw}S_{rw}+\tfrac{1}{2}S_{ws}P^\tau_{vw}(tu\mid vr)P^o_{tu}]\\
&M_{\tau,rs}=\beta\sum_t\sum_u\sum_v\sum_w [\tfrac{1}{2}P^o_{tu}(st\mid uv)P^\tau_{vw}S_{rw}+\tfrac{1}{2}S_{ws}P^\tau_{vw}(rt\mid uv)P^o_{tu}] &&(9)
\end{aligned}$$

and

$$P^o_{tu}=2\sum_m C_{tm}C_{um},\ P^c_{tu}=2\sum_k C_{tk}C_{uk},\ P^\tau_{tu}=P^c_{tu}+P^o_{tu}, \qquad (10)$$

in which the MO coefficients are normalized to half the number of electrons they represent, i.e. unity for closed-shell MO's, f for open-shell MO's. The P_{tu} are then elements of the density matrices $\boldsymbol{D}_r$, $\boldsymbol{D}_c$, $\boldsymbol{D}_o$; and $\boldsymbol{R}$ may be expressed as:

$$\begin{aligned}
&\boldsymbol{R}=(\boldsymbol{S}\boldsymbol{D}^\tau\boldsymbol{Q}+\boldsymbol{Q}\boldsymbol{D}^\tau\boldsymbol{S}),\\
&R_{rs}=\sum_v\sum_w (S_{rw}P^\tau_{wv}Q_{vs}+Q_{rv}P^\tau_{vw}S_{ws}). &&(11)
\end{aligned}$$

Within the ZDO approximation, the components of F_{rs} simplify to:

$$\begin{aligned}
&J_{c,rs}=\tfrac{1}{2}P_{c,tt}\delta_{rs}\sum_t (rr\mid tt),\\
&J_{o,rs}=\tfrac{1}{2}P_{o,tt}\delta_{rs}\sum_t (rr\mid tt),\\
&K_{c,rs}=\tfrac{1}{2}P_{c,rs}(rr\mid ss), &&(12)\\
&K_{o,rs}=\tfrac{1}{2}P_{o,rs}(rr\mid ss),\\
&R_{rs}=\sum_v P_{\tau,ru}Q_{vs}
\end{aligned}$$

Using the INDO approximation for AO's r and r' on the same centre, some modification to (14) is required, as follows:

$$\begin{aligned}
J_{c,rr'} &= \tfrac{1}{2}P_{c,rr'}(rr' \mid rr'),\\
J_{o,rr'} &= \tfrac{1}{2}P_{o,rr'}(rr' \mid rr'),\\
K_{c,rr} &= \tfrac{1}{2}P_{c,rr}(rr \mid rr)+\tfrac{1}{2}\sum_{r'\neq r} P_{c,r'r'}(rr' \mid rr'),\\
K_{o,r} &= \tfrac{1}{2}P_{o,rr}(rr \mid rr)+\sum_{r'\neq r} P_{o,r'r'}(rr' \mid rr'),\\
K_{c,rr'} &= \tfrac{1}{2}P_{c,rr'}(rr \mid r'r')+\tfrac{1}{2}P_{c,rr'}(rr' \mid rr'),\\
K_{o,rr'} &= \tfrac{1}{2}P_{o,rr'}(rr \mid r'r')+\tfrac{1}{2}P_{o,rr'}(rr' \mid rr').
\end{aligned} \tag{13}$$

The most common systems for which the ground state energy is given by (2), and for which the open-shell SCF theory is applicable, are those containing half-closed shells, in which the open-shell consists of complete degenerate sets of orbitals containing single electrons of parallel spin. The wavefunction can be represented by a single Slater determinant, $f=\frac{1}{2}$, and α and β are subject to the restriction $(2a-b)=0$, usually being chosen as $\alpha=0$, $\beta=-2$.

To derive excited state wavefunctions of open-shell molecules by the same procedure we have been describing for ground states would be extremely complicated. We therefore represent excited states as mixtures of orthogonal configurations (CI). In the present case only singly excited configurations are taken into account.

If ϕ_f is the MO containing the unpaired electron, and is normalized to unity, and the other MO's are labelled ϕ_i, $\phi_j \ldots$ for orbitals filled in the ground state and ϕ_a, $\phi_b \ldots$ for those vacant in the ground state the ground state of the single open-shell orbital system is

$$^2\psi(G)=|1\bar{1}2\bar{2}\cdots i\bar{i}j\bar{j}f|. \tag{14}$$

The doublet excited configurations corresponding to the transitions $(\phi_i \rightarrow \phi_f)$, $(\phi_f \rightarrow \phi_a)$ and $(\phi_i \rightarrow \phi_a)$ are:

$$^2\psi(A)_i^f=|1\bar{1}2\bar{2}\cdots i\bar{f}j\bar{j}f|, \tag{15}$$

$$^2\psi(B)_f^a=|1\bar{1}2\bar{2}\cdots i\bar{i}j\bar{j}a|, \tag{16}$$

$$^2\psi(C)_i^a=\tfrac{1}{2}[\Delta_1+\Delta_2], \tag{17}$$

$$^2\psi(D)_i^a=\frac{1}{\sqrt{6}}[2\Delta_3-\Delta_1+\Delta_2], \tag{18}$$

where

$$\begin{aligned}
\Delta_1 &= |1\bar{1}2\bar{2}\cdots i\bar{a}j\bar{j}f|,\\
\Delta_2 &= |1\bar{1}2\bar{2}\cdots a\bar{i}j\bar{j}f|,\\
\Delta_3 &= |1\bar{1}2\bar{2}\cdots iaj\bar{i}\bar{f}|.
\end{aligned} \tag{19}$$

The nomenclature of these configurations follows that of Longuet-Higgins and Pople [11], except that the columns i and a in the Δ_2 Slater determinant are interchanged, thus altering the sign of the coefficient of Δ_2 in the expressions for $^2\psi(C)_i^a$, $^2\psi(D)_i^a$.

The CI matrix elements are most easily obtained in terms of the open-shell Fock operator F by first expressing them in terms of an operator F^*, where:

$$F^* = H + 2J_c - K_c + 2J_o, \tag{20a}$$

$$F_{gh} = H_{gh} + \sum [2(jj \mid gh) - (gj \mid hj)] + (gh \mid ff). \tag{20b}$$

Now for the case of $f = \frac{1}{2}$, and the solution ($\alpha = 0$, $\beta = -2$) satisfying $(2a - b) = 0$, (20) gives:

$$F = H + 2J_\tau - K_\tau + 2(M_\tau - K_o), \tag{21}$$

from which

$$(F - F^*) = 2M_\tau - 3K_o. \tag{22}$$

CI elements expressed in terms of F^* can then be transformed to elements of F by (24). This procedure gives the CI matrix shown in Table 1. In using Table 1 it must be remembered that ϕ_f is normalized to unity; whilst the open-shell orbital, ϕ_m, calculated by the Roothaan SCF procedure, is normalized to the fractional occupancy of the open-shell, $\frac{1}{2}$. The equations of Table 1 may be converted to expressions in ϕ_m by using:

Table 1. Open-shell configuration interaction matrix elements

$$\langle {}^2\psi(A)_i^f | H | {}^2\psi(G) \rangle = F_{if}$$

$$\langle {}^2\psi(B)_f^a | H | \psi(G) \rangle = F_{fa}$$

$$\langle {}^2\psi(C)_i^a | H | \psi(G) \rangle = \sqrt{2F_{ia}}$$

$$\langle {}^2\psi(D)_i^a | H | \psi(G) \rangle = \sqrt{\tfrac{3}{2}}(if \mid fa)$$

$$\langle {}^2\psi(A)_i^f | H | {}^2\psi(A)_i^f \rangle = \delta_{ij}(F_{ff} + \tfrac{1}{2}J_{ff}) - F_{ij} + \tfrac{3}{2}(jf \mid fi) - (ji \mid ff)$$

$$\langle {}^2\psi(B)_f^a | H | {}^2\psi(B)_f^b \rangle = \delta_{ab}(-F_{ff} + \tfrac{1}{2}J_{ff}) + F_{ab} - (ff \mid ab) + \tfrac{3}{2}(fa \mid fb)$$

$$\langle {}^2\psi(C)_i^a | H | {}^2\psi(C)_j^b \rangle = \delta_{ij}[F_{ab} + (bf \mid fa)] - \delta_{ab}[F_{ij} - (if \mid fa)] + 2(ia \mid bf) - (ij \mid ba)$$

$$\langle {}^2\psi(D)_i^a | H | {}^2\psi(C)_j^b \rangle = \delta_{ij}[F_{ab} + 2(af \mid fb)] - \delta_{ab}[F_{ij} - 2(if \mid fj)] - (ij \mid ba)$$

$$\langle {}^2\psi(B)_f^a | H | {}^2\psi(A)_i^f \rangle = (fi \mid fa)$$

$$\langle {}^2\psi(C)_i^a | H | {}^2\psi(A)_j^f \rangle = \frac{1}{\sqrt{2}}[\delta_{ij}(F_{fa} + (ff \mid af)) + 2(fj \mid ia) - (fa \mid ij)]$$

$$\langle {}^2\psi(D)_i^a | H | {}^2\psi(A)_j^f \rangle = \sqrt{\tfrac{3}{2}}[-\delta_{ij}(F_{fa} + (ff \mid af)) + (ij \mid fa)]$$

$$\langle {}^2\psi(C)_i^a | H | {}^2\psi(B)_f^b \rangle = \frac{1}{\sqrt{2}}[\delta_{ab}(-F_{if} + (ff \mid if)) + 2(ia \mid bf) - (if \mid ba)]$$

$$\langle {}^2\psi(D)_i^a | H | {}^2\psi(B)_f^b \rangle = \sqrt{\tfrac{3}{2}}[\delta_{ab}(F_{if} - (ff \mid if)) - (ab \mid if)]$$

$$\langle {}^2\psi(D)_i^a | H | {}^2\psi(C)_j^b \rangle = \sqrt{\tfrac{3}{2}}[\delta_{ab}(if \mid fj) - \delta_{ij}(bf \mid fa)]$$

$$f = \sqrt{2\text{m}}. \tag{23}$$

Lowitz [12] has also derived some of the expressions of Table 1 for specific configurations of the TCNQ(−1) ion.

3. Results

3.1. *Iron(III) Complexes*

The metal core charges +0.50, +0.46 used in earlier work on the hypothetical mono complexes of Fe^{II}-phen and dipy [6] provide a reasonable starting point for calculations upon the corresponding open-shell species. Ground and excited state wavefunctions were computed by first using a Hückel calculation to produce trial wavefunctions, next generating the SCF basis using the Roothaan parameters ($f=0.5$, $\alpha=-2.0$, $\beta=-6.0$), and specifying that the coefficient of metal d_{xz} or d_{yz} AO in the open-shell MO be $\geqslant \frac{1}{2}$, then transforming this basis under ($f=0.5$, $\alpha=0.0$, $\rho=-2.0$) and finally carrying out CI.

The generation of the intermediate basis is necessitated by the failure to reach self-consistency of calculations in which the Roothaan parameters ($f=0.5$, $\alpha=0.0$, $\beta=-2.0$) are applied to approximate wavefunctions. The procedure just described avoids the difficulty for the following reason: if the MO's of a metal-ligand complex may be written to first-order as linear combinations of metal d and ligand π, π^* orbitals, the open-shell MO then takes the form:

$$\phi_m = N^{-1/2}\Big[\chi(d_{xz}) + \sum_j C_{mj}\phi(\pi_j) + \sum_k C_{mk}\phi(\pi_k^*)\Big] \tag{24}$$

The coefficients C_{mj}, C_{mk} depend by perturbation theory upon the reciprocal of the energy differences $(E(d_{xz})-E(\pi_j))$, $(E(d_{xz})-E(\pi_k^*))$. If one puts $f=0.5$, $\alpha=0.0$, $\beta=-2.0$, the metal d_{xz} and the upper ligand π_j orbitals take up similar eigenvalues, so that the small changes in $E(\pi_j)$ which occur between successive cycles of the refinement of approximate wavefunctions can significantly affect C_{mo}. Under these conditions the complex wavefunctions may oscillate rather than converge to self-consistency.

However, from (2) the eigenvalue of an orbital ϕ_i varies with the Roothaan α, β parameters as $(\phi_i|2\alpha J_0 - \beta K_o|\phi_i)$; so that:

$$\begin{aligned} E_i(f=0.5,\ \alpha=0.0,\ \beta=-2.0) = {} & E_i(f=0.5,\ \alpha=-2.0,\ \beta=-6.0) \\ & + 4(\phi_i|J_o|\phi_i) - 4(\phi_i|K_o|\phi_i); \end{aligned} \tag{25}$$

which for closed- and open-shell MO's respectively, simplifies to:

$$\begin{aligned} E_a(f=0.5,\ \alpha=0.0,\ \beta=-2.0) = {} & E_a(f=0.5,\ \alpha=-2.0,\ \beta=-6.0) \\ & + 4(\phi_m\phi_m \mid \phi_a\phi_a) - 4(\phi_m\phi_a \mid \phi_m\phi_a), \end{aligned} \tag{26}$$

$$E_m(f=0.5,\ \alpha=0.0,\ \beta=-2.0) = E_m(f=0.5,\ \alpha=-2.0,\ \beta=-6.0). \tag{27}$$

Now since the Coulombic integral $(\phi_m\phi_m \mid \phi_a\phi_a)$ is considerably larger than the exchange integral $(\phi_m\phi_a \mid \phi_m\phi_a)$, it follows that the eigenvalues of closed-shell MO's take lower values under ($f=0.5$, $\alpha=-2.0$, $\beta=-6.0$) than under ($f=0.5$, $\alpha=0.0$, $\beta=-2.0$). Thus, $E(d_{xz})$ and $E(\pi j)$ are well separated in the former case; so that the coefficients C_{mj} of (26) are less sensitive to $(E(d_{xz})-E(\pi_j))$, and self-consistent solutions are easily obtained. In trial calculations on $TCNQ^-$ it was found, as anticipated, that both choices of α, β gave identical results for physically observable ground state quantities such as charge and spin-densities.

Table 2. Calculated energies and intensities of low-energy excitations of Fe(III)-phen. The metal core-charge is fixed at +0.50; 40 configurations of $\pi(A)$, $\pi(B)$, $\pi(C)$ type, and $\pi(D)$ configurations corresponding to the $\pi(C)$, are employed in CI

Energy (kK)	$f(DL)$	$f(DV)$	Principal assignment[a]
a) Unpaired electron located principally in d_{xz}			
18.77	0.004	0.002	$\pi 1 \rightarrow \mathrm{M}, (\pi 1 \rightarrow \pi 2^*(D))$
21.30	0.003	0.003	$\pi 2 \rightarrow \mathrm{M}, (\pi 2 \rightarrow \pi 2^*(D))$
23.30	0.000	0.000	$\pi 2 \rightarrow \pi 1^*(D), \pi 3 \rightarrow \pi 2^*(D)$
23.82	0.000	0.000	$\pi 1 \rightarrow \pi 1^*(D)$
25.47	0.001	0.001	$\pi 1 \rightarrow \pi 2^*(D), (\pi 1 \rightarrow \mathrm{M})$
25.91	0.001	0.001	$\pi 2 \rightarrow \pi 2^*(D), \pi 3 \rightarrow \pi 1^*(D)$
30.47	0.044	0.013	$\pi 1 \rightarrow \pi 1^*$
31.46	0.001	0.001	$\pi 1 \rightarrow \pi 3^*(D), \pi 3 \rightarrow \pi 1^*(D)$
31.89	0.033	0.028	$\pi 3 \rightarrow \mathrm{M}, \pi 1 \rightarrow \pi 4^*(D)$
32.18	0.466	0.230	$\pi 1 \rightarrow \pi 2^*$
32.62	0.364	0.235	$\pi 2 \rightarrow \pi 1^*, (\pi 1 \rightarrow \pi 4^*(D))$
33.23	0.173	0.123	$\pi 3 \rightarrow \mathrm{M}, \pi 2 \rightarrow \pi 1^*$
35.71	0.138	0.043	$\pi 2 \rightarrow \pi 2^*, \pi 1 \rightarrow \pi 3^*$
b) Unpaired electron located principally in d_{yz}			
18.66	0.005	0.005	$\pi 1 \rightarrow \mathrm{M}$
22.19	0.000	0.000	$\pi 1 \rightarrow \pi 1^*(D)$
22.28	0.001	0.001	$\pi 2 \rightarrow \mathrm{M}$
23.38	0.000	0.000	$\pi 1 \rightarrow \pi 2^*(D), \pi 2 \rightarrow \pi 1^*(D)$
25.69	0.000	0.000	$\pi 1 \rightarrow \pi 2^*(D), \pi 2 \rightarrow \pi 1^*(D)$
26.50	0.000	0.000	$\pi 1 \rightarrow \pi 2^*(D), \pi 2 \rightarrow \pi 1^*(D)$
30.84	0.005	0.001	$\pi 1 \rightarrow \pi 1^*$
31.49	0.012	0.002	$\pi 1 \rightarrow \pi 2^*, \pi 2 \rightarrow \pi 1^*$
33.06	0.000	0.000	$\pi 1 \rightarrow \pi 4^*(D), \pi 1 \rightarrow \pi 5^*(D)$
33.61	1.116	0.608	$\pi 1 \rightarrow \pi 2^*, \pi 2 \rightarrow \pi 1^*$
33.62	0.004	0.001	$\pi 3 \rightarrow \mathrm{M}$
34.54	0.000	0.000	$\pi 1 \rightarrow \pi 3^*(D)$
35.41	0.000	0.000	$\pi 2 \rightarrow \pi 3^*(D), \pi 3 \rightarrow \pi 1^*(D)$
37.66	0.591	0.270	$\pi 2 \rightarrow \pi 2^*$

[a] π-orbitals are labelled in order of decreasing binding energy, as follows:

A_2: $\pi 1, \pi 3, \pi 5, \pi 7, \pi 1^*, \pi 3^*, \pi 6^*$;
B_1: $\pi 2, \pi 4, \pi 6, \pi 2^*, \pi 4^*, \pi 5^*, \pi 7^*$.

Configurations reported outside brackets contribute more than 10% to the state wavefunction; configurations reported within brackets contribute 5–10% to the state wavefunction.

Energies and intensities of low-energy (<40 kK) excitations of the $\mathrm{Fe^{III}}$-phen and dipy monocomplexes, calculated using the parameters originally employed by Sanders and Day [6] for the corresponding Fe complexes, are reported in Tables 2 and 3. The two modes of $(\pi \rightarrow d)$ CT interaction in tris complexes, i.e. $(A_2) \rightarrow d_{yz}$, $(B_1) \rightarrow d_{xz}$, are represented by separate calculations in which the spin-free electron is principally located in the d_{yz}, d_{xz} orbitals respectively. In addition, CI excited configurations of $\pi(D)$ type (Eq. (20)) are included.

Table 3. Calculated energies and intensities of low-energy excitations of Fe(III)-dipy. The metal core-charge is fixed as +0.46; 40 configurations of $\pi(A)$, $\pi(B)$, $\pi(C)$ type, and $\pi(D)$ configurations corresponding to the $\pi(C)$, are employed in CI

Energy (kK)	$f(DL)$	$f(DV)$	Principal assignment[a]
a) Unpaired electron located principally in d_{yz}			
17.07	0.005	0.001	$\pi1 \rightarrow \mathrm{M}, (\pi1 \rightarrow \pi1^*(D))$
22.80	0.000	0.000	$\pi2 \rightarrow \mathrm{M}, \pi1 \rightarrow \pi2^*(D),$ $\pi2 \rightarrow \pi1^*(D)$
24.15	0.009	0.005	$\pi1 \rightarrow \pi1^*(D), (\pi1 \rightarrow M)$
27.15	0.000	0.000	$\pi2 \rightarrow \mathrm{M}, \pi1 \rightarrow \pi2^*(D),$ $\pi2 \rightarrow \pi1^*(D)$
29.02	0.000	0.000	$\pi2 \rightarrow \mathrm{M}, \pi2 \rightarrow \pi1^*(D)$
29.17	0.000	0.000	$\pi1 \rightarrow \pi3^*(D), \pi3 \rightarrow \pi1^*(D),$
29.66	0.000	0.000	$\pi2 \rightarrow \pi2^*(D), \pi3 \rightarrow \mathrm{M}$
30.23	0.006	0.002	$\pi4 \rightarrow \mathrm{M}, \pi4 \rightarrow \pi1^*(D),$ $\pi3 \rightarrow \pi2^*(D)$
31.90	0.642	0.368	$\pi1 \rightarrow \pi1^*$
35.80	0.010	0.005	$\pi4 \rightarrow \mathrm{M}, (\pi4 \rightarrow \pi1^*(D))$
35.86	0.010	0.009	$\pi3 \rightarrow \mathrm{M}, (\pi3 \rightarrow \pi1^*(D))$
39.84	0.247	0.128	$\pi1 \rightarrow \pi2^*$
b) Unpaired electron located principally in d_{xz}			
18.35	0.002	0.001	$\pi1 \rightarrow \mathrm{M}, (\pi1 \rightarrow \pi2^*(D))$
21.90	0.000	0.000	$\pi1 \rightarrow \pi1^*(D), \pi2 \rightarrow \pi2^*(D)$
25.16	0.000	0.000	$\pi1 \rightarrow \pi2^*(D), \pi2 \rightarrow \pi1^*(D),$ $(\pi1 \rightarrow \mathrm{M})$
26.86	0.000	0.000	$\pi2 \rightarrow \mathrm{M}, (\pi1 \rightarrow \pi1^*(D))$
28.30	0.000	0.000	$\pi1 \rightarrow \pi4^*(D), \pi2 \rightarrow \pi1^*(D),$ $\pi2 \rightarrow \pi3^*(D), \pi1 \rightarrow \pi2^*(D)$
30.43	0.001	0.000	$\pi1 \rightarrow \pi3^*(D), (\pi2 \rightarrow \mathrm{M})$
30.48	0.003	0.002	$\pi3 \rightarrow \pi1^*(D), (\pi4 \rightarrow \mathrm{M})$
31.83	0.005	0.004	$\pi4 \rightarrow \pi1^*(D), \pi3 \rightarrow \pi2^*(D),$ $\pi4 \rightarrow \mathrm{M}$
32.28	0.820	0.508	$\pi1 \rightarrow \pi1^*$
33.91	0.012	0.005	$\pi4 \rightarrow \mathrm{M}, \pi3 \rightarrow \pi1^*(D))$
34.88	0.008	0.005	$\pi3 \rightarrow \mathrm{M}, (\pi3 \rightarrow \pi2^*(D))$
40.71	0.422	0.220	$\pi1 \rightarrow \pi2^*, (\pi2 \rightarrow \pi1^*)$

[a] Occupied π-orbitals are labelled in order of decreasing binding energy, followed by the unoccupied orbitals. Thus 1 is the highest filled and 1* the lowest empty orbital.

A_2: $\pi2, \pi4, \pi6, \pi1^*, \pi3^*, \pi5^*$;
B_1: $\pi1, \pi3, \pi5, \pi2^*, \pi4^*, \pi6^*$.

Configurations reported outside brackets contribute > 10% to the state wavefunction; configurations reported within brackets contribute ~5–10% to the state wavefunction.

Published experimental data for the complexes Fe^{III}(phen), Fe^{III}(dipy) are confined to detail of the CT band energies at about 18 kK [13]. Nonetheless, several useful theoretical results are indicated by the present study. First, the use of metal core charges appropriate to Fe^{II}(phen), Fe^{II}(dipy) gives calculated energies for the first CT bands of Fe^{III}(phen), Fe^{III}(dipy) at approximately the observed values. When the core-charges are lowered to $+0.30$ the energy of ($\pi 1 \rightarrow$ M) charge transfer is increased to about 29 kK. Second, the dipole length and velocity intensities of CT transitions in which the contributions of localized ligand excitations are negligible are approximately equal. Third, in no cases do low energy transitions of $\psi_0 \rightarrow \psi_i(D)$ character borrow sufficient intensity to be spectrally significant, other than in the induction of small perturbations to the energies of adjacent excitations. Fourth, the calculated intensities of $\pi \rightarrow$ Fe^{III} charge transfer are much lower than those of Fe$^{II} \rightarrow \pi^*$ charge transfer in the corresponding Fe^{II} complexes. A discussion of this effect is presented below.

Table 4. Calculated energies and intensities of the low-energy excitations of Ru(II)-phen. The metal core-charge is fixed as 0.20; 30 configurations are employed in CI

Energy (kK)	$f(DL)$	Principal assignment	Observed energy
20.14	0.005	$M(xz) \rightarrow \pi 2^*$	
20.97	0.015	$M(xz) \rightarrow \pi 1^*$, $M(yz) \rightarrow \pi 2^*$	22–24
22.65	0.055	$M(yz) \rightarrow \pi 1^*$	
25.25	0.132	$M(yz) \rightarrow \pi 2^*$, $M(xz) \rightarrow \pi 1^*$	
31.48	0.007	$M(yz) \rightarrow \pi 3^*$ $\pi 2 \rightarrow \pi 1^*$, $\pi 1 \rightarrow \pi 2^*$	30
32.68	0.278	$\pi 1 \rightarrow \pi 1^*$, $M(xz) \rightarrow \pi 3^*$	32.5
33.56	0.008	$\pi 1 \rightarrow \pi 1^*$, $\pi 2 \rightarrow \pi 2^*$ $M(xz) \rightarrow \pi 3^*$	
34.34	0.003	$M(yz) \rightarrow \pi 3^*$, $\pi 1 \rightarrow \pi 2^*$	
35.98	0.863	$\pi 2 \rightarrow \pi 2^*$	36
37.55	0.170	$\pi 2 \rightarrow \pi 1^*$	38
44.32	0.644	$\pi 1 \rightarrow \pi 3^*$ ($\pi 2 \rightarrow \pi 1^*$)	44

3.2. *Spectra of Ruthenium-Phenanthroline, Dipyridyl Complexes*

The spectra of Ru^{II}(phen)$_3$, Ru^{III}(phen)$_3$, Ru^{II}(dipy)$_3$, Ru^{III}(dipy)$_3$ have been reported by Mason [13] and Crosby *et al.* [1]. MO calculations upon the hypothetical monocomplexes parallel those described for the corresponding iron species. However, it should be noted that the VOIP of ruthenium atoms is expressed as a function of core-charge, Z, by applying the procedure of Basch, Viste and Gray [14] to the atomic spectral data of Moore [15]. VOIP(0), VOIP(1) are calculated as 6.9, 15.4 eV respectively. Lack of experimental data precludes estimation of VOIP(2), but consideration of iron VOIP data reveals that the function VOIP(Z) is approximately linear for $Z<2$. On this basis a linear relationship between VOIP(0) VOIP(1) may be assumed to indicate the appropriate value of VOIP(Z) for ruthenium.

3.2.1 Ruthenium(II) Complexes

The spectra of $\mathrm{Ru^{II}(phen)_3}$, $\mathrm{Ru^{II}(dipy)_3}$ are generally similar to those of the corresponding iron complexes. Absorption from 20–30 kK may be assigned to $\mathrm{Ru^{II}} \rightarrow$ ligand π^* charge transfer whilst peaks from 30–45 kK correspond to internal excitations of the ligand. The observed CT energies are reproduced in SCF-MO calculations on $\mathrm{Ru^{II}}$-phen, $\mathrm{Ru^{II}}$-dipy, if in each case a value $+0.20$ is assigned to the ruthenium atom core-charge, Z_{Ru}. Energies, intensities and principal assignments of all transitions in the spectral region below 45 kK are reported in Tables 4 and 5, with their correspondence to the observed band energies in the corresponding tris-complexes, $\mathrm{Ru^{II}(phen)_3}$ and $\mathrm{Ru^{II}(dipy)_3}$. Note, in particular, that the transitions at 36 and 44 kK in $\mathrm{Ru^{II}(phen)_3}$ and at 35 and 40 kK in $\mathrm{Ru^{II}(dipy)_3}$, are calculated to be strongly allowed, in agreement with experiment. The absolute intensities of the CT excitations are discussed in Sect. 3.2.3.

Table 5. Calculated energies and intensities of low-energy excitations of Ru(II)-dipy. The metal core-charge is fixed as 0.20; 30 configurations are employed in CI

Energy (kK)	$f(DL)$	Principal assignment	Observed energy
18.80	0.004	$M(xz) \rightarrow \pi 1^*$	(18)
21.10	0.058	$M(yz) \rightarrow \pi 1^*$	22
27.06	0.047	$M(xz) \rightarrow \pi 2^*$	
29.47	0.109	$M(yz) \rightarrow \pi 2^*$	29
31.38	0.068	$M(xz) \rightarrow \pi 3^*$ $(\pi 1 \rightarrow \pi 1^*)$	31
31.39	0.009	$M(yz) \rightarrow \pi 3^*$	
34.11	0.861	$\pi 1 \rightarrow \pi 1^*$ $(M(xz) \rightarrow \pi 3^*)$	35
37.75	0.045	$M(xz) \rightarrow \pi 4^*$ $(\pi 1 \rightarrow \pi 2^*, \pi 2 \rightarrow \pi 1^*)$	
38.44	0.032	$M(yz) \rightarrow \pi 4^*$ $(\pi 1 \rightarrow \pi 1^*)$	
40.82	0.190	$\pi 1 \rightarrow \pi 2^*, \pi 2 \rightarrow \pi 1^*,$ $M(xz) \rightarrow \pi 4^*$	40

3.2.2 Ruthenium(III) Complexes

Mason [13] assigned the visible and near-UV absorption in the spectra of $\mathrm{Ru^{III}(phen)_3}$, $\mathrm{Ru^{III}(dipy)_3}$ to ligand $\pi \rightarrow$ metal t_{2g} charge transfer. As in the corresponding $\mathrm{Ru^{II}}$, $\mathrm{Fe^{II}}$, $\mathrm{Fe^{III}}$ complexes, absorption from 30–45 kK is dominated by localized ligand excitations.

Tables 6 and 7 show the energies, intensities and principal assignments of low-energy transitions of $\mathrm{Ru^{III}}$-phen, dipy, as given by MO calculations using the method outlined in Sect. 2 and the parametrization scheme employed for the $\mathrm{Ru^{II}}$ complexes. From the viewpoint of the "average" ligand in a tris(ligand)-metal

Table 6. Calculated energies and intensities of low-energy excitations of Ru(III)-phen. The metal core-charge is fixed at +0.20; 40 configurations of $\pi(A)$, $\pi(B)$, $\pi(C)$ type, and $\pi(D)$ configurations corresponding to the $\pi(C)$, are employed in CI

a) Unpaired electron located principally in d_{yz}

Energy (kK)	$f(DL)$	Principal assignment
14.74	0.004	$\pi1 \rightarrow \mathrm{M}, (\pi1 \rightarrow \pi2^*(D))$
18.53	0.005	$\pi2 \rightarrow \mathrm{M}, (\pi1 \rightarrow \pi1^*(D))$
22.83	0.002	$\pi2 \rightarrow \pi2^*(D), (\pi2 \rightarrow \mathrm{M})$
23.39	0.001	$\pi1 \rightarrow \pi2^*(D), \pi2 \rightarrow \pi1^*(D)$
24.48	0.000	$\pi2 \rightarrow \pi1^*(D), \pi1 \rightarrow \pi2^*(D)$
26.19	0.003	$\pi2 \rightarrow \pi2^*(D), (\pi2 \rightarrow \mathrm{M})$
27.85	0.002	$\pi3 \rightarrow \mathrm{M}, \pi5 \rightarrow \mathrm{M}$
29.77	0.001	$\pi5 \rightarrow \mathrm{M}, \pi1 \rightarrow \pi4^*(D),$ $\pi2 \rightarrow \pi1^*(D), \pi2 \rightarrow \pi3^*(D),$ $\pi3 \rightarrow \pi2^*(D), \pi4 \rightarrow \pi1^*(D)$
30.38	0.002	$\pi1 \rightarrow \pi1^*, (\pi2 \rightarrow \pi2^*)$
30.75	0.000	$\pi1 \rightarrow \pi3^*(D), \pi2 \rightarrow \pi4^*(D),$ $\pi3 \rightarrow \pi1^*(D), \pi4 \rightarrow \pi2^*(D)$
31.65	0.018	$\pi1 \rightarrow \pi2^*, \pi2 \rightarrow \pi1^*$
33.68	0.758	$\pi1 \rightarrow \pi2^*, \pi2 \rightarrow \pi1^*$
34.13	0.219	$\pi3 \rightarrow \mathrm{M}, \pi5 \rightarrow \mathrm{M},$ $\pi2 \rightarrow \pi1^*$
35.81	0.005	$\pi4 \rightarrow \mathrm{M}, (\pi2 \rightarrow \pi4^*(D))$
36.24	0.213	$\pi2 \rightarrow \pi2^*, (\pi1 \rightarrow \pi1^*),$ $(\pi1 \rightarrow \pi3^*)$
42.82	0.272	$\pi1 \rightarrow \pi3^*, \pi2 \rightarrow \pi2^*,$ $\pi3 \rightarrow \pi1^*$

b) Unpaired electron located principally in d_{xz}

Energy (kK)	$f(DL)$	Principal assignment
14.53	0.009	$\pi1 \rightarrow \mathrm{M}, (\pi1 \rightarrow \pi1^*(D))$
17.12	0.006	$\pi2 \rightarrow \mathrm{M}, (\pi2 \rightarrow \pi1^*(D))$
22.96	0.009	$\pi2 \rightarrow \pi2^*(D), (\pi1 \rightarrow \mathrm{M}),$ $\pi3 \rightarrow \pi1^*(D), (\pi3 \rightarrow \mathrm{M})$
23.69	0.003	$\pi1 \rightarrow \pi2^*(D)$
24.82	0.003	$\pi1 \rightarrow \pi1^*(D),$ $(\pi1 \rightarrow \mathrm{M}), (\pi3 \rightarrow \mathrm{M})$
27.11	0.021	$\pi2 \rightarrow \mathrm{M}, \pi4 \rightarrow \mathrm{M},$ $\pi2 \rightarrow \pi1^*(D), \pi4 \rightarrow \pi1^*(D)$
28.19	0.001	$\pi4 \rightarrow \mathrm{M}, \pi2 \rightarrow \pi1^*(D),$ $\pi1 \rightarrow \pi4^*(D)$
29.66	0.007	$\pi3 \rightarrow \mathrm{M}, \pi1 \rightarrow \pi3^*(D)$ $\pi2 \rightarrow \pi2^*(D)$
30.99	0.000	$\pi1 \rightarrow \pi1^* (\pi2 \rightarrow \pi2^*)$
31.82	0.117	$\pi1 \rightarrow \pi2^* (\pi2 \rightarrow \pi1^*)$

b) Unpaired electron located principally in d_{xz}—cont.

Energy (kK)	$f(DL)$	Principal assignment
33.26	0.002	$\pi4 \rightarrow \mathrm{M}$, $\pi2 \rightarrow \pi3^*(D)$, $\pi3 \rightarrow \pi2^*(D)$
34.06	0.828	$\pi2 \rightarrow \pi1^*$, $(\pi3 \rightarrow \pi2^*)$
34.19	0.055	$\pi3 \rightarrow \mathrm{M}$, $\pi1 \rightarrow \pi3^*(D)$, $\pi4 \rightarrow \pi2^*(D)$
36.26	0.171	$\pi2 \rightarrow \pi2^*$ $(\pi1 \rightarrow \pi1^*)$
42.76	0.228	$\pi1 \rightarrow \pi3^*$, $(\pi3 \rightarrow \pi1^*)$
43.70	0.152	$\pi4 \rightarrow \mathrm{M}$, $\pi4 \rightarrow \pi2^*(D)$, $(\pi1 \rightarrow \pi3^*)$, $(\pi2 \rightarrow \pi2^*)$

(d^5) complex, the t_{2g} hole spends approximately one-third of its time in each of the d_{xy}, d_{xz}, d_{yz} orbitals. Ligand to metal CT interaction in the "average" metal-ligand pair is then in equal (one-third) parts of $\pi2 \rightarrow d_{xy}$, $\pi2 \rightarrow d_{xz}$, $\pi2 \rightarrow d_{yz}$ character, and is mirrored three times in the complex. Tables 6a and 7b show spectra calculated assuming ligand ($\pi2$) → metal (d_{yz}) CT interaction, while Tables 6b and 7a show spectra calculated assuming ligand ($\pi2$) → metal (d_{xz}) CT interaction. Since ligand ($\pi2$) → metal (d_{xy}) CT resonance is forbidden by symmetry, the summed CT intensities of Tables 6a and 6b and 7a and 7b should be comparable with experimental data for $\mathrm{Ru^{III}(phen)_3}$, $\mathrm{Ru^{III}(dipy)_3}$ respectively.

As for the $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$ complexes, such comparison shows that the observed energies of CT transitions in the oxidized species are accurately reproduced by MO calculations using values of metal atom core-charge empirically deduced for the reduced species, i.e. by $Z_{\mathrm{Ru}} = +0.20$. The following band assignments are indicated:

Band	Assignment
	$\mathrm{Ru^{III}(phen)_3}$
19 kK	gains intensity from elements of $\pi1 \rightarrow \mathrm{M}$, $\pi2 \rightarrow \mathrm{M}$ charge-transfer within excitations of $\pi \rightarrow \mathrm{M}$, $\pi \rightarrow \pi(D)$ type.
27 kK	the principal transition is of $\pi2 \rightarrow \mathrm{M}$, $\pi4 \rightarrow \mathrm{M}$, $\pi \rightarrow \pi(D)$ type, but gains intensity from admixture of ~2.5% $\pi2 \rightarrow \pi1^*$ character.
33 kK	$\pi1 \rightarrow \pi2^*$
37 kK	$\pi2 \rightarrow \pi1^*$
43 kK	$\pi1 \rightarrow \pi3^*$
	$\mathrm{Ru^{III}(dipy)_3}$
15 kK 25 kK	arise from transitions to states formed by combination of $\pi1 \rightarrow \mathrm{M}$, $\pi \rightarrow \pi(D)$ (principally $\pi1 \rightarrow \pi3^*(D)$) configurations. The two principal transitions ~25 kK gain intensity by admixture of 0.75, 2.5% $\pi1 \rightarrow \pi1^*$ character.
31 kK (sh)	composed of transitions of $\pi2 \rightarrow \mathrm{M}$, $\pi3 \rightarrow \mathrm{M}$, $\pi4 \rightarrow \mathrm{M}$, $\pi \rightarrow \pi(D)$ character.
35 kK	$\pi1 \rightarrow \pi1^*$
41 kK	arises from a transition to a state of $\pi1 \rightarrow \pi2^*$, $\pi2 \rightarrow \pi1^*$ character.

Table 7. Calculated energies and intensities of low-energy excitations of Ru(III)-dipy. The metal core-charge is fixed at +0.20; 40 configurations of $\pi(A)$, $\pi(B)$, $\pi(C)$ type, and $\pi(D)$ configurations corresponding to the $\pi(C)$, are employed in CI

Energy (kK)	$f(DL)$	Principal assignment
a) Unpaired electron located principally in d_{xz}		
17.21	0.004	$\pi1 \rightarrow \mathrm{M}$, $\pi1 \rightarrow \pi2^*(D)$
20.41	0.000	$\pi1 \rightarrow \pi1^*(D)$, $(\pi2 \rightarrow \mathrm{M})$
24.47	0.001	$\pi2 \rightarrow \mathrm{M}$, $\pi2 \rightarrow \pi3^*(D)$
25.23	0.001	$\pi2 \rightarrow \pi1^*(D)$, $\pi1 \rightarrow \pi2^*(D)$, $(\pi1 \rightarrow \mathrm{M})$
27.28	0.002	$\pi2 \rightarrow \mathrm{M}$, $\pi3 \rightarrow \mathrm{M}$, $\pi2 \rightarrow \pi3^*(D)$
27.85	0.000	$\pi2 \rightarrow \pi3^*(D)$, $\pi3 \rightarrow \pi1^*(D)$, $\pi1 \rightarrow \pi4^*(D)$, $\pi1 \rightarrow \pi2^*(D)$
29.35	0.007	$\pi2 \rightarrow \mathrm{M}$, $\pi1 \rightarrow \pi3^*(D)$, $\pi3 \rightarrow \mathrm{M}$, $\pi3 \rightarrow \pi2^*(D)$, $\pi4 \rightarrow \pi1^*(D)$
29.71	0.004	$\pi4 \rightarrow \mathrm{M}$, $\pi3 \rightarrow \pi1^*(D)$, $\pi4 \rightarrow \pi2^*(D)$
31.58	0.729	$\pi1 \rightarrow \pi1^*$
33.56	0.091	$\pi4 \rightarrow \pi1^*(D)$, $(\pi3 \rightarrow \mathrm{M})$
35.67	0.023	$\pi4 \rightarrow \mathrm{M}$, $\pi3 \rightarrow \pi1^*(D)$
38.80	0.154	$\pi1 \rightarrow \pi2^*$, $\pi2 \rightarrow \pi1^*$
b) Unpaired electron located principally in d_{yz}		
15.00	0.007	$\pi1 \rightarrow \mathrm{M}$, $\pi1 \rightarrow \pi1^*(D)$
21.07	0.000	$\pi2 \rightarrow \mathrm{M}$, $\pi1 \rightarrow \pi2^*(D)$, $\pi2 \rightarrow \pi1^*(D)$
24.06	0.018	$\pi1 \rightarrow \mathrm{M}$, $\pi1 \rightarrow \pi1^*(D)$ $\pi1 \rightarrow \pi3^*(D)$
26.17	0.018	$\pi1 \rightarrow \pi3^*(D)$, $(\pi1 \rightarrow \mathrm{M})$, $(\pi3 \rightarrow \mathrm{M})$
27.03	0.002	$\pi2 \rightarrow \mathrm{M}$, $\pi4 \rightarrow \mathrm{M}$, $\pi2 \rightarrow \pi3^*(D)$, $\pi1 \rightarrow \pi2^*(D)$
27.05	0.000	$\pi3 \rightarrow \mathrm{M}$, $\pi1 \rightarrow \pi3^*(D)$, $\pi3 \rightarrow \pi1^*(D)$, $\pi4 \rightarrow \pi2^*(D)$
29.17	0.008	$\pi2 \rightarrow \mathrm{M}$, $\pi1 \rightarrow \pi2^*(D)$, $\pi4 \rightarrow \mathrm{M}$, $\pi3 \rightarrow \pi2^*(D)$
29.80	0.002	$\pi2 \rightarrow \mathrm{M}$, $\pi4 \rightarrow \mathrm{M}$, $\pi2 \rightarrow \pi1^*(D)$, $\pi2 \rightarrow \pi3^*(D)$
31.70	0.625	$\pi1 \rightarrow \pi1^*$
34.57	0.024	$\pi3 \rightarrow \mathrm{M}$, $\pi3 \rightarrow \pi1^*(D)$, $\pi2 \rightarrow \pi4^*(D)$
37.07	0.011	$\pi4 \rightarrow \mathrm{M}$, $\pi3 \rightarrow \pi2^*(D)$, $\pi4 \rightarrow \pi1^*(D)$
39.74	0.313	$\pi1 \rightarrow \pi2^*$

3.2.3. Intensities of CT Transitions in Ru^{II} and Ru^{III} Complexes

A striking feature of the charge-transfer transitions in the Ru^{II} and Ru^{III} complexes is that the former are very much more intense than the latter. This feature is reproduced very successfully by the present calculations, as shown below. (The calculated oscillator strengths are obtained using the dipole-length approximation):

	E	f(calc)	f(obs)
$Ru(phen)_3^{2+}$	22 kK	0.62	0.42
$Ru(phen)_3^{3+}$	19 kK	0.042	0.033
$Ru(dipy)_3^{2+}$	22 kK	0.19	0.20
$Ru(dipy)_3^{3+}$	15 kK	0.011	0.007

A qualitative explanation for the difference may be found in the following considerations. The intensities of metal → ligand, ligand → metal CT excitations are approximately proportional to the squares of the appropriate metal-ligand resonance integrals, $(\pi_i|H|\mathrm{M})$, $(\pi_j^*|H|\mathrm{M})$:

$$(\pi_i|H|\mathrm{M}) \sim C_{i\mathrm{A}}\beta_{\mathrm{MA}} + C_{i\mathrm{B}}\beta_{\mathrm{MB}},$$
$$(\pi_j^*|H|\mathrm{M}) \sim C_{j\mathrm{A}}^*\beta_{\mathrm{MA}} + C_{j\mathrm{B}}^*\beta_{\mathrm{MB}},$$

where A, B are the ligand nitrogen atoms; and β_{MA}, β_{MB} are resonance integrals between the metal atom and A, B. Since VSIP(N) > VSIP(C) the nitrogen Fock elements F_{NN} are more negative than those for carbon, F_{CC}. In consequence, the largest values of $C_{i\mathrm{A}}$, $C_{i\mathrm{B}}$ and $C_{j\mathrm{A}}^*$, $C_{j\mathrm{B}}^*$ are found in the lowest energy MO's πm, πn^* (where $m = 5,6$ for dipy, 6,7 for phen; $n = 1,2$).

The integrals $(\pi 1^*|H|\mathrm{M})$, $(\pi 2^*|H|\mathrm{M})$, governing the intensities of low-energy M^{II}-ligand transitions, are then somewhat larger than the integrals $(\pi 1|H|\mathrm{M})$, $(\pi 2|H|\mathrm{M})$, which determine the intensities of low-energy CT excitations in the M^{III} complexes. Together with the fact that any one of six electrons may be transferred in an $M^{II}(d^6)$ → ligand CT process, as opposed to only one in a ligand → $M^{III}(d^5)$ transition, this accounts for the much greater CT intensity in the M^{II} complexes.

4. Conclusions

We have shown that Roothaan's open-shell SCF-MO theory, when approximated at the INDO level, is quite successful in explaining the main features of the spectra, both charge transfer and intra-ligand, of Fe(III) and Ru(III) complexes with conjugated heterocycles such as phenanthroline and dipyridyl. Energies and oscillator strengths of the transitions are reproduced by only a single freely variable parameter, the core charge of the metal atom. This gives us confidence that excited state properties of complexes with other ligands which may be of interest from the point of view of luminescence or photochemistry could be predicted.

Other physical insights also result. For example, all the calculated states of Ru(II) phen and dipy below 30 kK are overwhelmingly of Ru → π^* CT type, no

$\pi \rightarrow \pi^*$ configurations contributing as much as 10% to the wavefunctions. The electron distribution in these excited states is therefore quite close to Ru(d^5) $(\pi 1^*)^1$ or Ru(d^5) $(\pi 2^*)^1$, and the reason why they should combine strong reducing properties with moderately strong oxidizing properties is immediately clear. A further point which has assumed some importance for the detailed interpretation of both absorption and luminescence of the Ru(II) dipy and phen complexes concerns the symmetry type of the π^* orbital into which the excited electron is placed. Crosby and his colleagues [1, 16] assume that the lowest empty π^* orbitals of phen and dipy, which can act as electron acceptors, are of a_2 type. From Tables 4 and 5 we see that whilst Crosby's assumption is justified in the case of Ru(II) dipy, in the phen complex states of $M \rightarrow \pi 1^*$ and $M \rightarrow \pi 2^*$ type are intermingled with one another.

Turning to the results for the open-shell complexes, our most striking conclusion is that the oscillator strengths of the $\pi \rightarrow M$ CT bands should be so much less than those of the $M \rightarrow \pi^*$. This agrees with observation, but also makes it harder to disentangle the CT and intraligand states, not only because the two kinds of state are closer in energy, but also because the former gain a good fraction of their intensity from admixture with the latter (see Tables 6 and 7). One consequence is that we would not expect the CT excited states of the Fe(III) and Ru(III) complexes to have especially marked oxidizing properties.

Finally, two caveats are necessary when comparing the results of calculations of the kind described here with the excited state properties of these complexes. First, no account is taken of ligand field excited states, and second, spin-orbit coupling has not been included. On the scale of the energies we have been discussing, spin-orbit splittings are relatively minor although they may have important consequences, especially for the luminescence. Crosby and his colleagues [1] have noted that spin-orbit coupling determines the level sequence of the luminescent states of $\mathrm{Ru^{II}}$ tris-dipy and tris-phen complexes, which consist of three states. Nevertheless the three states in question span only about 0.07 kK. The absence of low-lying ligand field states, which could provide a radiationless pathway back to the ground state, is probably the substantial reason why the Ru(II) dipy and phen complexes luminesce from their charge transfer states, in contrast to the corresponding Fe(II) complexes, which do not luminesce. Our calculations say nothing about the location of ligand-field states, since we have only included orbitals of the t_{2g} manifold.

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