

Synthesis and Luminescence of $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{EUO})$ Complexes with $\text{phpyH} = 2\text{-Phenylpyridine}$ and $\text{EUOH} = \text{Tropolone, Flavonol and Lumichrome}$

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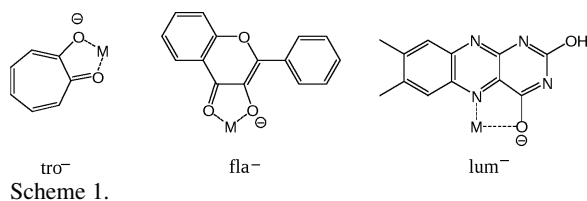
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The complexes $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{EUO})$ with $\text{phpy}^- = \text{deprotonated 2-phenylpyridine}$ and $\text{EUO}^- = \text{bidentate anions of the biologically important compounds EUO (troH = tropolone, flaH = flavonol and lumH = lumichrome)}$ have been prepared and characterized with regard to their optical properties. The $\text{Rh}^{\text{III}}(\text{phpy})_2$ fragment is a useful probe for the emission behavior of these complexes since the phpy IL triplet can serve as a marker. Only the IL states of tp^- and lum^- are located below the phpy IL states. While $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{fla})$ is quite remarkable because it shows an IL (fla) fluorescence, $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{lum})$ displays an IL (lum) phosphorescence as expected owing to the heavy-atom effect.

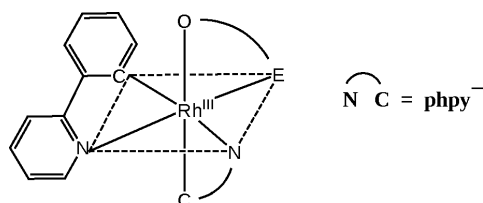
Key words: Electronic Spectra, Luminescence, Rhodium Complexes, Tropolone, Flavonol, Lumichrome

Introduction

Coordination compounds of transition metals play an important role as metalloenzymes in biochemistry. Moreover, suitable metal complexes may be utilized for therapeutic and diagnostic purposes in medical applications. Owing to their coordinating ability a variety of biomolecules such as DNA bases, amino acids and certain coenzymes can be attached to transition metals. Some of such complexes are of natural origin. In other cases they do not occur in nature, but their study could help to reveal their natural functions. Light-induced processes including photochemistry and photoluminescence are of particular interest since they are inherent in biological systems. For the present study we selected the biologically important compounds tropolone (troH), flavonol (flaH) and 7,8-alloxazine or lumichrome (lumH) as targets. The anions tro^- , fla^- and lum^- , which are obtained by deprotonation of the neutral compounds, can serve as bidentate ligands (Scheme 1).



Scheme 1.



Scheme 2.

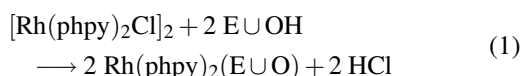
The complex fragment $[\text{Rh}^{\text{III}}(\text{phpy})_2]^+$ with $\text{phpyH} = 2\text{-phenylpyridine}$ was chosen as a very useful probe for the spectroscopic properties of these ligands. First of all, monoanionic bidentate ligands can be easily coordinated to this complex moiety [1, 2]. Accordingly, the complexes $\text{Rh}(\text{phpy})_2(\text{EUO})$ with $\text{EUO}^- = \text{tro}^-$, fla^- and lum^- (Scheme 2) were expected to be accessible by simple synthetic procedures.

The resulting octahedral complexes should be characterized by luminescence properties, which are largely determined by the ligands EUO^- , but are modified by the complex fragment $[\text{Rh}(\text{phpy})_2]^+$ in a well-defined manner [2]. The lowest-energy excited state of the $[\text{Rh}^{\text{III}}(\text{phpy})_2]^+$ moiety is an IL (intraligand) triplet with a diagnostic phosphorescence spectrum [3–6]. If the lowest excited state of EUO^- is located at lower energies, the complex $\text{Rh}(\text{phpy})_2(\text{EUO})$ is expected to emit from this IL state. Owing to the heavy-atom effect of rhodium this luminescence may be a phospho-

rescence, which could appear under ambient conditions. Since $\text{Rh}(\text{III})$ is generally rather redox inert, any interference by low-energy MLCT or LMCT excited states is excluded. LF states of complexes containing the $\text{Rh}(\text{phpy})_2$ fragment occur also at accessible energies, but are not expected to be luminescent at r. t. [7]. In conclusion, our target complexes $\text{Rh}(\text{phpy})_2(\text{EUO})$ seem to be well suited to reveal excited state properties of coordinated EUO^- anions, which may be obscured in complexes of redox-active metals owing to the presence of low-energy CT states.

Results and Discussion

The complexes of the general composition $\text{Rh}(\text{phpy})_2(\text{EUO})$ with $\text{EUO}^- = \text{tro}^-$, fla^- and lum^- were synthesized according to Eq. 1:



The compounds $\text{Rh}(\text{phpy})_2(\text{EUO})$ with $\text{EUO}^- = \text{tro}^-$ and fla^- are sufficiently soluble in common organic solvents in order to perform spectroscopic measurements. The complex $\text{Rh}(\text{phpy})_2(\text{lum})$ is insoluble in polar and non-polar solvents.

The electronic spectrum of $\text{Rh}(\text{phpy})_2(\text{tro})$ in CH_2Cl_2 (Fig. 1) shows absorptions at $\lambda_{\text{max}} = 425$ (sh), 402 (sh), 353, and 243 nm. Tropolone in ethanol displays absorptions at 402 (sh), 368, 351, and 319 nm. The compound $\text{Rh}(\text{phpy})_2(\text{tro})$ is not luminescent at r. t. in solution or in the solid state. In a glass of ethanol, methanol and CH_2Cl_2 (4 : 1 : 1) at 77 K the complex exhibits an emission with $\lambda_{\text{max}} = 462, 497$

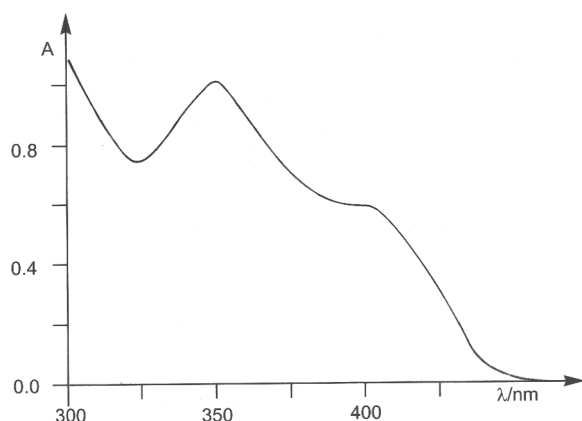


Fig. 1. Electronic absorption spectrum of $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{tro}) \cdot \text{H}_2\text{O}$ in CH_2Cl_2 at r. t. (1 cm cell).

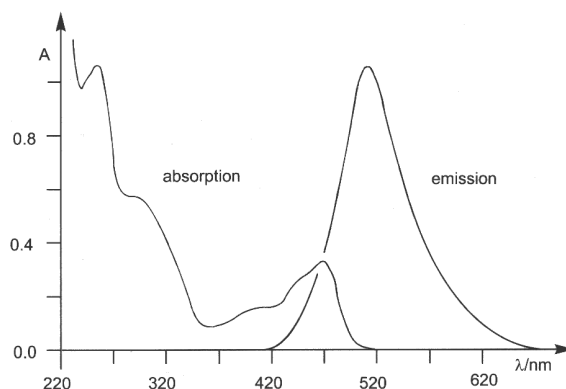


Fig. 2. Electronic absorption and emission spectrum of $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{fla}) \cdot \text{H}_2\text{O}$ in CH_2Cl_2 at r. t. (1 cm cell; emission intensity in arbitrary units).

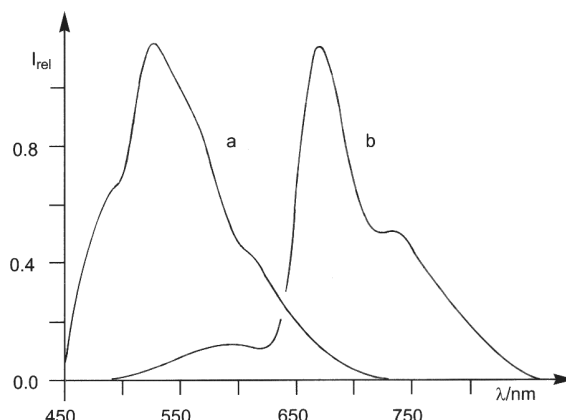


Fig. 3. Electronic emission spectrum of solid lumichrome (a) and $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{lum}) \cdot 2.5\text{H}_2\text{O}$ (b) at r. t. (intensity in arbitrary units).

and 536 nm which is practically identically to that of $[\text{Rh}(\text{phpy})_2\text{Cl}]_2$ [3].

The absorption spectrum of $\text{Rh}(\text{phpy})_2(\text{fla})$ in CH_2Cl_2 (Fig. 2) displays absorptions at $\lambda_{\text{max}} = 469, 432$ (sh), 405 (sh), 290 (sh), 254, and 245 (sh) nm. The complex is slightly solvatochromic. The longest-wavelength band appears at $\lambda_{\text{max}} = 469$ nm in CH_2Cl_2 , 463 nm in CH_3CN and 447 nm in EtOH. The compound is luminescent at r. t. in solution. A green emission (Fig. 2) appears at $\lambda_{\text{max}} = 510$ nm. This emission is not quenched by oxygen. The luminescence of solid $\text{Rh}(\text{phpy})_2(\text{fla})$ occurs at 542 nm. The emission of the complex resembles that of the protonated ligand flaH which shows also a single emission band at $\lambda_{\text{max}} = 525$ nm (in CH_3CN).

Unfortunately, $\text{Rh}(\text{phpy})_2(\text{lum})$ is rather insoluble in all common solvents. The solid complex exhibits a

quite intense red emission (Fig. 3) at $\lambda_{\text{max}} = 669 \text{ nm}$. Solid lumichrome shows a green emission (Fig. 3) at $\lambda_{\text{max}} = 524 \text{ nm}$.

Pseudooctahedral complexes of the type $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{LUL})$ with $\text{LUL} =$ bidentate anion are easily formed from $[\text{Rh}^{\text{III}}(\text{phpy})_2\text{Cl}]_2$ by substitution of the bridging chloride. The excited state properties of the resulting compounds are determined by the IL states of LUL^- provided these states are located at lower energies than those of the orthometalated phpy^- ligand [2]. The identification of the phpy^- IL emission is facilitated by the observation that the IL phosphorescence shows a characteristic structure [2–7], which is observed for various $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{LUL})$ complexes [2].

Tropolone is present in various natural compounds such as colchicine, hinokitiol, thujaplicine, and purpurogallin. While complexes with deprotonated tropolone as a bidentate ligand are well known, they do not seem to occur in biologic materials. However, the tropolonate complexes of In are applied for labelling blood cells [8]. There is very little known about the electronic spectra of tropolonate complexes. In this context it is quite interesting that complexes $\text{M}(\text{tro})_3$ with $\text{M} = \text{Al}$ and Ga have been reported to show a blue electroluminescence [9]. The absorption spectrum of $\text{Rh}(\text{phpy})_2(\text{tro})$ (Fig. 1) displays its longest-wavelength spin-allowed band at 400 nm. An additional spin-forbidden transition may give rise to a very weak absorption near 450 nm [2, 3] which, however, is obscured by the 400 nm band. Since the longest-wavelength band of the $\text{Rh}^{\text{III}}(\text{phpy})_2$ fragment, as well as that of tropolone appear also at approximately 400 nm, the origin of the lowest-energy absorption of $\text{Rh}(\text{phpy})_2(\text{tro})$ at 400 nm is not clear. Fortunately, the luminescence of $\text{Rh}(\text{phpy})_2(\text{tro})$ which occurs only at low temperatures can be unambiguously identified as an IL phosphorescence of the phpy^- ligand. It follows that the phpy^- IL triplet is the lowest excited state of the complex.

Flavonol (or 3-hydroxyflavone) is the parent compound of a variety of polyhydroxy flavones such as quercetin or morin which are present in various plants as yellow dyes. Quercetinase is a copper containing dioxygenase which catalyzes the oxidative degradation of quercetin [10]. A variety of coordination compounds with ligands derived from polyhydroxy flavones have been prepared and characterized. Diverse flavonolate complexes, in particular those of main group metal ions such as Al^{3+} , Ga^{3+} , In^{3+} , Ge^{4+} , and Sn^{2+} , have been reported to exhibit an in-

tense fluorescence [11–13]. In contrast, a copper(I) flavonolate complex does not only show an IL fluorescence but an additional phosphorescence, which appears even under ambient conditions [14]. However, the lowest-energy IL state of this Cu(I) complex may contain some LMCT character which enhances the electronic coupling between metal and ligand and facilitates the occurrence of the IL phosphorescence at r. t. The longest-wavelength absorption of $\text{Rh}(\text{phpy})_2(\text{fla})$ (Fig. 2) shows a maximum at 469 nm including shoulders at 432, 405, 290, and 245 nm. This spectrum resembles that of $\text{Cu}^{\text{I}}(\text{PPh}_3)_2(\text{fla})$, which shows a longest-wavelength absorption consisting of three structural features at 486, 434 and 414 nm [14]. In the case of the copper complex, the central absorption at 434 nm has the highest intensity while the other two features appear as shoulders at higher and lower energies.

$\text{Rh}(\text{phpy})_2(\text{fla})$ shows a green luminescence at $\lambda_{\text{max}} = 510 \text{ nm}$ in solution (Fig. 2) and at 542 nm in the solid state. We attribute this emission to an IL (fla) fluorescence. As expected for a fluorescence, the emission strongly overlaps the absorption. In agreement with the emission of $\text{Rh}(\text{phpy})_2(\text{thiooxinate})$ [2] the fluorescence of $\text{Rh}(\text{phpy})_2(\text{fla})$ is not quenched by oxygen. Moreover, the fluorescence of flaH occurs at a wavelength ($\lambda_{\text{max}} = 525 \text{ nm}$) close to that of $\text{Rh}(\text{phpy})_2(\text{fla})$. However, in distinction to $\text{Rh}(\text{phpy})_3(\text{thiooxinate})$, the complex $\text{Rh}(\text{phpy})_2(\text{fla})$ does not display an additional IL (fla) phosphorescence. This is a remarkable observation and requires a comment since the heavy-atom effect of rhodium might be expected to facilitate the appearance of an IL phosphorescence under ambient conditions in analogy to $\text{Rh}(\text{phpy})_2(\text{thiooxinate})$ [2]. As mentioned above, $\text{Rh}(\text{III})$ is rather inert and does not participate in CT transitions. Accordingly, the electronic coupling between rhodium and its ligands is probably rather weak and reduces the heavy-atom effect in ligands. In the case of $\text{Rh}(\text{phpy})_2(\text{fla})$, the IL fluorescence is apparently fast enough to compete successfully with intersystem crossing. As an alternative, or as an additional influence, the IL phosphorescence can be also quenched by low-energy LF states, which may be rapidly populated from other states at higher energies. In this context it should be emphasized that quite recently various complexes have been observed to show an IL fluorescence while an IL phosphorescence is absent although the central metals such as Re [15], Pt [16] and Gd or Th [17] are expected to exert a strong heavy-atom effect. Accordingly, it is

not trivial to predict for IL states the nature of the emission (fluorescence or phosphorescence) on the basis of the position of the metal in the periodic table.

Flavins, isoalloxazines and alloxazines are tricyclic compounds, which are basic constituents of various redox-active enzymes. Since they function also as bidentate ligands, their metal complexes have attracted considerable attention [18, 19]. Although the metal-free compounds are involved in diverse light-induced processes, the photochemical and photophysical properties of metal complexes with these ligands have been largely ignored [20]. In this context we prepared and examined the compound $\text{Rh}(\text{phpy})_2(\text{lum})$. In analogy to various other coordination compounds with similar ligands [18, 19] it is quite reasonable to assume that the complexation takes also place at a nitrogen and an oxygen atom of two adjacent six-membered rings forming a five-membered chelate ring.

Since $\text{Rh}(\text{phpy})_2(\text{lum})$ is insoluble in all common solvents its luminescence spectrum was measured in the solid state. The complex shows a red emission at r. t. (Fig. 3) with $\lambda_{\text{max}} = 669$ nm. We suggest that this emission is an IL (lum) phosphorescence while the short-wavelength shoulder at 593 nm might belong to the corresponding IL (lum) fluorescence. In this case the heavy-atom effect of rhodium is apparently strong enough to enhance intersystem crossing with concomitant fluorescence quenching and appearance of the phosphorescence under ambient conditions. In solution free lumichrome shows at r. t. only a fluorescence with a maximum near 430 nm [21, 22], while at 77 K in addition a structured phosphorescence occurs between 500 and 700 nm including a maximum at 545 nm and a pronounced shoulder at 580 nm [21, 23]. In the solid state at r. t., lumichrome shows a greenish emission (Fig. 3) with $\lambda_{\text{max}} = 524$ nm and shoulders at 493, 565, and 614 nm. This is certainly a fluorescence which is red-shifted in comparison to the fluorescence in solution. However, excited-state proton transfer complicates the fluorescence properties of lumichrome [22]. Irrespective of these details it makes sense to attribute the red emission of $\text{Rh}(\text{phpy})_2(\text{lum})$ to the IL (lum) phosphorescence since it appears at distinctly longer wavelength than the fluorescence and even the phosphorescence of lumichrome.

Conclusion

In summary, complexes of the type $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{EUO})$ with $\text{phpyH} =$ deprotonated 2-phenylpyridine

are useful for the assignment of IL (EUO^-) emissions (fluorescence and/or phosphorescence) provided these IL states are located at energies below those of the phpy^- ligand. The $\text{Rh}^{\text{III}}(\text{phpy})_2$ fragment was thus used as a probe for the biologically important chelating ligands tropolonate (tropolone = troH), flavonolate (flaH) and lumichrome (lumichrome = lumH) in their deprotonated form. In the case of $\text{Rh}(\text{phpy})_2(\text{tro})$ the IL (tro) states are apparently situated above the phpy states. Accordingly, the emission is of the phpy IL type. In the complex $\text{Rh}(\text{phpy})_2(\text{fla})$ and $\text{Rh}(\text{phpy})_2(\text{lum})$ the IL states of fla^- and lum^- are located below the phpy states. Both complexes show a r. t. luminescence. $\text{Rh}(\text{phpy})_2(\text{lum})$ displays a IL (lum) phosphorescence as expected owing to the heavy-atom effect. In contrast it is quite surprising that the emission of $\text{Rh}(\text{phpy})_2(\text{fla})$ is apparently an IL (fla) fluorescence.

Experimental Section

All solvents for spectroscopic measurements were of spectrograde quality. $[\text{Rh}(\text{phpy})_2\text{Cl}]_2$, tropolone (troH), 3-hydroxyflavone or flavonol (flaH), 7,8-dimethylalloxazine or lumichrome (lumH), KOCMe_3 (potassium *tert.*-butoxide), and TIPF_6 were commercially available (Aldrich) and used without further purification.

Absorption spectra were measured with a Varian Cary 50 or a Kontron Uvikon 860 spectrophotometer. Emission spectra were recorded on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations.

Rh(phpy)₂(tro)

To a solution of $[\text{Rh}(\text{phpy})_2\text{Cl}]_2$ (450 mg, 0.5 mmol) in 30 mL of DMF was added tropolone (250 mg, 2 mmol). This mixture was refluxed for 12 h. The resulting, dark yellow solution was cooled to r. t. Upon addition of cold water (50 mL) a yellow precipitate was formed. It was collected by filtration, washed with water, ethanol and diethyl ether, and dried over silica gel; yield 440 mg (80 %). – Analysis for $\text{Rh}(\text{phpy})_2(\text{tro}) \cdot \text{H}_2\text{O}$: calcd. C 63.92, H 4.26, N 5.55; found C 63.28, H 4.21, N 5.09.

Rh(phpy)₂(fla)

To a solution of flavonol (140 mg, 0.58 mmol) in 50 mL of ethanol was added KOCMe_3 (65 mg, 0.58 mmol) and $[\text{Rh}(\text{phpy})_2\text{Cl}]_2$ (258 mg, 0.29 mmol). This mixture was stirred for 3 h at 50 °C. In the resulting yellow solution a

precipitate was formed. The solvent was removed by evaporation under reduced pressure. Diethyl ether (150 mL) and acetone (250 mL) were added to the yellow residue. The mixture was stirred for 30 min and yellow impurities removed by filtration. The solvent of the filtrate was removed by evaporation leaving a yellow product; yield 310 mg (80 %). – Analysis for $\text{Rh}(\text{phpy})_2(\text{fla}) \cdot 0.5\text{H}_2\text{O}$: calcd. C 67.54, H 3.90, N 4.24; found C 67.55, H 3.94, N 4.24.

Rh(phpy)₂(lum)

A mixture of $[\text{Rh}(\text{phpy})_2\text{Cl}]_2$ (258 mg, 0.29 mmol) and TiPF_6 (200 mg, 0.58 mmol) in 50 mL of CH_3CN was re-

fluxed for 30 min. A precipitate of TiCl was removed by filtration. To this solution were added lumichrome (140 mg, 0.58 mmol) and a solution of KOCMe_3 (65 mg, 0.58 mmol) in 5 mL of ethanol. This mixture was refluxed for 6 h. An orange precipitate was formed and isolated from the brownish solution by filtration, washed with methanol, acetone and diethyl ether, and finally dried; yield 312 mg (77 %). – Analysis for $\text{Rh}(\text{phpy})_2(\text{lum}) \cdot 2.5\text{H}_2\text{O}$: calcd. C 58.60, H 3.64, N 11.97; found C 58.54, H 4.43, N 12.05.

Acknowledgement

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