Ligand-centered Luminescence and Deactivation by Ligand Field States in Alizarin Complexes

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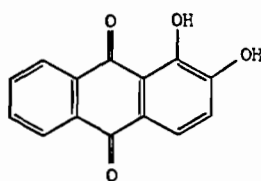
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Abstract

The red/near-infrared emission spectra of alizarin (1,2-dihydroxyanthraquinone), the potassium salt of alizarin and the aluminum and zinc complexes of alizarin in the solid state are reported. The emission is assigned to an alizarin localized transition from an in plane non-bonding orbital delocalized over the anthraquinone nucleus to a predominantly π^* quinone C=O acceptor orbital ($n\pi^*$ ligand localized excited state). The cobalt, nickel and copper complexes do not emit from their $n\pi^*$ excited state. In these complexes, metal centered d–d excited states which lie lower in energy than the ligand localized $n\pi^*$ state effectively deactivate the luminescence.

Introduction

Alizarin, 1,2-dihydroxyanthraquinone, and its metal complexes have historically been of great interest. It is the principle coloring material of madder, one of the most ancient dyestuffs [1]. Alizarin gives colored compounds with metals ('lakes'), the color of which depends upon the metal [2, 3]. In addition to its use in dyes and pigments, alizarin is used for the spectrophotometric determination of metals [4–7].

The structural and spectroscopic properties of alizarin, its salts and metal complexes have been investigated by several workers [2, 3, 8–16]. The free alizarin molecule is shown below. Metals com-

plex to this ligand through the ionized 1-hydroxyl oxygen and the adjacent carbonyl oxygen forming a six-member chelate ring structure [2, 3]. Salt

formation (i.e. potassium alizarinate) occurs by association of a cation with the ionized 2-hydroxyl group [8]. The lowest energy visible absorption band of alizarin has been assigned by Issa *et al.* to an intramolecular charge transfer from the anthracene nucleus out to the C=O acceptor groups [10]. Luminescence spectra of alizarin in isopropanol glass and of alizarin and its aluminum, gallium and indium complexes in the solid state as well as in aqueous solution have been reported [15, 16].

In this paper, we report an investigation of the absorption and luminescence properties of alizarin, its potassium salt and its Al(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes. Absorption spectra were taken of halocarbon grease mulls of each compound to eliminate solvent effects. For comparison, spectra were also taken of *N,N*-dimethylformamide (DMF) solutions. Emission is observed from the lowest energy ligand localized excited state for alizarin, potassium alizarinate and the Al(III) and Zn(II) complexes. The Co(II), Ni(II) and Cu(II) complexes do not emit from their lowest ligand based excited state. The lowest lying excited electronic states are assigned and the effect of the metal on the luminescence is discussed.

Experimental

Synthesis

Alizarin was purchased from Aldrich and used without further purification in the synthesis of potassium alizarinate. It was recrystallized once from acetic acid prior to use in the synthesis of calcium aluminum alizarinate.

Preparation of Ca[Al(OH)(C₁₄H₆O₄)₂(OH₂)] · 6H₂O

Preparation of $Ca[Al(OH)(C_{14}H_6O_4)_2(OH_2)] \cdot 6H_2O$

Calcium aluminum alizarinate was prepared according to the reported synthesis [3]. The crude product was recrystallized from hot DMF, washed with absolute ethanol followed by ether, then dried at 80 °C overnight. The purified product is a deep red powder. The product is soluble in DMF. It is insoluble in water and diethyl ether. *Anal.* Calc. C, 48.98; H, 3.96. Found: C, 48.55; H, 3.56%.

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Preparation of $K(C_{14}H_7O_4) \cdot (H_2O)$

Potassium alizarinate was prepared using the procedure of Weiland and Binder with some modifications [17]. Alizarin (5 g, 0.02 mol) was dissolved in 1 l of hot absolute ethanol. The solution was filtered and a solution of 2 g (0.02 mol) of potassium acetate dissolved in 20 ml absolute ethanol was added with stirring. Approximately $\frac{2}{3}$ of the alcohol was distilled off and the solution was cooled overnight. The resulting precipitate was filtered, washed with absolute ethanol and then dried at 90 °C for 2 h. This procedure yielded a dark purple powder which contained residual alizarin as evident from the yellow solution which developed when diethyl ether was added to the sample. The residual alizarin proved difficult to wash out using ether. However, the product could be purified by dissolving it in DMF followed by addition of ether to cause precipitation. Alternatively, using a ten-fold excess of potassium acetate in the synthesis yields a product free of alizarin contamination. The dark purple product is soluble in water, ethanol and DMF. It is insoluble in diethyl ether. *Anal.* Calc.: C, 56.75; H, 3.06. Found: C, 57.14; H, 2.50%.

Preparation of $M(II)(C_{14}H_7O_4)_2 \cdot 2H_2O$

Complexes, $M(II) = Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$

The divalent cobalt, nickel, copper and zinc complexes of alizarin were prepared according to Bakola-Christianopoulou with modifications [2]. Potassium alizarinate (2 mmol) was dissolved in 150 ml distilled water. To this solution, a solution of 1 mmol of the metal chloride or acetate in a 75% aqueous ethanol solution was added with stirring. The solution was stirred at room temperature for at least 3 h and then refrigerated at 0 °C overnight. The dark purple precipitate was filtered and washed with warm water until traces of unreacted potassium alizarinate were gone. Further washing with copious amounts of diethyl ether failed to remove all traces of unreacted alizarin contaminant as evidenced from the light yellow colored washings. Unlike the case of potassium alizarinate, addition of a large excess of the reacting metal did not eliminate the trace alizarin contamination in the product and the product could not be easily recrystallized from DMF. Although trace alizarin contamination existed, the resulting air dried products gave satisfactory elemental analysis for the cobalt, nickel and zinc complexes. *Anal.* for Co(II): Calc.: C, 58.65; H, 3.16. Found: C, 58.59; H, 3.21%. For Ni(II): Calc.: C, 58.68; H, 3.16. Found: C, 58.97; H, 2.74%. For Zn(II): Calc.: C, 58.00; H, 3.13. Found: C, 57.74; H, 3.19%. An unsatisfactory analysis was achieved for the dihydrated copper complex. However, if three waters of hydration are considered the analysis is satisfactory. *Anal.* for $Cu(C_{14}H_7O_4)_2 \cdot 3H_2O$: Calc.: C, 56.43; H, 3.38. Found: C, 56.09; H, 3.20%.

The solid Ni(II) and Cu(II) complexes are reddish brown while the Co(II) and Zn(II) complexes are both black.

Small amounts of pure samples could be obtained for emission studies by dissolving the product in DMF then passing the solution over a column of Bio-Beads SX-12. The purple fraction containing the complex elutes first, followed by a yellow fraction containing free alizarin. The complexes are insoluble in diethyl ether and water.

Absorption Spectra

Absorption spectra were taken of the recrystallized samples of alizarin, the calcium aluminum alizarinate and the potassium alizarinate. Since it was difficult to obtain the Co(II), Ni(II), Cu(II) and Zn(II) complexes completely free of trace alizarin contamination in quantities large enough for absorption measurements, the unchromatographed products were used for these measurements. UV–Vis spectra were taken of halocarbon grease mulls and DMF solutions of all of the compounds using a Cary 219 spectrophotometer. Near infrared spectra from DMF solutions were recorded with a Cary 14 spectrophotometer. The DMF was dried over potassium hydroxide and vacuum distilled at 80 °C immediately prior to use.

Emission Spectra

Room temperature and low temperature (10 K) emission spectra of recrystallized alizarin and calcium aluminum alizarinate were taken from samples mounted on a copper block inside a displex closed cycle helium refrigeration unit. An argon ion laser served as the excitation source. Emission from the samples was collected at approximately 45° from the laser beam, sent through a SPEX model 1702 3/4 meter monochromator, then detected using an RCA C31034 photomultiplier tube. The signal from the photomultiplier tube was processed through an EG&G model 1105 photon counter and stored digitally on an Apple II computer. The spectra shown are corrected for instrumental response.

Emission spectra of the recrystallized potassium alizarinate and the chromatographed Zn(II) complex were measured at 4.2 K. The samples were mounted inside a liquid helium dewar. An argon ion laser chopped at 110 Hz was used to excite the samples. The light was collected at approximately 45° from the excitation source, sent through a PTi 1/4 meter monochromator, then detected with a germanium IR detector. The signal from the detector was fed into a Princeton Applied Research model 121 lock-in amplifier and then stored digitally on a PC Prime 88 computer. The spectra shown are corrected for instrumental response.

Lifetimes

Emission lifetimes were measured at 11 K. The samples were irradiated with 406 nm pulsed light from a XeCl Excimer pumped dye laser (DPS in p-dioxane). The signal was passed through a Spex 1702 3/4 meter single monochromator, detected by an RCA C31034 photomultiplier tube and then collected, stored and displayed using a Tektronix RTD 710 transient digitizer interfaced to an IBM XT computer. The limiting system response time was 15 ns.

Results

Absorption Spectra

The mull spectra of alizarin, its potassium salt and its aluminum, zinc, cobalt and nickel complexes are shown in Fig. 1. Table 1 lists the position in
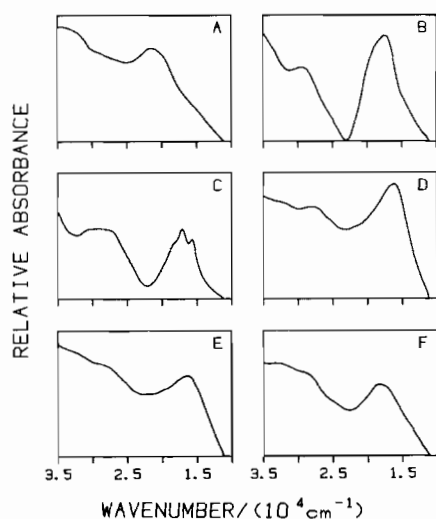
wavenumbers of the lowest energy resolved transition observed in the visible mull spectrum for each of the compounds studied. This transition, which occurs at 21 450 cm^{-1} in the mull spectrum of alizarin, is red shifted in the spectra of the metal complexes. It is also red shifted in the potassium salt. The extent of the shift depends upon the metal. Structure with a spacing of 1300 ± 50 cm^{-1} is observed in this band for the potassium salt and the nickel complex, although it is most prominent in the spectrum of the salt.

Figure 2 shows the DMF solution absorption spectra of the compounds. In DMF, the spectrum of free alizarin changes dramatically as compared to the mull spectrum with the lowest energy transition red shifting by over 3600 cm^{-1}. Furthermore, this transition does not obey Beer's law. In contrast, the solution spectra of potassium alizarinate and

Fig. 1. UV–Vis Halocarbon grease mull absorption spectra for alizarin and its complexes: (A) uncomplexed alizarin; (B) calcium aluminum(III) alizarinate; (C) potassium alizarinate; (D) zinc(II) alizarinate; (E) cobalt(II) alizarinate; (F) nickel(II) alizarinate.
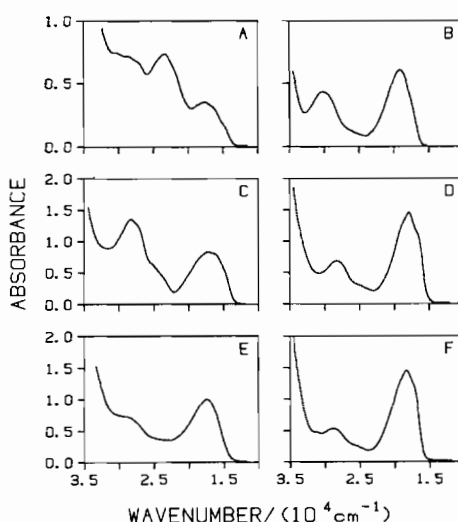

Fig. 2. DMF solution UV/Vis absorption for alizarin and its complexes: (A) uncomplexed alizarin, 1.69×10^{-4} M; (B) calcium aluminum(III) alizarinate, 1.56×10^{-5} M; (C) potassium alizarinate, 1.43×10^{-4} M; (D) zinc(II) alizarinate, 7.35×10^{-5} M; (E) cobalt(II) alizarinate, 7.21×10^{-5} M; (F) nickel(II) alizarinate, 6.74×10^{-5} M.

TABLE 1. Ligand localized $n\pi^*$ absorption maxima observed in the visible halocarbon grease mull and N,N-dimethylformamide solution spectra of alizarin and its complexes

Compound	Band maximum in mull (cm^{-1})	Band maximum in DMF (cm^{-1})	$\log(\epsilon)$ (DMF) (M^{-1} cm^{-1})
Alizarin	21450	17766	a
$K(C_{14}H_7O_4) \cdot H_2O$	17085	17287	3.75
$Ca\{Al(OH)(C_{14}H_6O_4)_2(OH_2)\} \cdot 6H_2O$	17510	19217	4.56
$\{Zn(C_{14}H_7O_4)_2\} \cdot 2H_2O$	16200	17912	4.28
$\{Co(C_{14}H_7O_4)_2\} \cdot 2H_2O$	16360	17472[b]	4.10
$\{Ni(C_{14}H_7O_4)_2\} \cdot 2H_2O$	18480	18224[c]	4.34

[a]Does not obey Beer's Law.   [b]Weak lower energy bands centered at 8000 cm^{-1} are also observed.   [c]A weak tail extending out to about 7000 cm^{-1} is also observed.

of the metal complexes do not change as dramatically when compared to their mull spectra. The overall features of these spectra remain about the same with smaller shifts (less than 1800 cm^{-1}) in the lowest energy visible transition. Table 1 lists the position in wavenumbers of this transition along with the log of the extinction coefficient. Weak structure is observed on this band for free alizarin, the potassium salt and the zinc and nickel complexes. In the solution spectra, the structure is less well resolved than that observed in the mull spectrum of potassium alizarinate.

The near-infrared spectra of the Co(II), Ni(II) and Cu(II) complexes exhibit a weak lower lying absorption band which is not observed for any of the other compounds. As shown in Fig. 3, this transition is well separated from the visible band in the Co(II) complex, but it is observed only as a long tail extending out to about 7000 cm^{-1} for the Ni(II) complex. Two weak bands at 10 230 and 8860 cm^{-1} have been previously reported for the nickel complex [2]. In the Co(II) complex, this transition is a broad band which is composed of more than one component and is centered around 8000 cm^{-1}. It has an extinction coefficient of about 10 M^{-1} cm^{-1}. The extinction coefficient for the tail observed in the spectrum of the nickel complex is of the same magnitude. The Cu(II) complex also exhibits a weak, well separated absorption band lower in energy than the ligand localized transition. This band is broad, contains more than one component and is centered at about 7500 cm^{-1} for the copper complex.

Emission Spectra

The emission spectra of alizarin, potassium alizarinate and the zinc and aluminum complexes were independent of the wavelength of excitation. The low temperature emission spectra of alizarin excited at 457.9 nm is shown in Fig. 4. Figure 5 shows the low temperature emission from calcium aluminum alizarinate, potassium alizarinate and
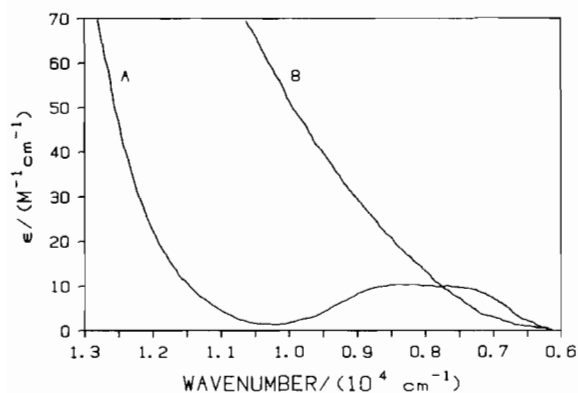

Fig. 3. Near infrared DMF solution absorption spectra for: (A) cobalt(II) alizarinate; (B) nickel(II) alizarinate.
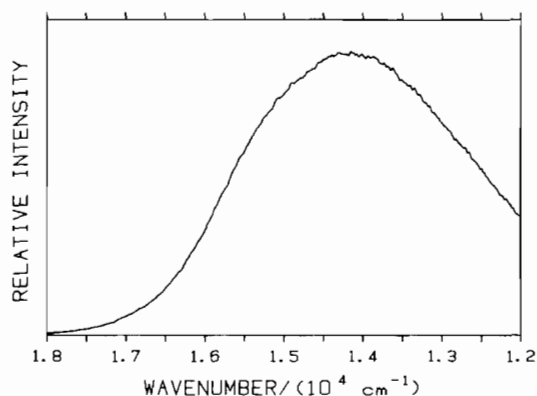

Fig. 4. Low temperature (10 K) emission spectrum of the uncomplexed, solid state alizarin. The wavelength of excitation was 457.9 nm.
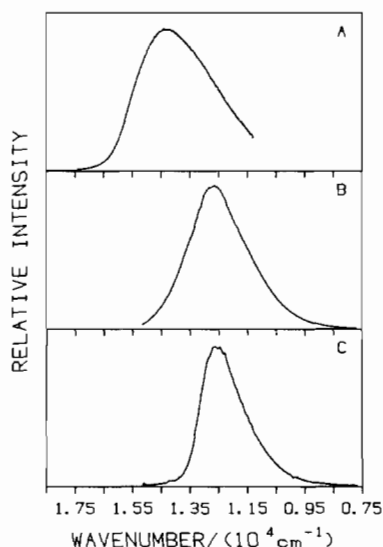

Fig. 5. Emission spectra of: (A) calcium aluminum(III) alizarinate (T = 10 K, λ_{ex} = 457.9 nm); (B) potassium alizarinate (T = 4.2 K, λ_{ex} = 514.5 nm); (C) zinc(II) alizarinate (T = 4.2 K, λ_{ex} = 514.5 nm).

zinc alizarinate. The spectrum of the aluminum complex was obtained using 457.9 nm excitation while the potassium alizarinate and zinc complex spectra were obtained with 514.5 nm excitation. Table 2 lists the position of the emission maximum in wavenumbers for each of these compounds. The emission band is red shifted greatly in potassium alizarinate and zinc alizarinate compared to alizarin. The onset of emission for calcium aluminum alizarinate is red shifted compared to that of the free ligand whereas its maximum is slightly blue shifted. Karyakin et al. reported values of 14 144 and 14 388 cm^{-1} for emission maxima of crystalline samples of alizarin and calcium aluminum alizarinate, respectively [16]. The room temperature emission spectrum of alizarin is shifted approximately 300

TABLE 2. Emission maxima and lifetimes for alizarin and its complexes

Compound	Emission maximum (cm^{-1})	Emission lifetime (ns)
Alizarin	14179[a]	<15
$K(C_{14}H_7O_4)\cdot H_2O$	12714[b]	<15
$Ca\{Al(OH)(C_{14}H_6O_4)_2(OH_2)\}\cdot 6H_2O$	14301[a]	<15
$\{Zn(C_{14}H_7O_4)_2\}\cdot 2H_2O$	12635[b]	<15
$\{Co(C_{14}H_7O_4)_2\}\cdot 2H_2O$	does not emit	
$\{Ni(C_{14}H_7O_4)_2\}\cdot 2H_2O$	does not emit	

[a]T = 10 K; wavelength of excitation = 457.9 nm.   [b]T = 4.2 K; wavelength of excitation = 514.5 nm.

cm^{-1} to higher energy compared to its low temperature spectrum, while the room temperature spectrum of calcium aluminum alizarinate remained virtually unchanged compared to its low temperature spectrum. Emission was not detected from the Co(II), Ni(II) and Cu(II) complexes.

Emission Lifetimes

Emission lifetimes were measured at 14251, 12658, 14329 and 12658 cm^{-1} for alizarin, potassium alizarinate and the Al(III) and Zn(II) complexes, respectively. In all cases the emission decay curves were system limited (≤15 ns).

Discussion

The lowest energy electronic absorption band of alizarin has been assigned to an intramolecular charge transfer from the anthracene nucleus out to the C=O acceptor groups [10]. Extended Hückel MO calculations indicate that the HOMO is an in plane non-bonding orbital delocalized over the anthraquinone nucleus and that the LUMO is predominantly π^* quinone C=O. We will thus refer to this band as an $n\pi^*$ transition. Based upon the overlap of the emission and absorption bands and the short lifetime of the emission, emission from alizarin is assigned to a spin allowed transition from this excited state. Alizarin molecules can readily associate within the solid lattice through intermolecular hydrogen bonding [10], however this type of association is not expected to take place in the potassium salt or in the metal complexes of alizarin. It is reasonable to assume that the $n\pi^*$ excited state observed in the solid state absorption and emission spectra of free alizarin emanates from associated molecules. For this reason, the spectra of uncomplexed alizarin will be considered separately from the others. The spectra of potassium alizarinate, which represents an ionized or basic form of alizarin, will be used for comparison with the metal complexes. Uncomplexed alizarin will be considered first followed by a discussion of its potassium salt and its zinc and

aluminum complexes. Finally, the non-emitting cobalt, nickel and copper complexes will be discussed.

Uncomplexed Alizarin

The lowest energy $n\pi^*$ transition of alizarin is centered at 21450 cm^{-1} in the solid state mull absorption spectrum, but is shifted to 17766 cm^{-1} in the DMF solution spectrum. This shift could arise from two causes. First, the energy of this transition is readily influenced by solvent effects [10, 13]. For example, solvents capable of forming intermolecular hydrogen bonds with the β-OH group have been shown to red shift this band by up to about 1200 cm^{-1} compared to solvents which do not hydrogen bond [10]. This shift caused by hydrogen bonding is smaller than that observed in the mull spectrum versus the spectrum in DMF. Secondly, the energy of this transition is lowered considerably upon hydrogen dissociation [9, 11]. The position of the $n\pi^*$ transition in aqueous solution has been reported to shift from 455 nm (21978 cm^{-1}) to 570 nm (17544 cm^{-1}) when the pH was changed from 7.35, where the molecule is essentially fully protonated, to 11.7, at which point dissociation has occurred [9].

The 3000 cm^{-1} shift of the low energy band in DMF is dominated by hydrogen dissociation. DMF is a weak base in which dissociation may occur to some extent. Furthermore, in the DMF solution spectrum, this band is at almost the same energy and exhibits similar structural features as that observed for potassium alizarinate (*vide infra*) in which the β-OH is dissociated. When a small amount of concentrated hydrochloric acid was added to the DMF solution of alizarin the band at 17766 cm^{-1} disappeared while the absorbance of the next higher energy band at 23364 cm^{-1} increased. Thus, the lowest energy absorption observed in the mull spectrum is assigned to the $n\pi^*$ transition associated with the fully protonated alizarin molecule, whereas the lowest energy absorption observed in its DMF solution spectrum is assigned to the $n\pi^*$ transition associated with singly deprotonated alizarin. Further-

more, the band at $23\,364$ cm^{-1} in the DMF solution spectrum can be assigned to the nπ^* transition of the fully protonated alizarin molecule in the solution. The emission observed from solid alizarin is assigned to fluorescence from the fully protonated nπ^* excited state.

Potassium, Zn(II) and Al(III) Alizarinate

The lowest energy visible absorption band in both the mull and solution spectra of potassium alizarinate is also assigned to the alizarin localized nπ^* transition. This is the same transition observed in the mull spectrum of alizarin, but it has been red shifted due to ionization of the β-OH group. This band is at almost the same energy in both media. In addition, it exhibits similar structural features in the DMF solution spectrum and the mull spectrum, although the structure is much weaker in the solution spectrum. The emission observed from potassium alizarinate is assigned to fluorescence from this ligand localized nπ^* excited state.

The lowest energy absorption band in the mull absorption spectra of the Zn(II) and Al(III) complexes are in the same region as that of the potassium alizarinate, but show a metal dependent shift compared to the salt. In the Zn(II) complex this transition is red shifted by 885 cm^{-1}, whereas for the Al(III) complex it is blue shifted by 425 cm^{-1}. This band is assigned to the ligand localized nπ^* transition which has been perturbed by complexation. The shifts observed in the emission spectrum for the Zn(II) and Al(III) complexes compared to the potassium salt parallel those observed in the absorption spectra; emission from the zinc complex is red shifted by 79 cm^{-1} whereas emission from the aluminum complex is blue shifted by 1587 cm^{-1} with respect to the potassium salt. The emission lifetimes of the zinc and aluminum complexes are less than 15 ns. Thus, we assign the emission from these complexes to fluorescence from the perturbed ligand localized nπ^* excited state.

Co(II), Ni(II) and Cu(II) Alizarinate

The cobalt, nickel and copper complexes of alizarin do not emit from their ligand localized nπ^* excited state. This absence of emission, even at low temperature, can be explained by the presence of low lying d–d excited states on the metals. Careful examination of the absorption spectra of these complexes in the near-infrared region revealed the presence of weak absorbances at energies lower than that of the ligand localized nπ^* band. The presence of metal centered d–d excited states in this energy region is typical for divalent cobalt, nickel and copper complexes [18]. For these complexes the nπ^* band is present and is not significantly changed in energy, width or extinction coefficient from that in the potassium salt or the other metal complexes.

The deactivation of luminescence from ligand localized excited states in metal complexes by low-lying metal centered d–d excited states is well known [19, 20]. The lower-energy states can provide channels for rapid radiationless decay. Only in rare circumstances are states so uncoupled that Kasha's rule is not obeyed in condensed media [21].

Conclusions

Fluorescence is observed from the alizarin localized nπ^* excited state for potassium, zinc and aluminum alizarinate. The absence of emission from the cobalt, nickel and copper complexes is attributed to the existence of d–d bands which lie lower in energy than the ligand localized band. Thus, the d–d excited states are sufficiently coupled to the ligand localized states to provide an efficient pathway for non-radiative decay from the ligand localized states. Metal complexes and mordanted dyes of alizarin will not be expected to emit from their ligand localized excited state if the compound contains ligand field excited states lying lower in energy than the ligand based state.

Acknowledgements

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