Luminescence Properties of Transition-Metal Ions in Double Complex Salts

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Dedicated to Prof. D. Reinen on the occasion of his 60th birthday

The luminescence spectra and radiative lifetimes of a series of d^3 and d^6 double complex compounds with bipyridine (bip), phenanthroline (phen), ammonia and ethylenediamine (en) ligands in the cations and chloride, cyanide, thiocyanide and oxalate (ox) ligands in the anions have been investigated at temperatures down to 2 K. Although energy transfer between the component ions is predicted from the Förster and Dexter theory to be effective due to the finite overlap of the donor emission and the acceptor absorption spectra, no emission could be detected for most of the double complexes. Only $[Ru(bip)_3]tr-[Cr(NH_3)_2(NCS)_4]_2$, $[Ru(bip)_3][PtCl_6]$ and $[Cr(d^4-en)_3][Rh(SCN)_6]$ exhibit characteristic luminescence spectra which in part are enhanced compared to their component emissions. For rationalizing the results, radiationless deactivation by various decay channels which compete with the energy transfer mechanism must be considered.

Key words: Interionic Energy Transfer, Low Temperature Luminescence Spectrometry

1. Introduction

Double complex compounds containing MA_n cations and $M'B_m$ complexes as anions exhibit luminescence spectra with band positions similar to those of the component ions but have in general drastically altered intensity properties [1–3]. While the luminescence of one component is quenched, in many cases leading to complete extinction, the intensity of the other component emitting from a lower energy level is very much increased. A straightforward explanation for this observation is offered by an energy transfer mechanism from the absorber (donor) to the counterion (acceptor) with an electronic level somewhat lower than that of the absorber followed by an emission of the acceptor which, due to concentration of energy on the acceptor site, emits with much higher intensity than the single complex [1–4]. This mechanism has been proposed also for explaining similar luminescence properties of coordination compounds in solutions [5–7]. In the solid state, however, parallel to this the influence of the medium on an emitting ion in the lattice of a double salt is of large importance [8] so that the luminescence properties (intensity, quantum yield, temperature dependence) of the emitter are changed essentially. This salt effect may lead to an enhancement of the emission [8] but

also to a drastric quenching [9] due to energy dissipation by phonon energy transfer into the surrounding medium.

It is difficult to find out which of the two mechanisms is the more effective one in a certain compound, in particular in doubtful cases where experimental results can be interpreted in different ways [8]. In general, from luminescence and routine lifetime measurements this question cannot be solved unambiguously. Therefore we will not address this particular problem but rather limit our investigation to explaining the measured luminescence intensities of double complex salts by considering the possible operation of both mechanisms (energy transfer *and* salt effects), demonstrating the competing contributions of these deactivation processes in some selected systems.

2. Theory

Relevant models for explaining energy transfer between molecules in condensed media are the resonance theory of Förster and Dexter [10–12] and various theories of propagating excitons [13, 14]. Since double complex salts have a predominantly localized electronic structure exhibiting no photoconductivity, so that transportation of excitation over a longer range can be neglected, the more appropriate model would be that of Förster and Dexter. It yields for dipolar coupling (applicable when the electronic transitions in

the donor and acceptor are electric dipole allowed) an R^{-6} dependence of the radiationless transfer rate between neighbouring molecules at distance R [15]. In the phenomenological treatment this rate is proportional to the overlap of the donor emission band $f_D(\tilde{v})$ and the acceptor absorption band profile $\varepsilon_A(\tilde{v})$, where both integral areas below these curves are normalized to unity [16], i.e.

$$k_{nr}^{ET}(dd) \sim \frac{1}{\tau_D R^6} \int_0^\infty \frac{\varepsilon_A(\tilde{v}) f_D(\tilde{v})}{\tilde{v}^4} d\tilde{v},$$

in which τ_D is the lifetime of the donor complex. A corresponding relation holds for dipole-quadrupole and exchange interactions, the latter arising from antisymmetrization of donor and acceptor wave functions. In these events the descent of interaction proceeds steeper than R^{-6} [12]. For the present double complex systems the component compounds, in many cases, exhibit absorption and emission bands originating from ligand field (d-d electron) transitions which are electric dipole forbidden, giving rise to relatively small intensities also in systems lacking an inversion center. Electric dipole transitions are, however, induced by vibronic coupling to odd levels which supply distinct but still relatively weak absorptions and emissions [17]. In this case the dipole-quadrupole $k_{nr}(dq)$ or the exchange interaction rate $k_{nr}(ex)$ will contribute to the radiationless energy transfer, the corresponding formulas having been worked out by Dexter [12].

According to the resonance theory [10–12], the energy transfer proceeds by several stages (cf. Fig. 1): (1) absorption of photon energy of $\approx E_0$ by the donor, (2) relaxation of the complex nuclear framework and/ or of the lattice environment around the donor arriving at an electronic energy $E_1 < E_0$, (3) radiationless transfer of $\approx E_1$ to the acceptor molecule , (4) relaxation of the acceptor in the same way as in (2), leading to the energy $E_2 < E_1$ and (5) followed by a photon emission of energy E_2 by the acceptor. All energy levels are diffuse (not well defined) since the molecular states are coupled to lattice vibrations of the crystal, thus entailing normalization problems for the wave functions. The resonance theory considers only the aforementioned steps which represent a very idealized path of the deactivation mechanism. Radiationless deactivation of component complexes, e.g. from E_1 of the donor and E_2 of the acceptor molecule leading to the ground states by phonon energy transfer into the
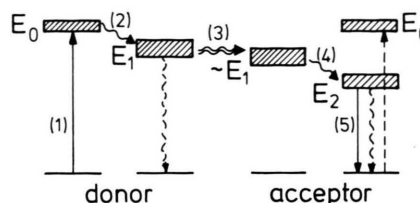

Fig. 1. Possible deactivation mechanisms in a double complex on excitation by an energy E_0 (see text).

lattice (see broken curled arrows in Fig. 1), is assumed to be small [16]. Also an energy loss due to possible phonon coupling during the donor-acceptor energy transfer has been neglected. A further complication for verifying the theoretical results from experiment arises from the fact that only the donor component of the system should absorb near the energy E_0; an absorption of the acceptor at this energy must be negligibly small (broken arrow in Fig. 1) if effective energy transfer is to be proved conclusively. Since for the present compounds obviously some of these requirements are not met, we cannot expect that the Förster and Dexter theory can be applied without restrictions. In any case radiationless deactivation into the ground state must be considered in addition to step (2) to (4) of the Förster-Dexter mechanism.

3. Experimental

Materials: Double complex salts are in general very insoluble. They are prepared by mixing stoichiometric amounts of component complexes in aqueous solution from which the double complexes will precipitate immediately. For avoiding co-precipitation of starting materials, diluted solutions are used. The products are collected on a filter, washed with water, ethanol and ether and dried in a desiccator over P_2O_5. The deuterated compounds were handled in D_2O medium. For checking on absorbed or crystalline water, some of the compounds were exposed for 2–3 days to temperatures close to 120 °C. Since no weight decrease could be observed we can assume that the compounds are largely free of water.

By the procedure described, 17 double complexes could be prepared which may be grouped by different aspects into seven series of compounds which allows to compare similar systems. They are compiled in Table 1. Some other combinations one may think of could not be established due to the failure of synthe-

sizing the corresponding compounds. Double complexes, for instance, of $[Cr en_3]^{3+}$ with $[RhCl_6]^{3-}$ or $[Rh ox_3]^{3-}$ and of cationic Rh(III) complexes with the Reinecke salt anion, tr-$[Cr(NH_3)_2(NCS)_4]^-$, decompose or are not stable enough for optical investigations.

Spectral recording: The emission spectra were taken from excitation with an argon ion laser, Spectra Physics, model 165, or with a mercury high-pressure lamp HBO 100 W/2 (Osram) using appropriate interference filters. For spectral dispersion a McPherson 0.5 m double monochromator was used; detection was achieved by a thermoelectrically cooled photomultiplier RF-TSA C31034 equipped with a GaAs photocathode (RCA). For low temperature recordings, a contact gas cryostat type k 1104/So and a bath cryostat, both furnished by CryoVac, were used which allow to obtain temperatures of about 4.2 K and 2.0 K, respectively. The temperature was monitored by a carbon resistor.

For a comparison of luminescence intensities of double complexes with the component compounds, identical optical conditions were used, applying exactly equal powers for excitation from the light source and turning the sample holder with the microcrystalline samples such that in each case maximal emission intensitiy is obtained. This procedure was repeated several times for estimating reliable error limits.

Emission lifetimes were measured by multi-channel scaling using an ND 66B multi-channel analyzer. Light pulses were produced either by a mechanical chopper or by applying an Edinburgh Instruments flashlamp, model 199 F. For this measurement, dispersion was achieved from a 25 cm Jarrell-Ash monochromator fitted with a 2400 lines/mm grating blazed at 500 nm.

4. Results and Discussion

For most of the presently investigated compounds an emission spectrum has been obtained which is extremely quenched compared to the spectra of their component ions. In general, except for a few cases, no luminescence could be detected even at temperatures as low as liquid helium. This finding is different from that earlier reported on, e.g., $[CrA_6][Cr(CN)_6]$ where A (or A–A) is a mono- or bidentate neutral ligand of oxygen and nitrogen coordinating atoms [1, 4, 8] and on $[Ru(bip)_3]_3[CrB_6]_2$ with B (or B–B) equal to oxalate, malonate, cyanide or thiocyanate [2, 3]. In these cases a drastic enhancement of luminescence intensity of the anion (acceptor) has been observed, which is attributed to an energy transfer or an intrinsic salt effect. For the present compounds the quenching of luminescence, different to what is expected beforehand from the theory of Förster and Dexter, must be explained by radiationless deactivation of the donor or acceptor molecules by phonon-assisted energy transfer into the surrounding lattice (see theoretical section) [16]. In these systems the deactivation due to vibronic coupling of energy levels in the component ions is favoured over the energy transfer mechanism. Decay channels may be obtained also from coupling to vibrational modes of crystalline water, if present. Internal molecular relaxation processes, like step (2) $E_0 \rightarrow E_1$ and step (4) $E_1 \rightarrow E_2$ (cf. Fig. 1) are, e.g., possible by virtue of the energy conservation law if vibronic coupling of molecular levels to lattice modes (phonons) is effective. For strong coupling, when allowed by the symmetry, the radiationless deactivation can proceed further, leading to the ground state, and no emission will be observed. Some of the double complexes which we have looked at exhibit substantial overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor, the emission being at higher energy than the absorption and the donor possessing a strong transition dipole moment. But although the prerequisites of the Förster-Dexter theory are fulfilled, no emission could be detected in systems such as $[Rh(phen)_3][RhCl_6]$, $[Rh(phen)_3][Rh(ox)_3]$ and $[Rh(bip)_3][Rh(ox)_3]$. From $[Rh(bip)_3][Rh(Cl)_6]$ a cation emission and from $[Rh(bip)_3][Rh(SCN)_6]$ an anion emission much weaker than for the component complexes [18–21] were measured. The donor components of these systems exhibit an electric dipole allowed $\pi - \pi^*$ transition giving rise to a strong dipole moment which would be very suitable for initiating energy transfer, and the acceptors in mono-complexes are known to be relatively poor emitters [22, 23].

Also, the phen and bip cation complexes of Rh combined with $[Rh(SCN)_6]^{3-}$ or $[PtCl_6]^{2-}$ anions, although their emission and absorption spectra overlap to a certain extent, do not show any sign of luminescence even at low temperature. The same is true for other double complex salts listed in Table 1 which contain ions exhibiting d-d transitions. This finding is, however, to be expected from the lack of overlap between the emission and the absorption spectra of their constituents.

Table 1. Series of similar systems supplied by the list of d^3-, d^6-double complexes A_nB_m considered.

Cationic Series		Anionic Series	
A	B	A	B
1. [Rh(phen)$_3$]	[RhCl$_6$] [Rh(SCN)$_6$] [Rh(ox)$_3$] [PtCl$_6$]	4. [Ru(bip)$_3$]	[PtCl$_6$] [Rh(bip)$_3$] [Rh(phen)$_3$]
2. [Rh(bip)$_3$]	[Co(CN)$_6$] [RhCl$_6$] [Rh(SCN)$_6$] [Rh(ox)$_3$] [PtCl$_6$]	5. [Cr(en)$_3$] [Cr(d^4-en)$_3$] [Rh(en)$_3$] [Rh(NH$_3$)$_5$Cl] [Rh(bip)$_3$] [Rh(phen)$_3$]	[Rh(SCN)$_6$]
3. [Ru(bip)$_3$]	tr[Cr(NH$_3$)$_2$(NCS)$_4$] [Co(CN)$_6$] [Rh(SCN)$_6$] [PtCl$_6$]		
		6. [Rh(bip)$_3$]	[Rh(ox)$_3$] [Rh(phen)$_3$]
		7. [Ru(bip)$_3$]	[Co(CN)$_6$] [Rh(bip)$_3$]

The only appreciable luminescence obtained from the present double complexes will be discussed in the following. These systems are characteristic examples for different decay mechanisms which work competitively and with various strengths.

4.1. [Ru(bip)$_3$] tr-[Cr(NH$_3$)$_2$(NCS)$_4$]$_2$

The emission intensities of the component complexes are very different. While [Ru(bip)$_3$]Cl$_2$ exhibits strong luminescence due to parity allowed metal-to-ligand charge transfer transitions [3, 24], the corresponding spectrum of the Reinecke salt arising from d-d transitions is very weak [5, 25]. Excitation of the double complex from the 454 nm Ar laser line results in an enhancement of the anion emission by a factor of 30 compared to the Reinecke salt, whereas the luminescence of the Ru cation is completely quenched at low temperature (cf. Figure 2). The anion in the double salt seems to be photochemically very stable, different from the Reinecke salt which like other Cr complexes decomposes when being irradiated by visible light of moderate intensity.

At the excitation wavelength of 454 nm the absorption spectrum of Reinecke salt has a minimum of the molar extinction coefficient, $\varepsilon = 45\ \mathrm{l\,mol^{-1}\,cm^{-1}}$, while the Ru-bip complex absorbs by a factor of about 200 stronger at this energy, therefore it is guaranteed

that most of the excitation energy is absorbed by the donor. Since the optical prerequisites are fulfilled, the experimental findings strongly support an energy transfer mechanism which fits into the series of Ru(II) – Cr(III) double complexes of Fujita and Kobayashi [2, 3]. A dipole-dipole interaction is, however, only possible applying Dexter's spin selection rules [12] from a singlet charge transfer excited state of the donor to the $^4B_2$ and ^4E (D_{4h} notation) ligand field levels of the acceptor, which are lower in energy by $\approx 2500\ \mathrm{cm^{-1}}$. Since for heavy metals the spins are not good quantum numbers due to intermediate coupling, a mixing of wave functions belonging to different spins is also possible. Therefore, energy transfer between lower excited states (triplet charge transfer levels of the donor and $^2A_1$, $^2B_1$ d-levels of acceptor, both occupied from the ground state by spinforbidden transitions) may also occur. The efficiency of the energy transfer is calculated from the amplification factor 30 to be about 0.3, in view of the fact that for a stoichiometric quotient of 1:2 the relation of the absorptivity between cations and anions is only ≈ 100, as estimated from ε coefficients at 454 nm.

4.2. [Ru(bip)$_3$] [PtCl$_6$]

The absorption and emission spectra of the component complexes have been recorded earlier and assigned to electronic energy level schemes [3, 24, 26, 27]. The emitting level of K$_2$PtCl$_6$ is a $\Gamma_3(^3T_{1g})$ ligand field state and the resulting luminescence spectrum taken from a single crystal is relatively strong for a d-d transition but well resolved, exhibiting three closely superimposed progressions due to the promoting modes $\tilde{\nu}_3(t_{1u})$, $\tilde{\nu}_4(t_{1u})$ and $\tilde{\nu}_6(t_{2u})$. The vibrational intervals of 323 cm^{-1} correspond to the $\tilde{\nu}_2(e_g)$ accepting mode (in octahedral notation) [27]. The spectrum of the double complex salt taken from a powder sample on excitation by $\lambda_{exc} = 365$ nm shows a similar progression with 315 cm^{-1} quanta, which is not as well resolved into vibrational components as in the K$_2$PtCl$_6$ spectrum of the crystal (cf. Figure 3). It also contains the almost unchanged emission spectrum of [Ru(bip)$_3$]$^{2+}$, and the intensity is comparable in strength to that of the superimposed spectra of the cation and the anion. On excitation with light of $\lambda_{exc} = 487$ nm only the spectrum of the Ru cation is observed.

The explanation for these findings from the energy level diagrams is straightforward. Since the overlap of
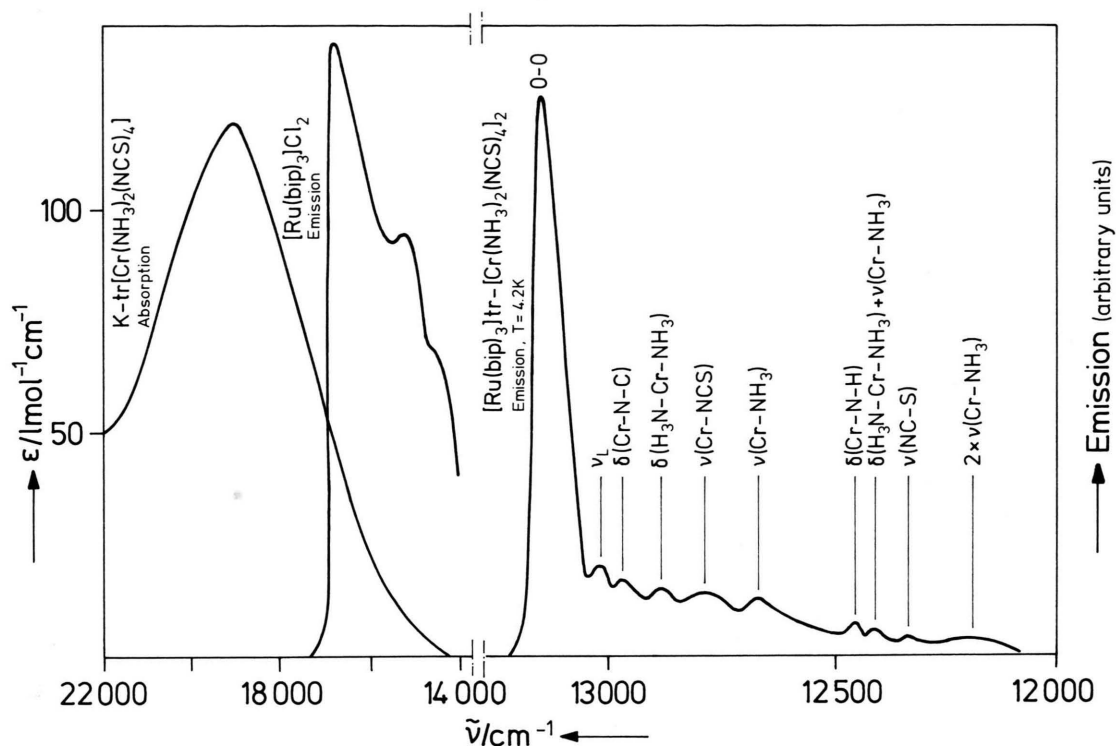
Fig. 2. The 4.2 K emission spectrum of $[Ru(bip)_3]tr-[Cr(NH_3)_2(NCS)_4]_2$ ($\lambda_{exc} = 454$ nm) and the absorption as well as the emission spectrum of the donor and acceptor complex, respectively. The vibrational fine structure is assigned following [25].

the emission spectrum of the cation and the absorption spectrum of the anion is very small, we do not expect much energy transfer from the Förster-Dexter mechanism. If the excitation energy is large enough, i.e. 27 400 cm^{-1} corresponding to $\lambda_{exc} = 365$ nm, both ions of the double complex are excited, each separately giving rise to emission from their excited levels. In case the excitation energy is low, i.e. 20 500 cm^{-1} corresponding to $\lambda_{exc} = 487$ nm, where $[PtCl_6]^{2-}$ can hardly be excited (the absorption coefficient at this wave number is extremely small compared to that of $[Ru(bip)_3]^{2+}$ (cf. Fig. 3), only the emission from $[Ru(bip)_3]^{2+}$ is observed. Since no trace of the characteristic $[PtCl_6]^{2-}$ emission is detected we can conclude that at this excitation energy, the transfer, if occurring at all, is negligibly small. The deactivation proceeds predominantly inside the Ru complex through intersystem crossing into the lowest triplet charge transfer states (^3CT) which are located at 16 000–18 000 cm^{-1} in the level scheme [3, 24, 28]. From these, no energy transfer to the lowest $[PtCl_6]^{2-}$ level at 21 000 cm^{-1} is possible, such that emission only from the Ru ^3CT

levels can be observed. On excitation at higher energy (i.e. at 27 400 cm^{-1}) the energy level scheme, in principle, allows for energy transfer between the ions in either direction. Since the absorbancy at this wave number is much higher for the Ru- than for the Pt-complex (cf. Fig. 3), possible energy transfer will proceed from the Ru- to the Pt-component in the double complex. However, as the energy is known to be collected mainly in the lowest excited states by fast relaxation processes, transfer from higher Ru levels to Pt is very unlikely. Since, moreover, the double complex spectrum exhibits both emission spectra of the cation and the anion with relative intensities comparable to their component spectra, we conclude that a noticeable energy transfer will not occur also in the event of excitation at higher energy.

Lifetime measurements support this mechanism. At the maximum of emission (≈ 600 nm) the lifetime of the double complex at 12 K is 19 μs, which compares to 17 μs for $[Ru(bip)_3]Cl_2$ at the same temperature. At slightly lower wavelength the lifetime of the double complex is also larger than for the single Ru complex,

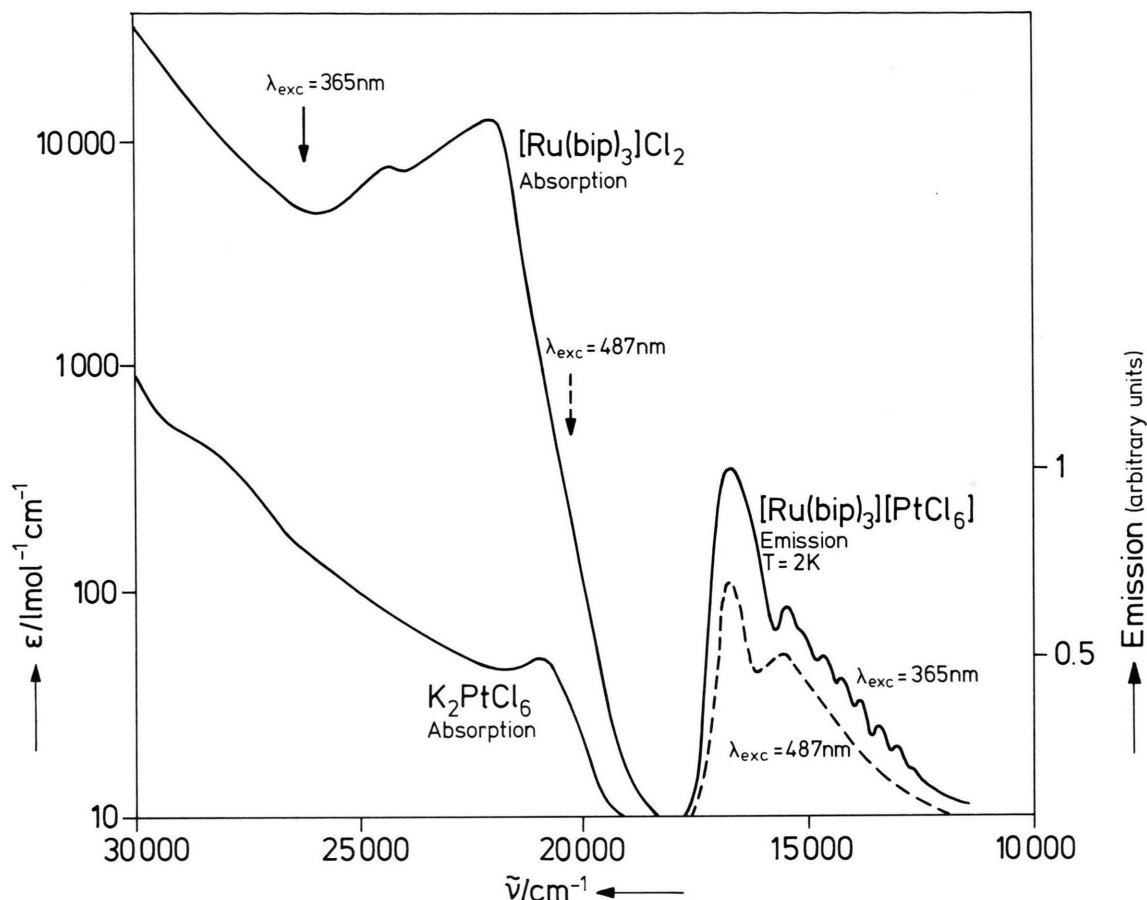Fig. 3. The 2 K emission spectrum of $[Ru(bip)_3][PtCl_6]$ for different excitations compared to the absorption spectra of corresponding mono-complexes [3, 29]. The emission spectrum of $[Ru(bip)_3]Cl_2$ is very similar to the double complex excited at 487 nm.

indicating as well the absence of any significant energy transfer in the double complex.

When varying the donor ion from Ru(II)- to the Rh(III)-complex (series 4 of Table 1) the emission completely disappears. Since overlap of the donor emission with the acceptor absorption spectrum is small, moderate energy transfer is expected from the Förster-Dexter theory. However, luminescence of the constituent ions is quenched due to a salt effect in the double complexes which may vary for different crystal structures expected for another stoichiometric relation. The same explanation for a lack of emission must hold when varying the acceptor ion to $[Rh(SCN)_6]^{3-}$ and $[Co(CN)_6]^{3-}$ in series 3. Since cation-anion spectral overlap is very poor, deactivation of $[Ru(bip)_3]^{2+}$ in these system must preferentially be due to intra-molecular radiationless transitions within this ion.

4.3. $[Cr(d^4\text{-}en)_3][Rh(SCN)_6]$

The luminescence spectrum of this double complex obtained from excitation at 454 nm, where the two component ions can absorb light, is depicted in Figure 4. It exhibits emissions from both complexes, the intensity of the Cr spectrum, however, is very much weakened and the Rh spectrum is strengthened by a factor of 1.5–2 compared to the component compounds at the same temperature. Although in either complexion the spectra originate only from weak d-d transitions, the experimental finding suggests the operation of an energy transfer mechanism as proposed for other similar systems [1, 4, 5]. The transition on excitation is spin allowed, and the fair overlap of the donor emission from levels of higher energy with the acceptor absorption spectrum towards lower
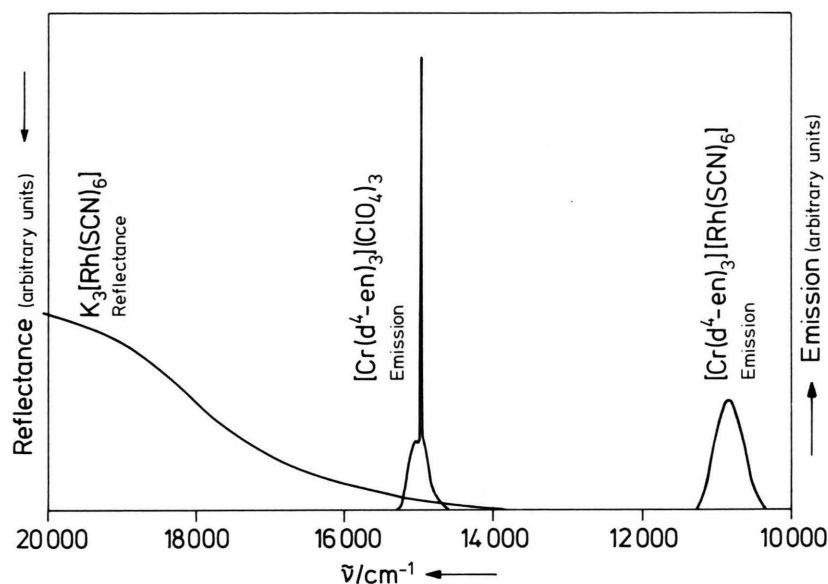
Fig. 4. The 10 K emission spectrum of $[Cr(d^4-en)_3][Rh(SCN)_6]$ ($\lambda_{exc} = 454$ nm) and the reflectance and emission spectrum of the donor and acceptor complex, respectively (the rest signal due to the Cr complex in the double complex is too weak to be reproduced at the scale applied).

energy fulfills the conditions imposed by the Förster and Dexter theory [10–12]. This is in contrast to the absence of any luminescence, also measured at very low temperature, of the protonated analogoue, $[Cr(en)_3][Rh(SCN)_6]$, in series 5 with an electronic structure and energy level scheme very similar to the deuterated compound. Rather different are, on the other hand, the vibrational structure and the radiative decay behavior of the deuterated species: while the ^2E level of $[Cr(en)_3]^{3+}$ in various environments has a lifetime of about 36 µs at 11 K, the $[Cr(d^4-en)_3]^{3+}$ level is much longer lived with a bi-exponential decay curve of 480 and 1160 µs lifetimes at this temperature [30]. In the deuterated double complex the cation lifetime is decreased to lower than 10 µs. According to the Förster-Dexter formula given above, the energy transfer rate for dipole-dipole interactions changes inversely proportional to the lifetime τ_D of the donor emission, i.e. $k_{nr}^{ET}(dd) \sim 1/\tau_D$ [12, 16]. The energy transfer therefore is larger for the protonated than for the deuterated system. If radiation is the only decay channel for deactivation, the protonated species should exhibit a luminescence of higher intensity. This is, however, at variance with the experimental result: an emission spectrum could only be observed from the deuterated double complex. Therefore, in addition to an energy transfer, another deactivation channel by radiationless transitions caused by vibronic coupling to internal molecular vibrations and to lattice modes

must be considered. In this context the effect of amine deuteration on vibronic coupling which strongly determines the decay rate of complex compounds becomes important [31, 32].

With these two mechanisms the experimental results can be explained satisfactorily. From the measured decay curves of the Cr trisethylenediamine monocomplexes, the relation obtained from the nonradiative decay constants of the protonated (p) and deuterated (d) cations is $k_{nr}^p > k_{nr}^d$ (the radiative constants k_r^p of the protonated species are negligibly small for all Cr complexes compared to their k_{nr}^p components). If in the protonated double complex the decay rate k_{nr}^p of the cation is large against the energy transfer rate k_{nr}^{ET}, the deactivation proceeds mainly through the radiationless decay channel of the cation, and energy transfer to the anion is very small such that emission from the acceptor will be weak. Direct emission from the cation can be completely quenched by environmental effects. For the deuterated double complex the rate constant k_{nr}^d of the cation for radiationless decay may be comparable to or smaller than the transfer rate k_{nr}^{ET}. In this case the total decay constant is $k_{nr} = k_{nr}^d + k_{nr}^{ET}$. Deactivation can in part proceed through cation-anion energy transfer, becoming apparent by a lower lifetime of the cation and leading to an enhanced emission of the anion. The slightly increased overlap observed for the constituent spectra of the deuterated species may also add to the

larger luminescence intensity. In all steps involved, environmental effects due to vibrational coupling to lattice modes will contribute to the respective rates. The importance of these contributions can, however, not be estimated from the present results. They are also responsible for the largely quenched emission measured for the other double complexes with Rh cations in Series 5.

5. Conclusion

A discussion of energy transfer processes between donor and acceptor ions in double complex salts on the basis of the rate formulas of Förster and Dexter should also consider possible decay mechanisms within the constituent complex molecules by radia-

tionless transitions (e.g. internal conversion and/or vibronic coupling to lattice modes). The two mechanisms are in competition which can lead in some cases to enhanced emission of the acceptor ion with or without quenching of the donor emission, in other events to simultaneous presence of almost unchanged emission of both the cation and the anion and more frequently to complete extinction of any emission.

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