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Synthesis and Characterization of a New Non-linear Trimetallic Complex, Hexakis(2,2'-bipyridine)-(μ-dipyrazino[2,3-f][2',3'-h]quinoxaline)-trisruthenium(II) and Related Compounds

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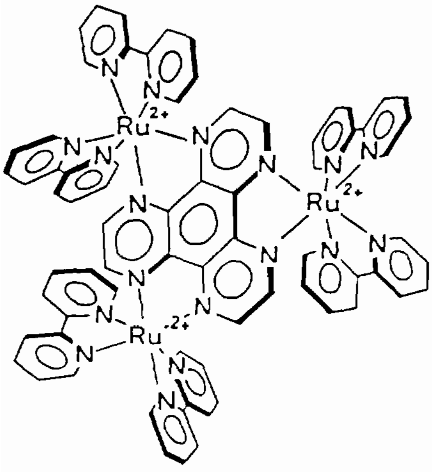
Quite recently, several works on bimetallic [1–7] and polymetallic [8–13] complexes have been published in the literature. These compounds are interesting in many respects. Some have been prepared in view of their possible optical activity [12]; others have been considered as new photosensitizers [8], as models for photochemistry and photophysics of large aggregated chromophores [10], for the study of intramolecular electron or energy transfer [6, 13] or electron transfer directionality [11].

A few years ago, an hexachelating, highly symmetric ligand, the dipyrazino[2,3-f][2',3'-h]quinoxaline, also known as 1,4,5,8,9,12-hexaazatriphenylene (HAT), was prepared [14]. This compound offers, in the context of polymetallic complexes, the advantage to build different organometallic edifices, using the HAT as bridging ligand. To investigate this attractive possibility, we thus synthesized the mononuclear $Ru(bpy)_2(HAT)^{2+}$ (yellow) (bpy = 2,2'-bipyridine), dinuclear $[Ru(bpy)_2]_2(HAT)^{4+}$ (aubergine-colored) and trinuclear $[Ru(bpy)_2]_3(HAT)^{6+}$ (deep blue):



We present in this note their redox and spectroscopic characteristics.

Experimental

$Ru(bpy)_2Cl_2$ [15] and HAT [14] were prepared according to known methods and the complexes synthesized following the procedure described by Belser and von Zelewsky [16] for mixed ligand complexes. A methanol–water (1:1) solution of n equivalents (n = 1,2 or 3) of $Ru(bpy)_2Cl_2$ was added dropwise to a boiling solution of HAT in the same solvent; the disappearance of the starting material was followed by silica gel TLC ($CHCl_3$–MeOH 95:5) while the complex appearance and transformation could be detected by reverse phase Whatman Si-C_{18} TLC (CH_3CN–MeOH 1:1, CH_3SO_3H 0.015 M). The desired complex $[Ru(bpy)_2]_n(HAT)^{2n+}$ was mainly formed with however small amounts of $[Ru(bpy)_2]_2(HAT)^{4+}$ in the $Ru(bpy)_2(HAT)^{2+}$, and of $Ru(bpy)_2(HAT)^{2+}$ plus $[Ru(bpy)_2]_3(HAT)^{6+}$ in the $[Ru(bpy)_2]_2(HAT)^{4+}$; the trimetallic compound was obtained alone.

The complexes were separated and purified by ion exchange chromatography (IEC) [16] on Sephadex SP-C25 Na^+ form (H_2O–$(CH_3)_2CO$ 5:3, NaCl 0.1 M for $Ru(bpy)_2(HAT)^{2+}$, 0.3 M for $[Ru(bpy)_2]_2(HAT)^{4+}$ and 0.5 M for $[Ru(bpy)_2]_3(HAT)^{6+}$); acetone was evaporated and the addition of KPF_6 precipitated respectively the mono-, di-, and trimetallic complexes in 47, 68 and 72% yield. Analytical data are given in Table I.

The NMR spectra were recorded on a Bruker 250 MHz and absorption on a Varian Cary 219 UV–Vis spectrophotometer. The emission spectra were determined with a RCA 7102 photomultiplier and emission lifetimes with a Hamamatsu R928 P.M.T. at room temperature in water.

Results and Discussion

NMR Spectra

Only the $Ru(bpy)_2(HAT)^{2+}$ gave a simple, interpretable ^1H NMR spectrum in full agreement with the expected structure. The di- and trimetallic compounds show, however, a very complicated spectrum probably for symmetry reasons; since a $Ru(bpy)_2Cl_2$ racemic mixture (with absolute configurations $\Lambda + \Delta$) has been used, two diastereoisomers belonging to different point groups can be formed in each polynuclear complex: the Λ^2 (+ its enantiomer Δ^2, C_2 group) and the $\Lambda\Delta$ (C_s group) for the $[Ru(bpy)_2]_2(HAT)^{4+}$, the Δ^3 (+ its enantiomer Λ^3, D_3 group) and the $\Lambda\Delta^2$ (+ its enantiomer $\Delta\Lambda^2$, C_2 group) for the

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TABLE I. Analytical Data (%) for the Ruthenium–HAT Complexes

Complex	*Anal.*, calc. (found)		
	C	H	N
$Ru(bpy)_2(HAT)(PF_6)_2$	40.99(40.04)	2.36(2.36)	14.95(15.05)
$[Ru(bpy)_2]_2(HAT)(PF_6)_4$	38.06(36.68)	2.33(2.36)	11.95(12.16)
$[Ru(bpy)_2]_3(HAT)(PF_6)_6$	36.89(35.93)	2.32(2.40)	10.75(11.04)

TABLE II. Electrochemical Data for the Ruthenium–HAT Complexes

Complex[a]	Oxidation[b]			Reduction[b]		
$Ru(bpy)_2(HAT)^{2+}$	+1.56			−0.84	−1.43	
$[Ru(bpy)_2]_2(HAT)^{4+}$	+1.53	+1.78		−0.49	−1.06	
$[Ru(bpy)_2]_3(HAT)^{6+}$	+1.61	+1.87	+2.12[c]	−0.25	−0.58	−1.07
HAT[d]				−1.46	−1.79	

[a] 10^{-3} M in acetonitrile, 0.1 M in $(n\text{-}Bu)_4N(PF_6)$ as supporting electrolyte. [b] Cyclic voltammetry on a Pt disc electrode, Saturated Calomel Electrode as reference electrode and large area Pt counter electrode; potentials are given *vs.* SCE; scan rate = 200 mV/s. [c] Poorly resolved. [d] Cyclic voltammetry on a Hg drop electrode, same conditions as above except with saturated [HAT] (*i.e.* $<10^{-3}$ M).

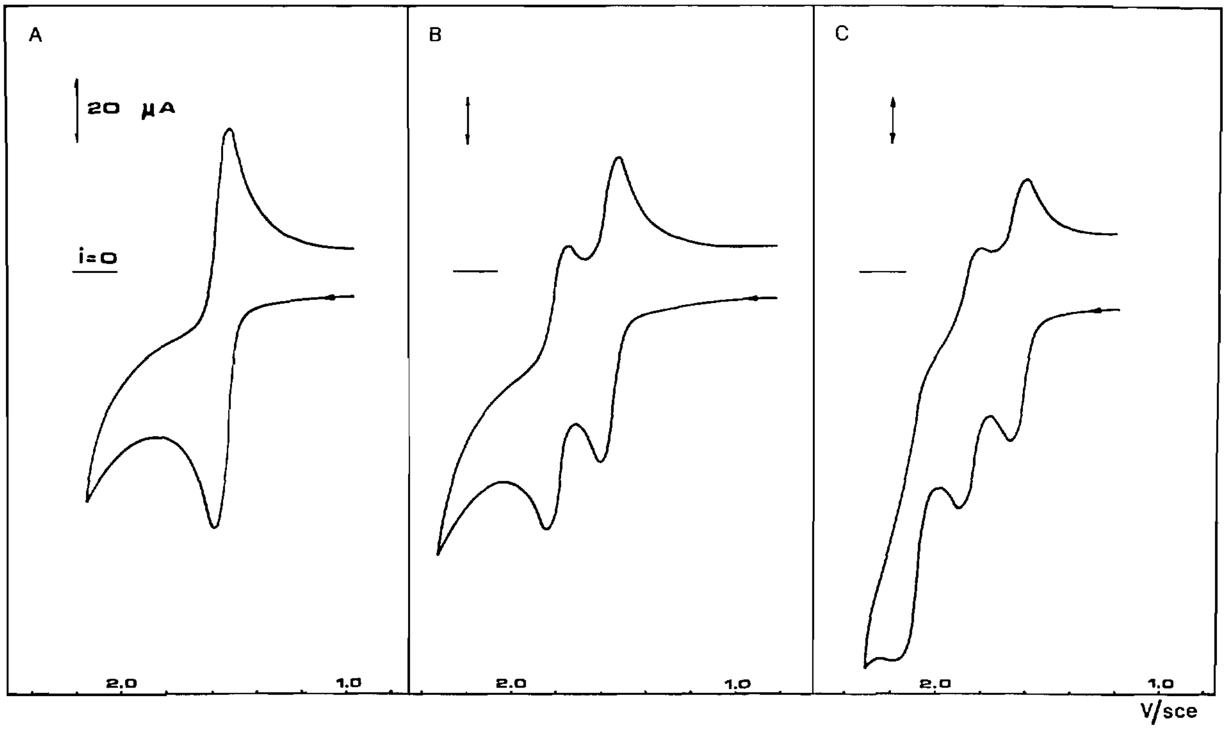

Fig. 1. Oxidation waves on a Pt disc electrode in acetonitrile, (a) $Ru(bpy)_2(HAT)^{2+}$, (b) $[Ru(bpy)_2]_2(HAT)^{4+}$, (c) $[Ru(bpy)_2]_3(HAT)^{6+}$.

$[Ru(bpy)_2]_3(HAT)^{6+}$. Obviously these diastereoisomers should not be separated by IEC since the main interaction involved in this chromatography is due to the charges; therefore only the NMR spectra of the mixtures can be obtained.

Redox Potentials

These are tabulated in Table II for the 3 complexes and the free HAT ligand; Fig. 1 shows the oxidation waves. It is clear that the number of one electron, reversible oxidation waves is correlated to

TABLE III. Absorption and Emission Data of the Ruthenium–HAT Complexes

Complex	Absorption[a] λ_{max} (nm), 10^{-4} ϵ (M^{-1} cm^{-1}) in parentheses	Emission[c] λ_{max} (nm), τ (ns) in parentheses[d]
$Ru(bpy)_2(HAT)^{2+}$	207(4.5), 277(5.9) 432(1.0), 484[b]	745(105)
$[Ru(bpy)_2]_2(HAT)^{4+}$	206(7.4), 243[b], 252[b], 276(10.5) 405(1.4), 490(1.4), 572(1.5)	825(148)
$[Ru(bpy)_2]_3(HAT)^{6+}$	206[b], 244(6.0), 251(6.1), 278(15.1) 364(1.7), 401(1.9), 525(3.2), 580(3.8)	880(40)

[a] In aqueous solution at 298 K. [b] Shoulder. [c] In aqueous solution at 298 K, uncorrected. [d] Under N_2.

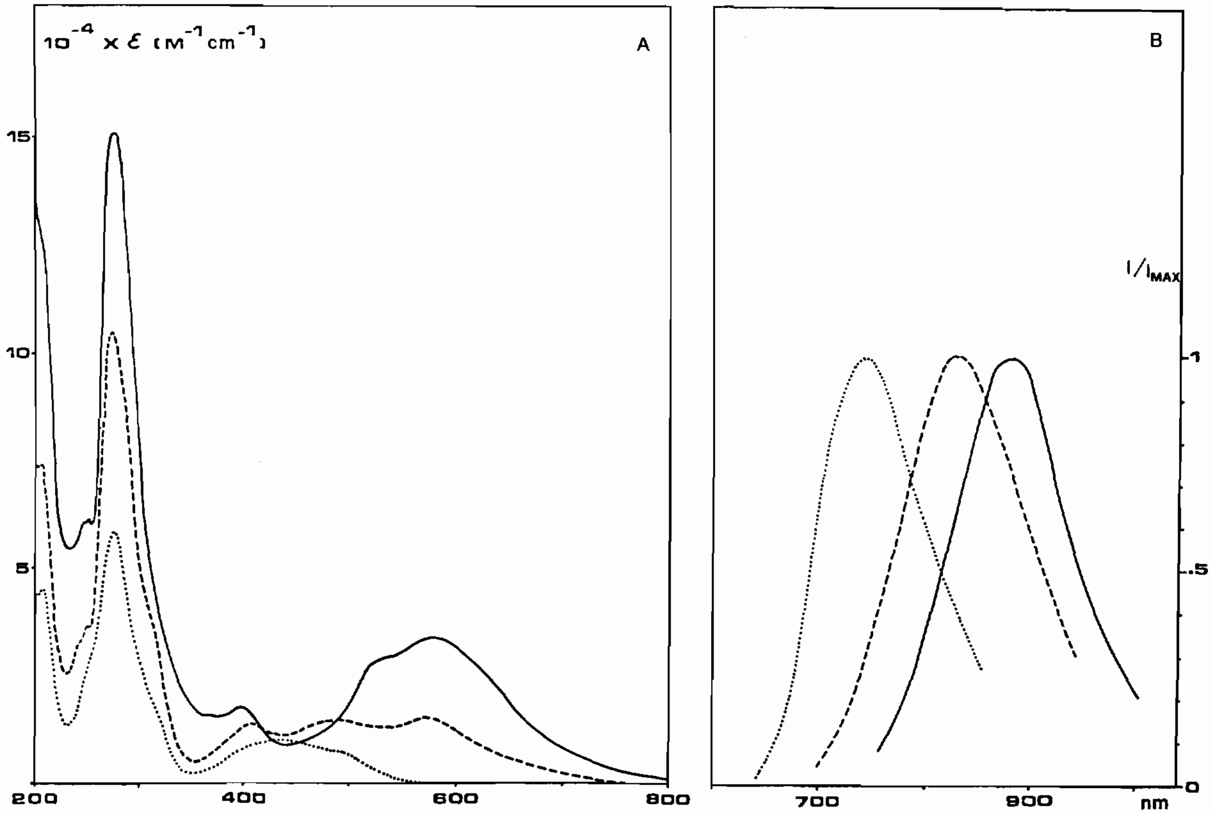

Fig. 2. (a) Absorption and (b) emission spectra of $Ru(bpy)_2(HAT)^{2+}$ (·······), $[Ru(bpy)_2]_2(HAT)^{4+}$ (– – –) and $[Ru(bpy)_2]_3(HAT)^{6+}$ (———), in water at room temperature; the emission spectra are uncorrected and normalized.

the number of Ru atoms, indicating a significant interaction between the metal ions, as generally observed with conjugated bridging ligands [3, 5, 8]. Moreover, the fact that the first oxidation wave of each complex remains at the same potential means that the highest occupied molecular dπ orbital (metal centered) is not much affected by the addition of $Ru(bpy)_2{}^{2+}$ moieties to form the di- and trimetallic compound. The reduction pathway is very complicated and only two or three reversible, one electron waves could be satisfactorily characterized (Table II). It is well known [17] that in this type of compound, the lowest unoccupied molecular orbital is a π^* ligand centered orbital, therefore, considering the relative oxidation power of the two ligands, the first electron added should be localized on the HAT. This is confirmed by the anodic shift of the first reduction wave with the increasing number of Ru, which should influence the HAT reduction but only slightly the bpy reduction. Moreover, since the second reduction wave is also affected by the Ru number, it would correspond to a second reduction of the HAT; in the trimetallic complex even the third electron could go on the bridging ligand since the third reduction occurs at a potential which is not negative enough for a bpy. Interestingly thus, the first three electrons would be all localized on the HAT bridging ligand in the $[Ru(bpy)_2]_3(HAT)^{6+}$.

Absorption and Luminescence Spectra

Unexpectedly, as shown in Table III and Fig. 2, the trimetallic complex is still luminescent with a lifetime of 40 ns. It is also clear that the intensity of the band around 280 nm, attributed to the bipyridine $\pi-\pi^*$ transition [15] is proportional to the number of $Ru(bpy)_2^{2+}$ moieties in the complex. The MLCT absorption band undergoes a strong bathochromic shift and hyperchromic effect from the mono- to the di- and trimetallic complexes; this red-shift is also observable on the MLCT triplet luminescence. This is in agreement with the fact that the highest occupied $d\pi$ molecular orbital remains unchanged whereas the lowest unoccupied π^* molecular orbital is stabilized by the addition of $Ru^{2+}(bpy)_2$ moieties as concluded from the electrochemistry.

In conclusion, the new ligand HAT allows the preparation of new polymetallic non-linear complexes which luminesce and present absorptions in a suitable region for photosensitization. Moreover, the mono- and dimetallic complexes, still having free chelation sites, should be useful as synthetic precursors for heterometallic compounds.

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