

A Comparison between "Second-Sphere Effects" in the Excited State Properties of Coordination Compounds and Nonmolecular Solids*

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In this paper we compare second-sphere effects as known from the field of photochemistry and photophysics of coordination compounds with similar phenomena in nonmolecular solids. Literature data, as well as new results, especially on cryptates, are used. The similarity between these phenomena in both classes of compounds is much larger than thought at first glance and has been overlooked for the most part. The following effects are considered: the influence of complex encapsulation on the yield of photochemical processes and the thermal quenching temperature of luminescence; the interaction in ion pairs resulting in new energy levels and luminescence quenching; and the influence of electric charges on the position of absorption bands. Since quantitative calculations of these effects are not easy to perform, it is beneficial to discuss information available from different fields of research. © 1987 Academic Press, Inc.

1. Introduction

A number of physical phenomena can be studied in coordination compounds as well as in nonmolecular solids and can be explained by the same theories. Examples are paramagnetism (including low-spin/high-spin transitions), ligand field spectroscopy, and luminescence (radiative as well as non-radiative transitions). Nevertheless, interaction among investigators of these two types of compounds has been limited.

Recently we reported on a comparison of the nonradiative transitions in rare-earth ions in both types of compounds (1). This comparison yielded results which were not clear from the published literature, e.g., the fact that the high-energy vibrations of the solvent do not influence the nonradiative transitions in the Eu^{2+} ion strongly, and the fact that nonradiative transitions in the Eu^{3+} ion can occur via the charge-transfer state in nonmolecular solids as well as in coordination compounds.

In the photochemistry and photophysics of coordination compounds there is nowa-

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days a strong interest in second-sphere effects (2). These are effects due to perturbations from outside the first coordination sphere of the central metal ion. The properties of the complex consisting of the central ion and its first coordination sphere are usually well known and nowadays well understood. However, second-sphere effects may bring about drastic changes in these properties. In solid state chemistry second-sphere effects as such are unknown. However, we will show that many observations in solids are immediately comparable to second-sphere effects in coordination compounds. It is our feeling that such a comparison has been neglected until now and may stimulate research in both areas. Since today's trend is to study more complex systems, a comparison between different fields of research may be useful, because it may simplify the situation or make a characterization easier.

We will restrict ourselves to photophysical and photochemical processes and, therefore, be interested in electronically excited states. These will be mainly of the charge-transfer type. Within the first coordination sphere we may distinguish ligand-to-metal charge transfer and metal-to-ligand charge transfer (3). When an interaction with the second sphere is present, there may also be excited states due to second-sphere charge transfer (also called outer-sphere charge transfer) (2). A large difference between the considerations in coordination chemistry in solution and nonmolecular solids considering second-sphere effects should be kept in mind. In coordination chemistry these effects are often observed in species which are due to an encounter between constituents which migrate through the solvent by diffusion. In solids the position of all particles is fixed for the time of the measurements. In spite of this, there remains a strong analogy as we will show now on several examples.

2. Complexes with Constrained Coordination Sphere

In coordination chemistry there exist nowadays many complexes in which the coordination sphere is constrained in some way. Examples are

a. Cage-Type Ligands

In the simplest case unidentate ligands are linked together by bonds (see Fig. 1), so that a cage results (4). In first approximation the coordination sphere is not changed much and the introduction of the extra bonds can be considered as a weak perturbation. In fact the absorption spectra do not change much. However, photochemical reactions and radiationless deactivation processes which involve nuclear displacements are influenced strongly (2). An interesting class of cage-type ligands are the macrobicyclic ligands called cryptands (5, 6,). Figure 2 gives as an example the 2.2.1 cryptand. We note that Eu^{2+} in aqueous solution at room temperature does not show any detectable luminescence, while under the same conditions the $[\text{Eu}^{2+} \subset 2.2.1]$ cryptate does show some luminescence, which obtains a high efficiency at lower temperatures (7, 8). Crown ethers are also able to cage the Eu^{2+} ion, resulting in efficient luminescence (9). Elsewhere we have shown that the cage-type ligands constrain the Eu^{2+} ion when it expands in the excited state (8, 1). This reduces the radiationless processes considerably.

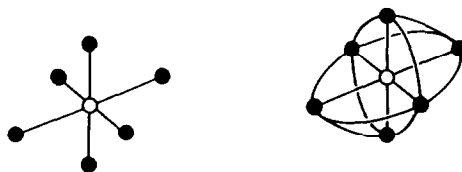


FIG. 1. Schematic representation of complexes containing monodentate and cage ligands (left- and right-hand side, respectively).

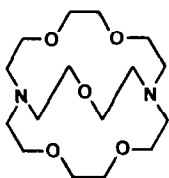


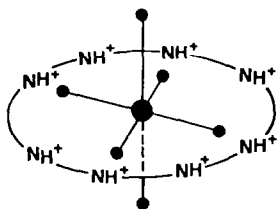
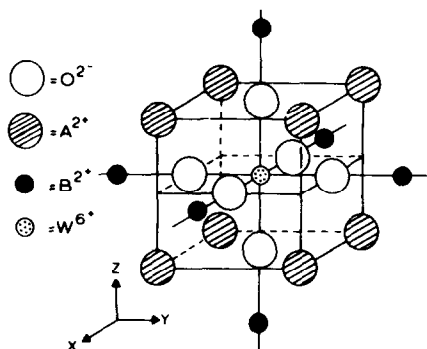
FIG. 2. The 2.2.1 cryptand.

b. Supercomplexes

It is also possible to enclose the coordination complex in an appropriate receptor, so that a supercomplex results (2). As an example we mention the complex $\text{Co}(\text{CN})_6^{3-}$ in the receptor $32\text{N}_8\text{H}_8^{8+}$, a polyammonium macrocyclic (see Fig. 3). In aqueous solution the complex $\text{Co}(\text{CN})_6^{3-}$ shows an aquation reaction upon irradiation into the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1T_{2g}$ transitions with a quantum yield of 30%. However, when the complex is in the receptor, the yield is considerably reduced (10).

After this superficial survey of complexes with a constrained coordination sphere, we now turn to nonmolecular solids.

Let us consider the ordered perovskite structure as an example. Figure 4 shows the part of the structure which is necessary for the discussion. The central metal ion is octahedrally coordinated by six O^{2-} ions. This we consider to be the first coordination sphere. This complex may be, for example, a tungstate or a uranate group (WO_6^{6-} or UO_6^{6-} , respectively). In compounds $A_2B\text{W}(\text{U})\text{O}_6$ this complex ion has a second coordination sphere consisting of the A^{2+} and

FIG. 3. Supramolecular structure of the adduct between $\text{Co}(\text{CN})_6^{3-}$ and $32\text{N}_8\text{H}_8^{8+}$.FIG. 4. The ordered perovskite structure of compounds $A_2BB'O_6$. Open circles: O^{2-} ; large, hatched circles: A^{2+} ; black circles B^{2+} ; small, dotted circles: $(B')^{6+}$.

B^{2+} cations, the larger A^{2+} ions forming a cube, the smaller B^{2+} ions forming an octahedron around the $\text{W}(\text{U})\text{O}_6$ octahedron. Since the A and B ions have noble-gas configuration (A and B may be Mg , Ca , Sr , Ba), the electronic levels of the central complex ion are hardly influenced by the second coordination sphere. In fact emission and excitation spectra of the tungstate or uranate luminescence are very much alike (11, 12).

However, the thermal quenching temperature of the luminescence is strongly influenced by the second coordination sphere (11, 12). Peculiarly enough, the A^{2+} ions do not have much influence, but the B^{2+} ions have (see Fig. 5). The smaller the B^{2+} ion, the higher the quenching temperature. The qualitative explanation, which has been confirmed by calculations (13), is as follows (12, 14). The central complex ion expands upon excitation; i.e., the O^{2-} ions move to the B^{2+} ions. The smaller (and the higher charged) the B^{2+} ions, the more this expansion is counteracted; i.e., the B_6 octahedron forms a constraint in the coordination sphere of the complex ion. As a matter of fact the A_8 cube is not very effective for this purpose. Figure 6 summarizes these arguments in a configurational coordinate diagram.

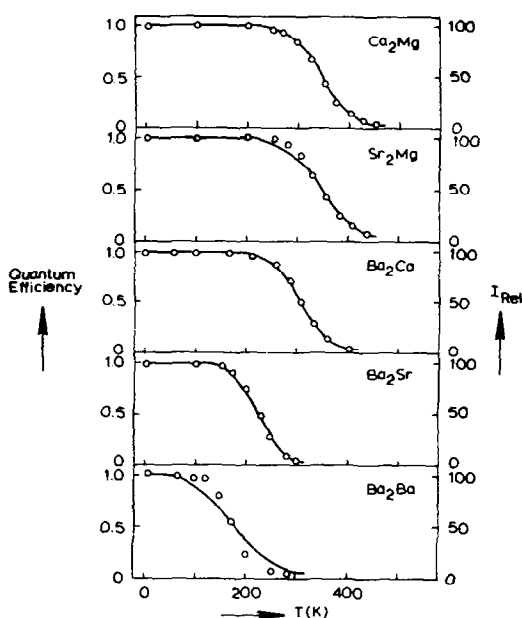


FIG. 5. Thermal quenching of the uranate luminescence in various U^{6+} -doped tungstates (from K. C. Bleijenberg, thesis, University of Utrecht, 1979).

This effect is even more pronounced in $Cs_2WO_2Cl_4$ (15) with the same crystal structure. Here the central complex ion is $[WO_2Cl_4]^{2-}$, the A ions are Cs^+ , and the sites of the B ions are empty. So there is no serious constraint to expansion of the chlorotungstate octahedron. As a consequence its luminescence is quenched above 80 K.

Actually it is an old rule of thumb in the field of luminescence in solids (14) that a constrained second coordination sphere is a necessary requirement in order to obtain high quenching temperatures (T_q) of the luminescence. Compare the luminescence of $Cs_2WO_2Cl_4$ with $T_q = 80$ K (15) with that of Ba_2MgWO_6 with $T_q = 500$ K (11). Note that the nature of the luminescent center is not involved in the discussion. In fact this rule has a very general validity.

In this way we see that a constraint in the second coordination sphere will lead to a reduction of the nonradiative losses in the luminescence transition. This runs parallel

with the reduction of photochemical quantum yields mentioned above. It is interesting that the dependence of quantum yields on a particular second coordination sphere can be predicted, because their value is often of large practical importance and their calculation is always tedious and often impossible.

Until now we have used only spatial arguments. The electronic energy levels of the second coordination sphere are at such a high energy that they do not influence those of the central complex involved. If this is no longer the case, a new situation occurs with unexpected results.

3. Ion Pairs

As in the previous paragraph, we first consider the situation in coordination chemistry following Ref. (2). Since coordination complexes are usually charged, ion pairs can be formed. Here we are interested in the case of weak interaction (outer-sphere ion pairs), so that the constituents maintain their individual spectroscopic properties. In addition second-sphere charge transfer is assumed to be possible. This results in the presence of energy levels which may be at very high energy, or in the range of levels of the constituents, or even below the lowest excited levels of the con-

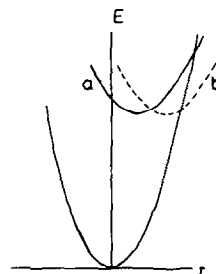


FIG. 6. Configurational coordinate diagram showing how a constraint in the lattice moves the excited state parabola from position b to position a , reducing in this way the nonradiative transition rate between the two parabolae.

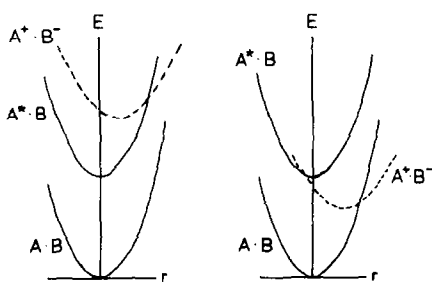
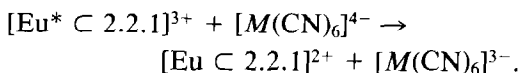


FIG. 7. Second-sphere charge-transfer states in the configurational coordinate diagram. $A \cdot B$ presents an outer-sphere ion pair in the ground state. Individual excitation of A leads to the species $A^* \cdot B$. The charge-transfer state is indicated by $A^* \cdot B^-$ and may be situated above or below the state $A^* \cdot B$. See also text.

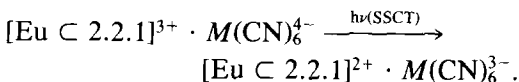
stituents. Figure 7 shows the two latter situations in a configurational coordinate diagram.

Let us illustrate this with some examples: the ion pair $[\text{Co}(\text{NH}_3)_6]^{3+} \cdot \text{I}^-$ shows under ultraviolet excitation a transition to the charge-transfer state $[\text{Co}(\text{NH}_3)_6]^{2+} \cdot \text{I}$. The latter species returns partly to the original ground state and decomposes partly into $\text{Co}_{\text{aq}}^{2+}$, NH_3 , and I_2 (16).

The luminescence of the cryptate $[\text{Eu}^{3+} \subset 2.2.1]^{3+}$ in solution is quenched by $[\text{M}(\text{CN})_6]^{4-}$ ions ($M = \text{Fe}, \text{Ru}, \text{Os}$) (17). At low quencher concentrations the quenching process is dynamic in nature and due to a bimolecular electron transfer:



At higher concentrations, ion pairs are formed and a new broad absorption band occurs at low energy (second-sphere charge transfer):



The luminescence of the Eu^{3+} cryptate is quenched, since the charge-transfer state returns nonradiatively to the ground state (Fig. 7).

Here we wish to present a couple of

cases of solids which are analogous to the second-sphere charge-transfer cases described above. First, we consider the vanadate group (VO_4^{3-}). This complex shows optical absorption in the ultraviolet region and an emission in the blue region. These transitions correspond to ligand-to-metal charge transfer within the vanadate group. One of us has proposed that the emission is from a spin triplet level (18). Recently van der Waals *et al.* have unraveled the structure of the excited state and shown that it is indeed a triplet state (19). A suitable system to study the spectral characteristics of the VO_4^{3-} complex is the solid solution series $\text{YP}_{1-x}\text{V}_x\text{O}_4$. The Y^{3+} ions can be replaced by other ions. If this is done by La^{3+} , Gd^{3+} , Lu^{3+} , or other noble-gas ions, the characteristics of the vanadate group do not change much. However, an ion like Bi^{3+} causes drastic changes. Although the Bi^{3+} ion in YPO_4 has its absorption and emission in the ultraviolet, $\text{YVO}_4\text{-Bi}$ shows an absorption band at very low energies (20, 21). Excitation into this band yields a yellow luminescence (see Fig. 8). These transitions can be ascribed to second-sphere charge-transfer transitions; i.e., the excited state has $\text{Bi}^{4+}\text{-V}^{4+}$ character. The appearance of a new absorption band is similar to observations in ion-pair coordination complexes.

Luminescence of a second-sphere charge-transfer state is rather exceptional, the offset of the excited state being large. In the case of $\text{YVO}_4\text{-Bi}^{3+}$, however, the

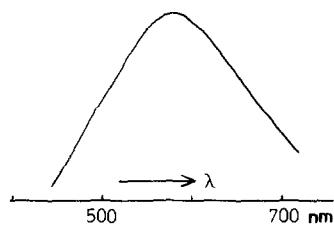


FIG. 8. Emission spectrum of $\text{YVO}_4\text{-Bi}$ at 300 K under 254 nm excitation. The undisturbed vanadate emission has its maximum at about 420 nm (20).

charge transfer starts from the filled, anti-bonding $6s^2$ orbital on the Bi^{3+} ion to the empty and only weakly antibonding d_e orbital on the V^{5+} ion. The decrease in bonding strength is therefore restricted, so that the offset will be relatively small.

If we introduce Tb^{3+} in YVO_4 , the Tb^{3+} as well as the VO_4^{3-} luminescence is quenched. This cannot be explained by energy transfer according to the Förster–Dexter theory (1). The quenching is ascribed to electron transfer between the metal ions concerned; i.e., on excitation a charge-transfer state $\text{Tb}^{4+}-\text{V}^{4+}$ is reached from where radiationless return occurs (Fig. 7). This charge transfer cannot be observed as an optical absorption band in the spectra. Obviously the corresponding absorption band is situated above the allowed transitions of the Tb^{3+} ion and the VO_4^{3-} complex. Its decisive role in the nonradiative transition is only possible due to the large offset.

In a very similar way the Ce^{3+} and the Eu^{3+} ions quench each other's luminescence (charge-transfer state $\text{Eu}^{2+}-\text{Ce}^{4+}$) (1).

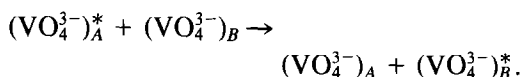
McGlynn *et al.* (22) have studied extensively the color of salts of heavy metal ions like Ag^+ and Pb^{2+} . Their arguments run parallel with those used in second-sphere charge-transfer phenomena. Recently Yamashita and Azumi (23) have shown that the absorption and emission of solid AgClO_4 are due to the perchlorate ion, although this ion has its energy levels in the vacuum ultraviolet when no Ag^+ is present. The Ag^+ ion induces the transitions observed in the luminescence study. Also the color of transition metal ions in titanates and related compounds is determined by second-sphere charge transfer (24).

Because the distance between the centers of the constituents of the ion pair are in solids often shorter than in coordination compounds, and because the concentration of the constituents can be varied more

widely in solids, a number of other effects are possible in solids and not in coordination chemistry.

a. Weak Interaction between Equal Species

In YVO_4 there exists a weak interaction between two neighboring VO_4^{3-} , leading to energy transfer between two VO_4^{3-} groups; i.e.,



The critical distance for this transfer is about 8 \AA (25). By repetition of this process the excitation energy can migrate through the crystal lattice which is the main reason why the host lattice YVO_4 yields very efficient luminescent materials upon doping. Energy transfer has also been observed in ion pairs in solution (26), but energy migration is impossible. In solid coordination compounds the distance is often too large for energy migration. Whereas efficient energy migration is possible in several non-molecular rare-earth compounds (27), we were not able to detect it in the rare-earth cryptates and rare-earth polytungstates (28), where the rare-earth distances amount to 11 and 13 Å , respectively. Whereas $\text{GdMgB}_5\text{O}_{10}-\text{Tb}^{3+}$ shows efficient Tb^{3+} emission upon excitation of the Gd^{3+} ions (29), solid $[\text{Gd} \subset 2.2.1]_{0.97}[\text{Tb} \subset 2.2.1]_{0.03}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ shows only (efficient) Gd^{3+} emission (${}^6P \rightarrow {}^8S$) upon excitation into the $\text{Gd}^{3+} {}^6I$ levels.

b. Strong Interaction between Equal Species

If the interaction is strong (wavefunction overlap), delocalization effects occur which have a strong influence on the luminescence properties (30), but fall outside the scope of this paper.

4. Charge Effects

If one replaces two out of the three H_2O molecules in the complex $[\text{Eu} \subset 2.2.1]^{3+} \cdot 3\text{H}_2\text{O}$ in aqueous solution by F^- ions, the position of the Eu^{3+} tertiary-amine nitrogen and Eu^{3+} ether oxygen charge-transfer bands shift from 33,500 and 41,300 cm^{-1} in the complex with H_2O molecules to 36,700 and 44,600 cm^{-1} in the complex with F^- ions, respectively (Fig. 9). The reason for this relatively large shift is at first sight not clear. If we compare the redox potentials of the $[\text{Eu} \subset 2.2.1]^{3+}$ complex and the $[\text{Eu} \subset 2.2.1]^{3+} \cdot 2\text{F}^-$ ion pair (31), we find that the presence of the F^- ions stabilizes the Eu^{3+} ion, as is also indicated by the shift in the charge-transfer bands.

This effect can be compared to what is known in solid state chemistry as the effect of an effective charge. A clear example of this is the position of the charge-transfer absorption band of the Eu^{3+} ion in six coordination in mixed-metal oxides. On experimental and theoretical grounds this position is expected to be independent of the $\text{Eu}^{3+}-\text{O}^{2-}$ distance (32). From spectroscopic measurements it is observed at $(42 \pm 1)10^3 \text{ cm}^{-1}$. However, for Eu^{3+} in CaO , 36,000 cm^{-1} is observed and for Eu^{3+} in ZrP_2O_7 , 45,000 cm^{-1} (33). The effective positive charge on the Eu^{3+} ion in CaO destabilizes

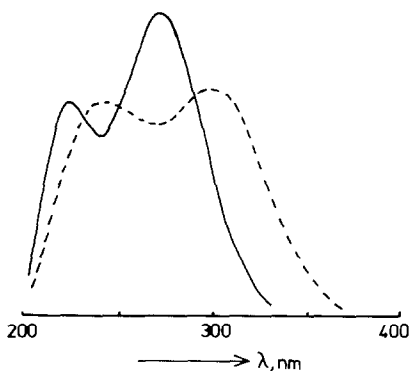


FIG. 9. Absorption spectra at 300 K of $[\text{Eu} \subset 2.2.1]^{3+}$ (broken curve) and $[\text{Eu} \subset 2.2.1]^{3+} \cdot 2\text{F}^-$ (drawn curve) in aqueous solution.

the Eu^{3+} ion relative to the Eu^{2+} ion, whereas the effective negative charge on Eu^{3+} in ZrP_2O_7 stabilizes the Eu^{3+} ion. This explains the shift in the charge-transfer spectra. Note the parallel with the replacement of H_2O by F^- in the Eu^{3+} -cryptate complex. The spectral shift observed in the latter case is of the same order of magnitude as that in the case of solids as a consequence of the presence of a formal effective charge.

We conclude that the photochemistry and photophysics of coordination compounds and nonmolecular solids often show similarities which are easily overlooked. They deserve attention because they facilitate and strengthen the arguments used. This is of importance because in many cases the arguments are of a qualitative nature only. This in turn is due to the fact that quantitative calculations of the effects described are cumbersome, which is partly related to the complicated nature of the phenomena involved (e.g., nonradiative transitions) and partly to the complicated nature of the complexes involved.

5. Experimental

The optical measurements on the cryptates were performed as described in Ref. (34). The Tb^{3+} -doped Gd^{3+} cryptate was made from Tb^{3+} cryptate and Gd^{3+} cryptate (prepared as described in Ref. (35)) by dissolving the cryptates in the required proportion. The Eu^{3+} cryptate-fluoride anion ion pair was obtained in H_2O solutions containing $5 \times 10^{-3} \text{ M}$ $[\text{Eu} \subset 2.2.1]\text{Cl}_3$ and 0.5 M NaF . Under these conditions the ion pair having 1:2 stoichiometry, $[\text{Eu} \subset 2.2.1]^{3+} \cdot 2\text{F}^-$, is formed (31).

Acknowledgments

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