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Spectrochemical Studies on Iridium(III) Pyridine Complexes. An Improved Procedure for Obtaining Purified Compounds

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The IR, UV absorption, and emission spectra of geometric isomers (including double complexes) of chloroiridium(III) complexes with pyridine have been measured. By emission spectroscopy impurities could be detected in several compounds prepared according to procedures as given in the literature. After appropriate purification normal emission properties were obtained for all complexes, resulting in band peaks, band shapes, and Stokes shifts as expected from simple theoretical models.

Introduction

All possible geometric isomers of iridium(III) with chlorine and up to 4 pyridine ligands including cation–anion double complexes are known [1–5]. They form a series of compounds which deserve attention in many respects. Looking at spectroscopic differences and regularities can supply insight into electronic structures and bonding properties, and their changes within this series. Ultraviolet absorption spectra of chloropyridine iridium(III) complexes were investigated some time ago [6, 7], while the corresponding emission spectra have been reported only for the bis(pyridine) complexes [8]. Infrared spectra are known for both $[Irpy_2Cl_4]^-$ isomers and for *tr*-$[Irpy_4Cl_2]^+$ [9]. As will be demonstrated in this article, the emission spectra can also be used for investigating the purity of the prepared compounds: irregular luminescence features are attributable to impurities which, due to the low concentrations, cannot be detected otherwise.

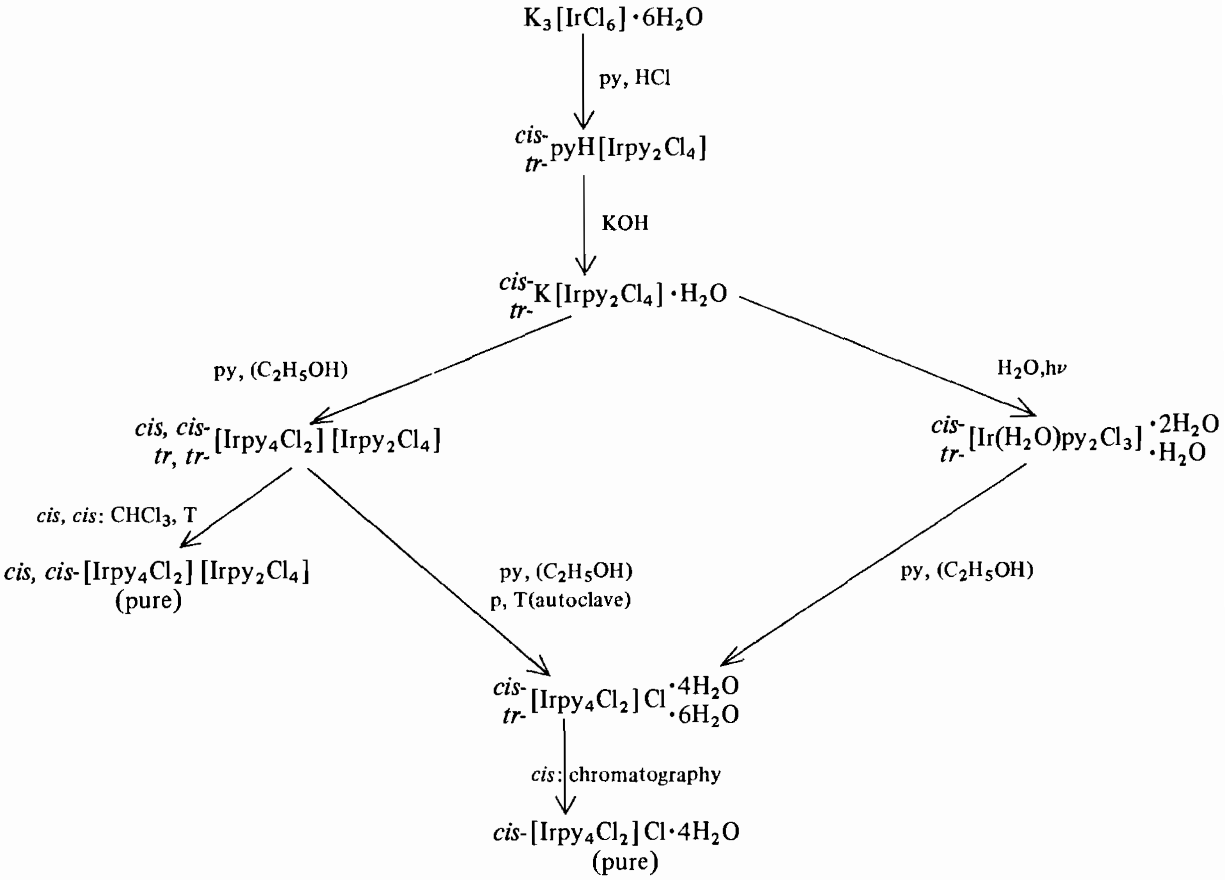
The luminescence spectrum of hexacoordinated low spin d^6 complexes usually exhibits broad bands, which are assigned to charge transfer or ligand field transitions [10–16]. Excitations to higher electronic states involve changes in the electron configuration with different minimum characteristics in the potential hypersurfaces. The electron transition induces distinct molecular vibrations [17] which in general are also coupled with normal lattice vibrations. The resulting bands are very broad; they show, in particular for ligand field transitions, no structural details down to liquid nitrogen temperatures [13–16]. Although no vibrational information can be obtained from broad band spectra, the peak positions, relative intensities, half-widths, *etc.*, can be useful for comparison with various theoretical, usually ligand field-based, models, and for the generation of empirical correlations within series of related compounds. When a pattern of regular behavior can be identified in such a series, the luminescence spectrum can be used as an analytical tool to identify very small amounts of impurities from the irregular features of the spectrum. This technique is particularly useful for identifying impurities closely related to the main compound, since the luminescence behavior of the two will be somewhat similar, and in such cases, the detection threshold is likely to be orders of magnitude below other techniques.

The present paper demonstrates by luminescence spectroscopy the existence of impurities in several complex compounds earlier considered as pure, in particular the bis- and tetrakis(pyridine)chloroiridium (III) complexes and their double complex salts. Procedures for purifying these compounds are presented.

Experimental

Syntheses of Compounds

The syntheses follow literature methods for the most part [1–5]. There are, however, some significant modifications, which are needed to obtain pure products and improve the yields. The procedure is conveniently presented in the following diagram. For maximum yield the preparation *via* the pyridinium salt is preferred. This can easily be converted into the potassium salt by neutralizing a hot pyridinium salt solution with 2*N* KOH. The product is purified by evaporating the solution almost to dryness and recrystallizing from a solution obtained by extraction with hot water, after accurate neutralization with HCl. The synthesis of *cis*(N)- and *tr*(N)-$[Ir(H_2O)py_2Cl_3]$ involves a photochemical hydrolysis. Instead of using sun light, which earlier had to be



applied for an extended period of time [1], the solution was irradiated for 140 hours by three 1000 Watt lamps, while cooled in a water bath. During the preparation of the *cis*-pyridine complex the temperature of the solution should not be higher than 40 °C in order to avoid ligand rearrangement leading to another isomer. The yields of the raw products were sufficiently high for further investigation. Only the *cis*-[Ir py_4Cl_2]Cl·$4H_2O$ was obtained in low yield (about 5%), since it had to be recovered from the mother liquor of the *trans* compound. The yield could not be increased by means of ion exchange chromatography, whereby the concentrated mother liquor was passed through a column (several packings were tried), in an effort to separate the iridium species present.

All compounds produced elementary analyses which agreed well with their formulas. Two compounds, however, were spectroscopically impure (see Discussion), and had to be purified by different procedures. *cis*-[Ir py_4Cl_2]Cl was treated by passing an aqueous solution through a DEAE-SEPHADEX A-25 (40–120 μ) ion exchange column and eluting with 0.05*M* KCl. All other complexes prepared here were also checked by additional purification through ion exchange and gel chromatography, using SEPHADEX materials. The almost insoluble *cis, cis*-[Ir py_4Cl_2] [Ir py_2Cl_4] was purified by stirring the thoroughly powdered material with chloroform under reflux for about one week, renewing the solvent several times. A repeated extraction with hot water or chloroform according to the procedure proposed by Delépine [3] did not remove the light-emitting impurity. All yellow chloroform fractions were collected and evaporated. In this way a yellow product was obtained (2/3 of solid starting material); it was identified as the pure *cis–cis* double complex. It is slightly soluble in chloroform. The other product (1/3 of the starting material), which remained insoluble during the chloroform extraction, had some brownish yellow color and represented an impurity of unknown composition. The products were washed several times with hot water.

Absorption and Emission Spectra

IR absorption spectra were recorded on Perkin–Elmer PE 325 using KBr mulls containing *ca.* 0.5% sample. In the region 400 to 2000 cm^{-1} the resolution was better than 2 cm^{-1}. For the 200 to 450 cm^{-1} region 1.5% CsI mulls were also used, permitting a recording precision of 0.2 cm^{-1}. The bands in this region were checked on a Beckman FIR interferometer model 720. Absorption and diffuse reflectance spectra were measured on a Cary 14 spectrophotometer, equipped with a Cary reflectance attachment model 1411.

The emission spectra were recorded using a Spex 1700 II Czerny–Turner monochromator with a grating blazed at 5000 Å and a Valvo CVP multiplier with S1 characteristics. Entrance and exit slit widths were maintained at 2.0mm. In order to avoid instrumental errors the spectra of *cis*-K[$Irpy_2Cl_4$], *tr*-[$Irpy_4Cl_2$]Cl, and *cis, cis*-[$Irpy_4Cl_2$] [$Irpy_2Cl_4$] were checked on another device, based on a McPherson 0.5m double-monochromator, an RCA C31034 multiplier with a GaAs photocathode, and a Keithley Instruments high speed picoammeter, model 417. The spectra did not change appreciably when the temperature was lowered from 77 K to 10 K. A number of light sources were used for excitation: the 365/366-nm and 436nm lines of a mercury high pressure lamp (Osram HBO 200) and various lines from an argon ion laser (Spectra-Physics, model 165-03), from which the plasma lines were removed by a Jarell–Ash 82410 monochromator and various glass filters. Intensities up to 100mW were used. The light stability of the compounds was checked by recording IR spectra before and after laser irradiation. In no case were any spectral changes observed. The thoroughly powdered samples were measured in general at 77 K or at room temperature.

Results and Discussion

Infrared Spectra

In Table I the long wavelength IR bands are listed, which are assigned to pyridine vibrations and to metal–halide and metal–pyridine vibrations [18]. The spectra of impure materials do not differ significantly from the pure compounds. For both bis(pyridine) isomers, and for the *trans*-tetrakis(pyridine) compound, the bands have been previously assigned, assuming no coupling between metal–halide and metal–pyridine vibrations [9]. A group theoretical consideration of an MA_4B_2 complex shows that, of the M–A stretching modes, only one is IR active in the *trans* complex, whereas four are active in the *cis* complex, and from the M–B stretching modes one is IR active in the *trans*, and two in the *cis* compound. The IR spectra do in fact exhibit a larger number of bands for the *cis* than for the *trans* geometries. In addition, for the *cis* complexes more modes assigned to M–A stretching are observed than those assigned to M–B stretches. When pyridine is coordinated the vibrations of the ring (a_1 in plane, and b_2 out of plane) usually exhibit a shift of about 50 cm^{-1} to higher frequencies [19]. A spectrum taken over the total IR range, typical for all compounds considered, is presented in Figure 1. Only very minor differences are detected for complexes with different geometry.

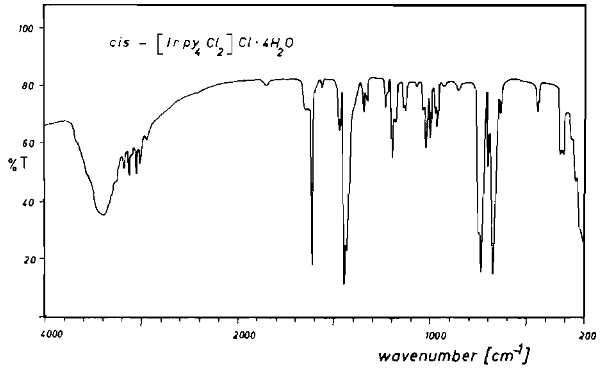


Figure 1. Infrared survey spectrum of *cis*-[$Irpy_4Cl_2$]Cl·$4H_2O$ in KBr.

TABLE I. Long Wavelength IR Band Assignments. Wave numbers in cm^{-1}.

Compound	Pyridine Ring[a] a_1	b_2	$\tilde{\nu}$(M–Cl)[b]	$\tilde{\nu}$(M–py)[b]
tr-pyH[$Irpy_2Cl_4$]		478w	331s, 304vs	265s
cis-pyH[$Irpy_2Cl_4$]	650vw,	458w	318vs[a], 304s, 300s	260s, 253sh
tr-K[$Irpy_2Cl_4$]·H_2O	648vw,	476w	330s, 303sh, 299s	266s
cis-K[$Irpy_2Cl_4$]·H_2O	650vw,	458w	321vs, 303s, 300s	260s, 253sh
tr-[$Ir(H_2O)py_2Cl_3$]·H_2O	642vw,	476w	328vs	271vs
cis-[$Ir(H_2O)py_2Cl_3$]·$2H_2O$	650vw,	460w	316vs, 301s	266s
tr, tr-[$Irpy_4Cl_2$] [$Irpy_2Cl_4$]	646vw,	468w	334sh[a], 318s[a] 311sh[a], 306sh[a]	257s, 254sh 216sh
cis, cis-[$Irpy_4Cl_2$] [$Irpy_2Cl_4$]	645sh,	466w	328s, 312s	270s, 267sh
tr-[$Irpy_4Cl_2$]Cl·$6H_2O$	645vw,	461w	338s	262s, 254sh
cis-[$Irpy_4Cl_2$]Cl·$4H_2O$	654w,	466w	332s, 325sh	287w, 272s

[a] In KBr. [b] In CsI.

Absorption and Reflectance Spectra

The measured absorption spectra agree for the most part with those published in the literature [6, 7]. The peaks, shoulders or band inflections can be assigned to triplet, and in some cases to singlet, ligand field transitions or to charge transfer transitions due to an electron transfer from the iridium central ion to a π^* orbital of the pyridine ligand, and also to internal pyridine transitions, which exhibit the usual vibrational structure. Small differences are observed, compared to earlier results, only in the first singlet-triplet ligand field transitions, which are found at longer wavelengths in some of the compounds. Band positions in the reflectance spectra of the insoluble double complexes are more or less superpositions of the absorption bands of their constituent complexes (*cf.* Figure 2). As usual little detail can be observed in the UV region reflectance spectra.

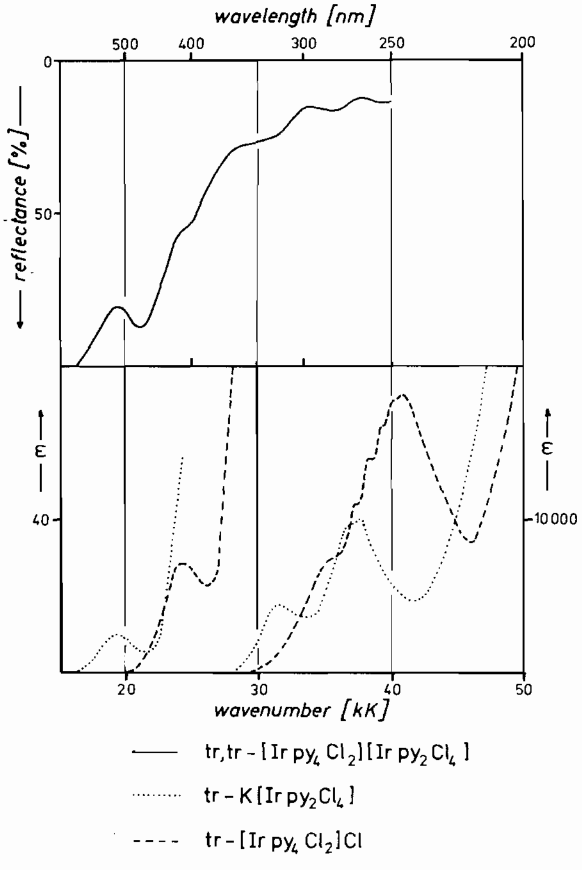


Figure 2. Diffuse reflectance spectrum of *tr, tr*-[$Irpy_4Cl_2$]-[$Irpy_2Cl_4$], diluted with LiF standard, and the absorption spectra of *tr*-K[$Irpy_2Cl_4$]·H_2O and *tr*-[$Irpy_4Cl_2$]Cl·6H_2O in aqueous solution for comparison.

Some model parameters, as defined by ligand field theory, can be determined using energy schemes obtained from usual model calculations. From the first singlet and triplet transitions of *tr*-[$Irpy_2Cl_4$]$^-$ a mean octahedral ligand field parameter 10Dq = 28kK and a Racah-parameter C = 2.9kK can be derived. If the rule of average environment is assumed to be valid, the ligand field parameter of a hypothetical [$Irpy_6$]$^{3+}$ can be estimated, referring to Co(III) and Rh(III) homologs, as 10Dq = 37kK. This leads to calculated parameters for the mixed complexes which agree well with those measured for the *trans* bis- and tetrakis(pyridine) compounds.

Emission Spectra

Luminescence spectra at 77 K were obtained only for the materials listed in Table II. The other compounds considered in the present work did not exhibit any detectable emission in the range 400–900 nm down to liquid nitrogen temperature, irrespective of the wavelengths and light intensity used for excitation. The reason for this may be found in the lower average ligand field for the *trans* configurations, so that radiationless transitions become more likely. At room temperature only the tetrakis(pyridine) complexes emit, the *trans* isomer showing a distinct shoulder. All other spectra exhibit only a broad, structureless band, as is common for ligand field transitions between levels involving different electron configurations [13–16], excepting only electron transfer transitions to antibonding orbitals of coordinated heterocycles, which often show some vibrational structure due to normal modes appropriate to the ring system [11–13]. However, if the temperature is decreased to liquid helium temperature, ligand field transitions may also exhibit vibrational structure [20]. The comparison with corresponding absorption spectra allows an assignment of these bands to be made to the lowest energy transition, *i.e.* in octahedral notation to $^3T_{1g}(t_{2g}{}^5e_g) \rightarrow {}^1A_{1g}(t_{2g}{}^6)$. This assignment is suggested in particular from the Stokes shifts, which can be compared with regular trends observed in other compounds. According to a simple model established for Rh(III) compounds, the Stokes shift for the first transition in octahedral low spin d^6 complexes is given by [15]

$$S.S. = 2ab^2\delta^2$$

where δ depends closely on the octahedral ligand field parameter 10Dq. Ligands with a larger ligand field should exhibit a higher Stokes shift. This is also observed for Ir(III) compounds. The Stokes shifts listed in Table II compare well with the values of ~17.2kK for [$Iren_3$]$^{3+}$, and 9.6kK for *tr*-[$Iren_2Cl_2$]$^+$ [13]; they are 3–5kK larger than for corresponding Rh(III) compounds, which is also in qualitative agreement with the above formula, since Ir complexes have higher ligand fields than their Rh homologs.

Contrary to experience in phenanthroline and bipyridine complexes, the charge transfer state in pyridine compounds is higher in energy than the first ligand field level [11–13]. This is supported by the fact that internal π–π^* excitations occur at higher energy in free (or coordinated) pyridine than in phenanthroline or bipyridine molecules.

Energy transfer inside the emitting *cis, cis* double complex is large enough that in the pure compound the emission is independent of the excitation wavelength. Obviously all light (although emission could be detected only for excitation within a small range in the long wavelength region, *cf.* Table II) absorbed by the complex with the higher ligand field, *i.e.* $[\mathrm{Irpy_4Cl_2}]^+$, is energetically transferred to the complex of lower ligand field strength, *i.e.* $[\mathrm{Irpy_2Cl_4}]^-$, from which light emission occurs. This mechanism seems to be more evident in the *trans, trans* double complex which does not show any luminescence as observed also for the *tr*-$[\mathrm{Irpy_2Cl_4}]^-$ compound itself.

On the other hand, the exchange of energy between the constituents in impure materials is not complete: the *cis, cis* double salt and the *tr*-$[\mathrm{Irpy_4Cl_2}]^+$, before being purified, show luminescence spectra which depend on the excitation energy. Both raw materials contain at least two species which emit at different wavelengths and which are excited to different degrees depending on their absorptivities at the excitation wavelength applied. This unusual behavior in the emission spectrum, therefore, can be used as an analytical tool to detect impurities in the compounds when usual procedures (elementary analysis, IR and UV spectra, chromatography *etc.*) fail. As described above, the *cis, cis* double complex was purified by refluxing the material obtained from the preparation with chloroform. The soluble product was identified as the pure double salt by comparing the luminescence and IR data with those of the precipitate obtained by mixing aqueous solutions of equivalent amounts of the *cis*-bis(pyridine) complex with the *cis*-tetrakis(pyridine) salt. The impurity, remaining insoluble during the reflux procedure, emits at 15.5kK at any laser excitation line. Before purification, the material, obviously because of different absorption properties of the constituents, exhibits luminescence from the pure complex at low wavelength excitation and from the impurity at long wavelength excitation. Only when excited by the 488nm line does emission occur from both compounds. The nature of the impurity could not be determined. It probably consists of a polymer containing three or more molecules of pyridine per iridium atom. The same treatment applied to the *trans, trans* double complex did not result in the isolation of any impurities or in any spectroscopic changes.

When prepared according to literature methods [3, 4], *cis*-$[\mathrm{Irpy_4Cl_2}]\mathrm{Cl}$ also exhibits inconsistent (wavelength-dependent) luminescence behavior. This may also be ascribed to luminescent impurities. A wavelenght-independent emission spectrum was

TABLE II. Emission Peaks and Shoulders, sh, for Various Excitations, Stokes Shifts Φ, and Half Widths of Bands $\Delta\bar{\nu}_{1/2}$.

Compound	λ_{exc}[nm]	$\lambda_{em}{}^{a}{}_{77}$[cm^{-1}]	$\lambda_{em}{}^{a}{}_{295}$[cm^{-1}]	Φ[cm^{-1}]	$\Delta\bar{\nu}_{1/2}$[cm^{-1}]
cis-pyH$[\mathrm{Irpy_2Cl_4}]$	b	12800	–	8800	2600
cis-K$[\mathrm{Irpy_2Cl_4}]$	b	12800	–	8800	2600
cis, cis-$[\mathrm{Irpy_4Cl_2}][\mathrm{Irpy_2Cl_4}]$					
impure	454.5	13100	–		
	457.9	13300	–		
	465.8	13300	–		
	472.7	13300	–		
	488.0	15600, 13400	–		broad band
	496.5	15900	–		
	514.5	15800	–		
purified	b	13300	–	9700	3000
insoluble impurity	b	15500	–		
tr-$[\mathrm{Irpy_4Cl_2}]\mathrm{Cl}$	b	15300	15400^c, 16300sh^c	9200	2600
cis-$[\mathrm{Irpy_4Cl_2}]\mathrm{Cl}$					
impure	363.8	14300	–		
	454.5	15500	–		
	457.9	15400	15400		
	465.8	18300, 15600sh	15500		very broad band
	472.7	18500, 15600sh			
	476.5	18200, 15600 sh			
purified	b	15300	15300^d	10900	2700

[a] Band maxima at 77 K and 295 K are determined within ±100 cm^{-1}. [b] All laser lines λ_{exc} as given for the *cis,cis* double complex. [c] λ_{exc} = 454.5;457.9;465.8nm. [d] λ_{exc} = 454.5nm.

obtained after ion exchange purification (see Experimental).

In addition, *cis*-K[$Irpy_2Cl_4$] and *tr*-[$Irpy_4Cl_2$]Cl showed, at 363.8nm excitation, a second, approximately a thousand times weaker luminescence, both reaching an intensity maximum at 21.4kK, and both exhibiting vibrational structure with a progression in 1100 cm^{-1} quanta, corresponding to a pyridine ring vibration. This luminescence band, since it is observed at the same position for both compounds, can probably be attributed to an emission from the charge transfer state. The different ligand field strengths are compensated by the relatively large difference in the Stokes shifts, which are about 10kK for the bis(pyridine) and 13kK for the tetrakis-(pyridine) complex, resulting in emission bands at similar spectral positions. However, the weak emission might also be caused by another impurity. A further analysis cannot be given at present.

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