

Synthesis and Luminescence of $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{SUE})$ Complexes with $\text{phpy}^- = \text{Deprotonated 2-Phenylpyridine}$ and $\text{SUE}^- = \text{Diethyldithiocarbamate, 2-Pyridinethiolate and 2-Quinoline-thiolate}$

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Complexes of the general composition $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{SUE})$ with $\text{phpy}^- = 2-(2\text{-pyridyl})\text{phenyl}$ and $\text{SUE}^- = \text{diethyldithiocarbamate, 2-pyridinethiolate and 2-quinolinethiolate}$ were prepared and characterized.

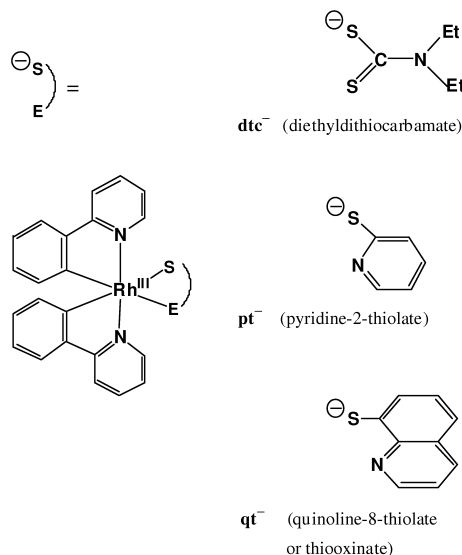
The complexes with $\text{SUE}^- = \text{diethyldithiocarbamate}$ and 2-pyridinethiolate show a low-temperature luminescence which originates from a $\text{phpy } \pi\pi^*$ intraligand triplet. For the complex with $\text{SUE}^- = 2\text{-quinolinethiolate}$ (or thiooxinate) the lowest-energy excited state is of the quinolinethiolate intraligand type. This complex displays a fluorescence as well as a phosphorescence under ambient conditions.

Key words: Electronic Spectra, Luminescence, Rhodium Complexes, Thiolate Complexes

Introduction

A variety of compounds of the type $\text{Rh}^{\text{III}}(\text{phpy})_2\text{LX}$ with $\text{phpy}^- = 2-(2\text{-pyridyl})\text{phenyl}$ as bidentate ligand has been prepared and characterized [1]. Generally, the electronic spectra of $\text{Rh}(\text{III})$ complexes do not display long-wavelength MLCT (metal-to-ligand charge transfer) and LMCT (ligand-to-metal charge transfer) absorptions [2] because $\text{Rh}(\text{III})$ is rather redox inert. The electronic spectra of $\text{Rh}(\text{phpy})_2\text{LX}$ complexes are dominated by $\pi\pi^*$ phpy IL (intraligand) transitions [3–5]. Frequently, these complexes show a lumines-

cence which originates from the phpy IL triplet provided it is located at energies well below the lowest-energy LF (ligand field) states [3–6]. The range of emissive $\text{Rh}^{\text{III}}(\text{phpy})_2$ complexes may be extended if other low-energy excited states are introduced by the appropriate choice of further ligands. We explored this possibility and selected the following compounds for the present study:



This choice was based on the following considerations. Thiolates are reducing anions and accordingly are strong CT donors. Since the phpy ligand has empty π^* orbitals available, low-energy thiolate to phpy LLCT (ligand-to-ligand charge transfer) transitions may occur. In this context it is of interest that numerous polypyridyl/thiolate mixed-ligand complexes have been observed to display thiolate \rightarrow polypyridyl LLCT transitions at low energies [7–9]. The desired compounds $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{SUE})$ were expected to be accessible by relatively simple procedures in analogy to various other $\text{Rh}^{\text{III}}(\text{phpy})_2$ complexes which contain an additional bidentate anionic ligand [1]. The synthesis of $\text{Rh}(\text{phpy})_2(\text{dtc})$ has been previously reported [10].

Experimental Section

Materials

All solvents for spectroscopic measurements were of spectrograde quality. $[\text{Rh}(\text{phpy})_2\text{Cl}]_2$, $\text{Nadtc} \cdot 3\text{H}_2\text{O}$ (sodium diethyldithiocarbamate), ptH (pyridine-2-thiol), $\text{qtH} \cdot \text{HCl}$

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SUE [−]	λ_{\max} [nm]	$(\epsilon [1 \text{ mol}^{-1} \text{ cm}^{-1}])$				
dtc [−]	237 (66 500)	275 sh (32 900)	340 sh (7400)	383 (4770)	455 sh (16)	
pt [−]	238 (45 100)	260 (39 200)	285 (24 400)	357 (5620)	384 sh (4600)	456 sh (15)
qt [−]	220 (58 600)	262 (39 100)	371 (6550)	456 (4900)		

sh = shoulder

Table 1. UV-vis spectral data of $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{SUE})$ with $\text{SUE}^- = \text{dtc}^-$, pt^- and qt^- in CH_3CN at r.t.

(quinoline-8-thiol hydrochloride) and KOCMe_3 (potassium *tert*-butoxide) were commercially available (Aldrich) and used without further purification.

$\text{Rh}(\text{phpy})_2(\text{dtc})$

To a solution of $\text{Na}(\text{dtc}) \cdot 3\text{H}_2\text{O}$ (225 mg, 1 mmol) in 40 ml of methanol was added $[\text{Rh}(\text{phpy})_2\text{Cl}]_2$ (450 mg, 0.5 mmol). This mixture was stirred for 30 h at r.t., then refluxed for 2 h. The solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 . The volume of the filtrate was reduced by evaporation. Upon addition of ether a yellow precipitate was formed. It was collected by filtration, washed with ether and dried over silica gel; yield 455 mg (81%).

Analysis for $\text{C}_{27}\text{H}_{26}\text{N}_3\text{S}_2\text{Rh}$ (559.57): calcd. C 57.94, H 4.68, N 7.51, S 11.46; found C 57.74, H 4.66, N 7.37, S 11.37.

$\text{Rh}(\text{phpy})_2(\text{pt})$

To a solution of ptH (112 mg, 1 mmol) in 20 ml of *n*-butanol were added $[\text{Rh}(\text{phpy})_2\text{Cl}]_2$ (450 mg, 0.5 mmol) and KOCMe_3 (115 mg, 1 mmol). The yellow suspension was refluxed for 2 h. A slightly yellow product precipitated. It was collected by filtration, washed with methanol and diethyl ether and dried over silica gel; yield 485 mg (93%).

Analysis for $\text{C}_{27}\text{H}_{20}\text{N}_3\text{SRh}$ (521.44): calcd. C 62.19, H 3.87, N 8.06, S 6.15; found C 61.53, H 3.88, N 8.09, S 6.28.

$\text{Rh}(\text{phpy})_2(\text{qt})$

To a solution of $[\text{Rh}(\text{phpy})_2\text{Cl}]_2$ (225 mg, 0.25 mmol) in 40 ml of CH_2Cl_2 was added $\text{qtH} \cdot \text{HCl}$ (100 mg, 0.5 mmol). This mixture was stirred until a red-orange solution was formed. To this solution was added KOCMe_3 (115 mg, 1 mmol) and stirred for 1.5 h. A precipitate of KCl was removed by filtration. Upon addition of diethyl ether an orange precipitate was formed, which was collected by filtration, washed with diethyl ether and dried over silica gel; yield 190 mg (31%).

Analysis for $\text{C}_{31}\text{H}_{26}\text{N}_3\text{O}_2\text{SRh} \cdot 2\text{H}_2\text{O}$ (607.53): calcd. C 61.29, H 4.31, N 6.92, S 5.28; found C 61.81, H 4.08, N 6.80, S 5.21.

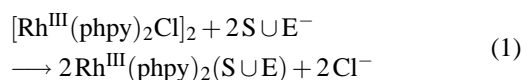
Instrumentation

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.

Results

The complexes $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{SUE})$ with $\text{SUE}^- = \text{dtc}^-$, pt^- and qt^- were synthesized according to the equation:



The compounds are neutral and sufficiently soluble in common organic solvents. The absorption spectra are displayed in Figs 1–3 and corresponding spectral data are presented in Table 1. The complexes $\text{Rh}(\text{phpy})_2(\text{SUE})$ with $\text{SUE} = \text{dtc}$ and pt are not luminescent at r.t. but show an emission in low-temperature glasses. This emission is almost identical for both compounds and is shown for the dtc complex in Fig. 1 with $\lambda_{\max} = 461 \text{ nm}$, 482, 493, 524, 532 and 567. The complex $\text{Rh}(\text{phpy})_2(\text{qt})$ is luminescent at r.t. (Fig. 3). In argon-saturated solutions two emission maxima appear

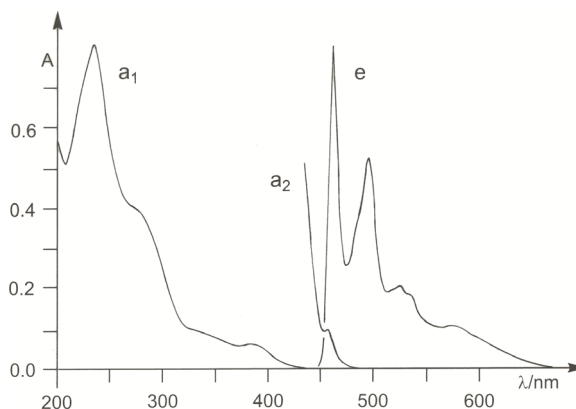


Fig. 1. Electronic absorption (a_1 , a_2) and emission (e) spectra of $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{dtc})$ under argon. Absorptions in CH_3CN at room temperature: a_1 , $1.25 \times 10^{-5} \text{ M}$, 1 cm cell; a_2 , $6.29 \times 10^{-2} \text{ M}$, 1 mm cell. Emission: in EtOH at 77 K, $\lambda_{\text{exc}} = 350 \text{ nm}$, intensity in arbitrary units.

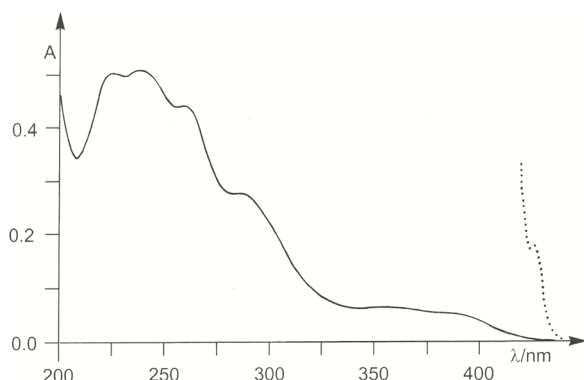


Fig. 2. Electronic absorption spectrum of 1.12×10^{-5} M (—, 1 cm cell) and 1.22×10^{-2} M (···, 1 mm cell) $\text{Rh}^{\text{III}}(\text{ppy})_2(\text{pt})$ in CH_3CN under argon at room temperature.

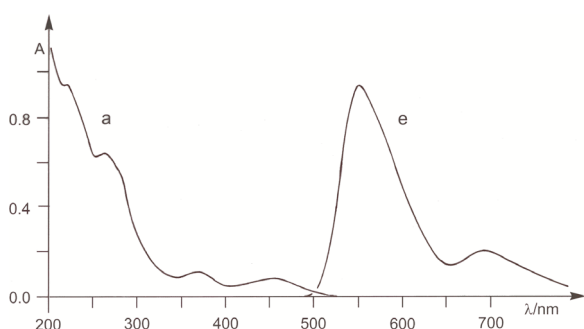


Fig. 3. Electronic absorption (a) and emission (e) spectrum of 1.63×10^{-4} M $\text{Rh}^{\text{III}}(\text{ppy})_2(\text{qt})$ in CH_3CN under argon at room temperature, 1 cm cell. Emission: $\lambda_{\text{exc}} = 450$ nm, intensity in arbitrary units.

at 558 and 690 nm. In air-saturated solutions only the shorter-wavelength band appears.

Discussion

The lowest-energy excited states of various $\text{Rh}^{\text{III}}(\text{ppy})_2$ complexes [3–5] including $[\text{Rh}(\text{ppy})_2\text{Cl}]_2$ [11] are apparently of the $\pi\pi^*$ (ppy) IL type. In the absorption spectrum these IL transitions appear as a relatively intense band at approximately 390 nm for the spin-allowed singlet-singlet and a rather weak band near 460 nm for the corresponding spin-forbidden singlet-triplet transitions. These complexes show an emission which originates from the lowest-energy ppy IL triplet. The phosphorescence spectrum displays well-developed vibrational features including a maximum at 461 nm which represents the 0,0 transition and coincides with the weak longest-wavelength absorption. A non-emissive

LF state is apparently located at energies slightly above the IL triplet. As a consequence the IL triplet emits only at low temperature but at r.t. undergoes a thermally activated transition to the non-emissive LF state.

All these observations and conclusions which apply to $[\text{Rh}(\text{ppy})_2\text{Cl}]_2$ and related complexes are also valid for $\text{Rh}(\text{ppy})_2(\text{SUE})$ with $\text{SUE} = \text{dtc}$ and pt as indicated by the similarity of the absorption and emission spectra. Although a $\text{SUE} \rightarrow \text{ppy}$ LLCT excited state should exist at relatively low energies it is not emissive because it is obviously situated well above the emitting ppy IL state. In contrast, a variety of complexes which contain polypyridines (*e.g.* 2,2'-bipyridyl) and thiolates as ligands are well known to show a phosphorescence from (thiolate \rightarrow polypyridine) LLCT states provided they are the lowest states of these complexes [7, 9]. However, such LLCT states are shifted to higher energies if the polypyridines are replaced by their ortho-metallated counterparts such as ppy which is a weaker CT acceptor since its π^* orbitals are located at higher energies [3–5]. Accordingly, the emission of $\text{Rh}(\text{ppy})_2(\text{SUE})$ with $\text{SUE} = \text{dtc}$ and pt originates from the ppy IL triplet. The spectroscopic properties of $\text{Rh}(\text{ppy})_2(\text{qt})$ are clearly different from those of $\text{Rh}(\text{ppy})_2(\text{SUE})$ with $\text{SUE} = \text{dtc}$ and pt . The complex $\text{Rh}(\text{ppy})_2(\text{qt})$ shows a fairly intense absorption in the visible part of the spectrum ($\lambda_{\text{max}} = 456$ nm, Fig. 3). We assign this band to the lowest-energy spin-allowed $\pi\pi^*$ IL transition of the coordinated qt^- ligand. Quinolinethiolate (or thiooxinate) complexes of main group metals such as $\text{Ga}(\text{III})$ and $\text{In}(\text{III})$ display this IL band near 400 nm [12–14]. The red shift observed for $\text{Rh}(\text{ppy})_2(\text{qt})$ ($\lambda_{\text{max}} = 456$ nm) is not so surprising since analogous shifts have also been reported for 8-quinolinolate (oxinate) complexes. For example, $\text{Al}(\text{oxinate})_3$ absorbs at $\lambda_{\text{max}} = 388$ nm while the corresponding band of $\text{Rh}(\text{oxinate})_3$ appears at 425 nm [15]. The luminescence of $\text{Rh}(\text{ppy})_2(\text{qt})$ which occurs in solution at r.t. (Fig. 3) is certainly also associated with the qt ligand. The shorter-wavelength band at $\lambda_{\text{max}} = 558$ nm is a fluorescence which overlaps with the absorption spectrum. This fluorescence occurs near 510 nm for the $\text{Ga}(\text{III})$ and $\text{In}(\text{III})$ complex [13, 14]. The longer-wavelength emission of $\text{Rh}(\text{ppy})_2(\text{qt})$ at $\lambda_{\text{max}} = 690$ nm is obviously an IL (qt) phosphorescence which is induced by the heavy-atom effect of rhodium. This phosphorescence is quenched by oxygen. Various oxinate complexes of

heavy metals show a comparable behavior. They exhibit a shorter-wavelength IL fluorescence which is not affected by oxygen and a longer-wavelength phosphorescence which is attenuated or absent in aerated solution [15, 16].

In summary, the lowest-energy excited states of the complexes $\text{Rh}^{\text{III}}(\text{phpy})_2(\text{SUE})$ with $\text{SUE}^- = \text{dtc}^-$, pt^- and qt^- are not as anticipated of the (SUE^- to phpy^-) LLCT type. In the case of the dtc and pt complexes

the lowest-energy states are $\pi\pi^*$ (phpy) triplets which undergo an emission, but only at low temperatures. In contrast, $\text{Rh}(\text{phpy})_2(\text{qt})$ shows a fluorescence and a phosphorescence under ambient conditions. Both emissions originate from an IL singlet and triplet of the qt^- ligand.

Acknowledgement

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