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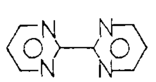
Ruthenium(II)-Bipyrimidine Complexes. Spectroscopic and Electrochemical Properties of a Novel Series of Compounds

Sir:

In our search for well-defined oligonuclear metal complexes we investigated the system ruthenium(II)-2,2′-bipyrimidine[1] (abbreviated as bipym). The four ligating sites of this molecule



are expected to lead to ligand bridged compounds of various complexity and various degrees of electronic interaction between the metallic centers. Related mononuclear ruthenium complexes have recently received considerable attention as systems capable of photodecomposing water.[2-5] This communication reports the syntheses and some spectroscopic and electrochemical properties of a series of novel Ru(II)bipym complexes.

The ion Ru(bipym)$_3^{2+}$ (I) was prepared by refluxing commercial $RuCl_3{\cdot}xH_2O$ (130 mg) with a fivefold excess of bipym in 30 mL of ethanol-water (2:1) for 30 h. The resulting hot solution was filtered and diluted with 50 mL of ethanol. Upon cooling the chloride salt was obtained in 90% yield as an orange microcrystalline solid. The same procedure using Ru(bipy)$_2$Cl$_2$[6] (bipy is 2,2′-bipyridine) in aqueous solution gave the mixed complex Ru(bipy)$_2$bipym^{2+} (II) which was isolated as the orange PF_6 salt. If a Ru:bipym ratio of 2:1 was used, the green binuclear complex [(bipy)$_2$RubipymRu(bipy)$_2$]$^{4+}$ (III) could be isolated in 88% yield. Refluxing an aqueous solution of Ru(bipym)$_3^{2+}$ with a slight excess of Ru(bipy)$_2$Cl$_2$ gave a dark green solution from which the tetranuclear complex [[(bipy)$_2$Rubipym]$_3$Ru]$^{8+}$ (IV) could be precipitated with saturated NH_4PF_6 solution. Ion-exchange chromatography showed no additional components. Elution of the complex was possible only with 12 M HCl demonstrating thus the high positive charge. Analytical data are summarized in Table I. The ligand bipym was prepared according to the method given in ref 1 and purchased from Lancaster Synthesis, LTD, Lancaster, England.

Table II. Charge-Transfer Absorption and Emission Spectra of Ruthenium(II)-Bipyrimidine Complexes

Complex	Absorption,[a] λ_{max} (nm)	$10^{-4}\,\epsilon$	Emission
I	452, 412, 331	0.74, 0.76, 1.48	644,[c] 616,[d] 674,[d] 740[b,d]
Ru(bipy)$_3^{2+}$ [e]	452, 423[b]	1.46	613,[c] 627[c]
II	475,[b] 415, 398[b]	1.13	~680,[c] 667,[d] 720,[d] 800[b,d]
III	606, 560,[b] 408	0.76, 3.13	769,[d] 850[d]
IV	613, 580,[b] 408	1.74, 4.94	

[a] Aqueous solution; ε is given only for band maxima. [b] Shoulder. [c] Aqueous solution, 25 °C, corrected. [d] Solid compound, 15 ± 4 K. [e] Reference 4.

Important spectroscopic data of the new compounds are given in Table II. The striking similarity in the charge-transfer absorption spectra of Ru(bipy)$_3^{2+}$ and Ru(bipym)$_3^{2+}$ is duplicated in the band position of the emission spectra. The quantum yield for I is 0.09 (2) (20 °C, aqueous solution) compared with 0.042 (2) for Ru(bipy)$_3^{2+}$ under the same conditions.[7] The emission intensity of I does not change in the pH range 4.5-8. At lower pH it rapidly decreases. No emission is observed below pH 1 indicating a slightly enhanced basicity of the excited state, pK_a of Ru(bipym)$_3^{2+}$ being approximately −1 as determined from a spectrophotometric titration. In remarkable contrast to other polypyridine complexes having emission lifetimes between 0.33 and 4.68 μs (25 °C),[4] the luminescence of I is not quenched by dioxygen. This observation is attributed to the significantly shorter lifetime of the excited state of I. In aqueous solution the emission lifetime of Ru(bipym)$_3^{2+}$ varies smoothly from 0.096 (2) μs at 1.5 °C to 0.064 (2) μs at 30 °C, whereas for a solid sample it increases from 0.11 (1) μs at 278 K to 7.25 (5) μs at 7.6 K. Low temperature luminescence spectra of I, II, and III as solids (Figures 1 and 2) exhibit the ~1.3 kK progression as typically observed in the emission of related ruthenium compounds.[8] No luminescence could be detected up to 900 nm for the tetranuclear complex IV.

Cyclic voltammetry in aqueous solution of the bipym com-

Table I. Analytical Data for the Ruthenium-Bipyrimidine Complexes. Experimental Values in Parentheses

Complex	Ru	C	H	N	F or Cl
[Ru(bipym)$_3$]Cl$_2$·4H_2O (I)	14.1 (14.4)	40.1 (40.1)	3.6 (3.3)	23.4 (23.4)	9.9 (9.9)
[Ru(bipy)$_2$bipym](PF_6)$_2$ (II)	11.7 (12.1)	39.0 (38.8)	2.6 (2.6)	13.0 (13.0)	26.5 (26.6)
[(bipy)$_2$RubipymRu(bipy)$_2$](PF_6)$_4$·H_2O (III)	12.8 (13.6)	36.4 (36.4)	2.5 (2.5)	10.6 (10.7)	28.8 (29.0)
[[(bipy)$_2$Rubipym]$_3$Ru](PF_6)$_8$·2H_2O (IV)	13.4 (13.4)	33.5 (33.8)	2.3 (2.5)	11.2 (11.1)	

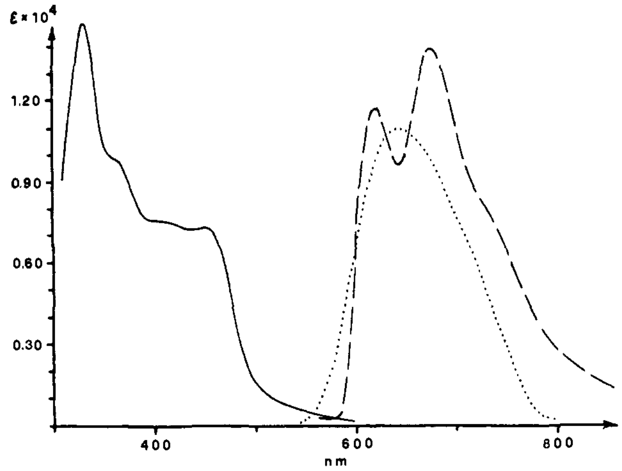


Figure 1. Absorption and emission spectra of Ru(bipym)$_3{}^{2+}$: —, absorption; ···, emission, aqueous solution 300 K; - - -, emission, solid complex 15 K.

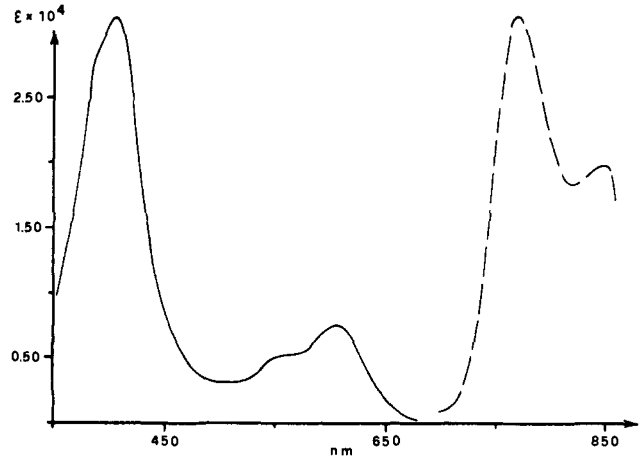


Figure 2. Absorption and emission spectra of [(bipy)$_2$RubipymRu(bipy)$_2$]$^{4+}$: —, absorption; - - -, emission, solid complex 15 K.

plexes did not show any reversible waves up to 1.3 V (vs. hydrogen). Spectrophotometric titration with Ce^{4+} indicates an oxidation rapidly followed by the reduction of the generated Ru(III) species by water. Formal reduction potentials were obtained from cyclic voltammograms on a Pt electrode in acetonitrile containing 0.1 M [(n-Bu)$_4$N]PF$_6$. Scan rates were varied between 100 and 500 mV/s. Owing to the onset of a steep increase of the base line at ~1.4 V, the cathodic and anodic waves were usually separated by more than 60 mV. Two well-defined waves were observed for the binuclear complex, the potential difference of 190 mV corresponding to a conproportionation constant of 1.63 × 10^3 for the generated mixed valence complex.[9] No reversible voltammogram was observed for the tetranuclear species IV. The formal reduction potentials (vs. hydrogen) of the various ruthenium(III)-bipyrimidine complexes are 1.64 V for I, 1.37 V for II, and 1.55 and 1.74 V for III. The value of 1.26 V for the Ru(bipy)$_3{}^{3+/2+}$ couple[4] was used to calibrate our measurements. The replacement of bipyridine by bipyrimidine thus shifts the reduction potential to considerably more positive values.

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A Quadruple Bond between Tungsten Atoms in an Air-Stable Compound

Sir:

The ability of transition metal atoms to form homonuclear multiple bonds (double,[1] triple,[2] and quadruple[3]) was first recognized, thus initiating an entirely new phase of transition metal chemistry, a relatively short time ago, but rapid progress has already been made in exploring this field.[4] The formation of quadruple bonds, which is restricted, so far as is presently known, to certain of the transition elements, mainly Re,[4] Mo,[4] Cr,[4] and Tc,[5] was only recently demonstrated for tungsten by the unequivocal characterization of the [W$_2$Me$_{8-x}$Cl$_x$]$^{4-}$ ions (x = ~2.5[6] or 0[7]), compounds of which are exceedingly reactive and thermally sensitive. We report here a method of preparation and proof of structure for a compound containing a quadruple W–W bond that is stable in air at ambient temperature, namely, W$_2$(C$_8$H$_8$)$_3$.

The existence of several compounds with the formula M$_2$(C$_8$H$_8$)$_3$ (M = Ti, V, Cr, Mo, W) was first announced a number of years ago.[8] However, except for Ti$_2$(C$_8$H$_8$)$_3$ no preparative methods nor any identifying physical or chemical properties were revealed. The structure of Ti$_2$(C$_8$H$_8$)$_3$, in which there is no M–M bond, was reported[9] in 1966. It was only with the report[10] last year that Cr$_2$(C$_8$H$_8$)$_3$ has a structure indicative of the presence of a quadruple Cr–Cr bond (but this report again reveals nothing about the preparation or other properties of the compound) that we became interested in the structure of W$_2$(C$_8$H$_8$)$_3$. It was possible (as Brauer and Kruger[10] themselves stated) that the molybdenum and tungsten compounds would be likely to have similar molecular structures. Our keen, long-standing[6,7,11] interest in the question of the stability of quadruple W–W bonds led us to examine the preparation and structure of W$_2$(C$_8$H$_8$)$_3$.

The preparation is quite simple. The reaction of WCl$_4$ with 2 molar equiv of K$_2$C$_8$H$_8$ in THF gave an intensely green solution from which a moderate yield of black crystals was obtained after removal of solvent and recrystallization from toluene. The mass spectrum has a prominent parent ion peak (m/e 680). The crystals appear to be stable in air for periods of at least a week.

Although the molecular structure of W$_2$(C$_8$H$_8$)$_3$ is quite similar to that of Cr$_2$(C$_8$H$_8$)$_3$ (vide infra) the compounds are not isomorphous. For W$_2$(C$_8$H$_8$)$_3$ we have space group $I\bar{4}$, a = 15.820 (3) Å, c = 15.041 (3) Å, Z = 8, meaning that the entire molecule constitutes the asymmetric unit. Using 2063 unique reflections with $I > 3\sigma(I)$ we have solved and refined the structure to convergence using anisotropic temperature parameters for all atoms. A spherical crystal was used to expedite the making of accurate absorption corrections, and both enantiomorphs were tested. The residuals obtained with the correct one (R$_1$ = 0.038, R$_2$ = 0.048) are significantly (*ca.* 0.006) lower than for the other one.