the O–H lengths of 1.00 (5) and 1.45 (5) Å. In [Pt(P(OH)(OMe)$_2$)$_2$(P(O)(OMe)$_2$)$_2$] the similarity in Pt–P (2.314 (3), 2.310 (3) Å) and P–O (1.527 (9), 1.525 (8) Å) distances was taken as further evidence of a symmetric O···H···O interaction. A stereoview of the unit cell contents is presented in Figure 2.

In [Pt(P(OH)(OEt)$_2$)$_2$(P(O)(OEt)$_2$)$_2$] the low melting point appears to manifest itself in very high thermal motion (see Experimental Section). There is, however, strong indication from the gross details of the structure that this compound also contains a symmetric O···H···O hydrogen bond.[24]

Acknowledgment. We are indebted to Professor Jerry L. Atwood for the use of his diffractometer. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. Pt(ETPB)$_4$, 63372-08-7; Pt(P(OMe)$_3$)$_4$, 41431-04-3; Pt(P(OEt)$_3$)$_4$, 23066-15-1; Pt(P(OH)(OMe)$_2$)$_2$(P(O)(OMe)$_2$)$_2$, 30053-63-5; Pt(P(OH)(OEt)$_2$)$_2$(P(O)(OEt)$_2$)$_2$, 32324-65-5; [Pt(P(OEt)$_3$)$_4$](ClO$_4$)$_2$, 88212-05-9; potassium tetrachloroplatinate(II), 10025-99-7.

Supplementary Material Available: Tables of thermal parameters, best planes results, and observed and calculated structure factors for [Pt(P(OH)(OMe)$_2$)$_2$(P(O)(OMe)$_2$)$_2$] (7 pages). Ordering information is given on any current masthead page.

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[24] Further details on the structure of [Pt(P(OH)(OEt)$_2$)$_2$(P(O)(OEt)$_2$)$_2$] are available from the authors.

Notes

Contribution from the Service de Chimie Organique,
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Synthesis and Spectroscopic and Electrochemical Properties of a New Ruthenium Complex: The Tris(1,4,5,8-tetraazaphenanthrene)ruthenium(II) Dication

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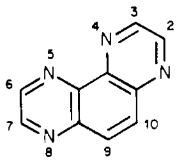
The Ru(bpy)$_3^{2+}$ complex ion has been extensively studied as a photosensitizer for the water-splitting reaction, with the hope of producing elemental hydrogen for use as a fuel.[2-5] The MLCT excited state of this complex is able, at least thermodynamically, to reduce and to oxidize water, leading to its decomposition into H_2 and O_2. Recently, Crutchley and Lever[6,7] have shown that Ru(bpz)$_3^{2+}$, where bpz is bipyrazine, is a strong oxidizing reagent in its MLCT excited state with an oxidizing potential close to +1.3 V (vs. SCE); Ru(bpz)$_3^{2+}$ should thus be thermodynamically able to oxidize water to O_2.

It seems of interest, in connection with this last result, to consider the potentialities of a still little explored ligand: 1,4,5,8-tetraazaphenanthrene, TAP (I),[8] which should show properties similar to those of bipyrazine and can be made with various substitution patterns. We report here the synthesis of Ru(TAP)$_3^{2+}$ (II) and its spectroscopic and electrochemical properties.



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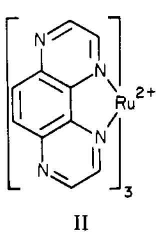

II

Synthesis

Hunziker and Ludi[9] synthesized Ru(bipym)$_3^{2+}$, where bipym is 2,2′-bipyrimidine, by refluxing RuCl$_3$·3H$_2$O and a fivefold excess ligand in ethanol–water. This procedure gives only a 5% yield in Ru(TAP)$_3$Cl$_2$ when the TAP ligand is used instead of the bipyrimidine. On the other hand, the synthesis of this salt was easily achieved by using Ru(Me$_2$SO)$_4$Cl$_2$ as starting material, according to the method described by Crutchley and Lever.[6,7] Refluxing this ruthenium complex with 6 equiv of TAP in ethanol–water (1:1) for 20 h yielded 71% of orange-red crystals recrystallizable from ethanol. The new complex was identified by X-ray diffraction analysis[10] and NMR spectroscopy.

^{1}H NMR Spectrum

When dissolved in D_2O, Ru(TAP)$_3$Cl$_2$ shows a singlet at 8.82 ppm (reference SDSS) with a relative intensity 2 and an AB system (J = 2.8 Hz) at 8.57 and 9.19 ppm, each doublet having also a relative intensity of 2 (Figure 1a).

The resonances of the heterocyclic protons were assigned unambiguously by using regioselectively monodeuterated TAP.[11] The spectra of Ru(TAP-*3-d*)$_3^{2+}$ (Figure 1b) and Ru(TAP-*2-d*)$_3^{2+}$ (Figure 1c) clearly show that the 8.82 ppm line corresponds to H(9) and H(10), the 8.57 ppm doublet to H(3) and H(6), and the 9.19 ppm signal to H(2) and H(7). Such a high-field shift of the protons adjacent to the complexation site has already been mentioned in the literature for the corresponding bipyridine,[12] bipyrazine,[6,7] and phenanthroline complexes[13] of ruthenium(II) and has been attributed to the ring current of one aromatic ligand exerting a shielding effect on the 3- and 6-protons of another ligand molecule. The X-ray diffraction analysis of a Ru(TAP)$_3$Cl$_2$.2H$_2$O monocrystal[10] shows indeed that the three TAP ligands are arranged quasi-octahedrally around the metal atom and that the 3- and 6-protons of one TAP ligand are located above the pyrazine

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(1) Research Associate of the National Fund for Scientific Research, Belgium.

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Table I. Reduction and Oxidation Potentials of TAP and $Ru(TAP)_3^{2+}$, by Polarography and Cyclic Voltammetry (0.5–1.5 V s^{-1}) on Hg and by Cyclic Voltammetry (0.20–0.25 V s^{-1}) on Pt

			oxidn pot.,	redn pot., V (vs. SCE)[a]				
compd	solvent	electrode	V (vs. SCE)	1	2	3	4	ref
TAP	DMF	Hg	. . .	−1.50 (r)	−2.10 (i)			
$Ru(TAP)_3Cl_2$	DMF	Hg	. . .	−0.76 (r)	−0.86 (r)	−1.05 (r)	−1.65[b] (i)	
$Ru(TAP)_3(PF_6)_2$	CH_3CN	Pt	~+1.93	−0.76 (r)	−0.89 (r)	−1.15 (r)	−1.59[b] (i)	
$Ru(TAP)_3(PF_6)_2$*[c]	CH_3CN		⩽−0.21	⩾+1.38				
$Ru(bpy)_3^{2+}$	CH_3CN	Pt	+1.354	−1.332	−1.517	−1.764	−2.4	19
	DMF	Hg	. . .	−1.25	−1.43	−1.68	−2.3	20
$Ru(phen)_3^{2+}$	CH_3CN	Pt	+1.40	−1.41	−1.54	−1.84	−2.24 (i)	19
$Ru(bpz)_3^{2+}$	CH_3CN	Pt	+1.86	−0.80	−0.98	−1.24	. . .	6, 7

[a] r = reversible; i = irreversible. [b] In polarography, the wave is irreversible; in cyclic voltammetry at 0.2 V s^{-1}, the wave becomes quasi-reversible with ΔE_p = 100 mV (difference between anodic and cathodic peak potential). [c] The oxidation and reduction potentials of the excited state[21] can be estimated provided the O–O transition energy is known, and this requires the knowledge of both the absorption and emission spectrum. Since no S_0–T_1 absorption was identified, the 580-nm emission band represents a lower limit of the O–O energy. The correct oxidation potential will thus be more negative than −0.21 V (SCE) and the reduction potential more positive than 1.38 V (SCE).

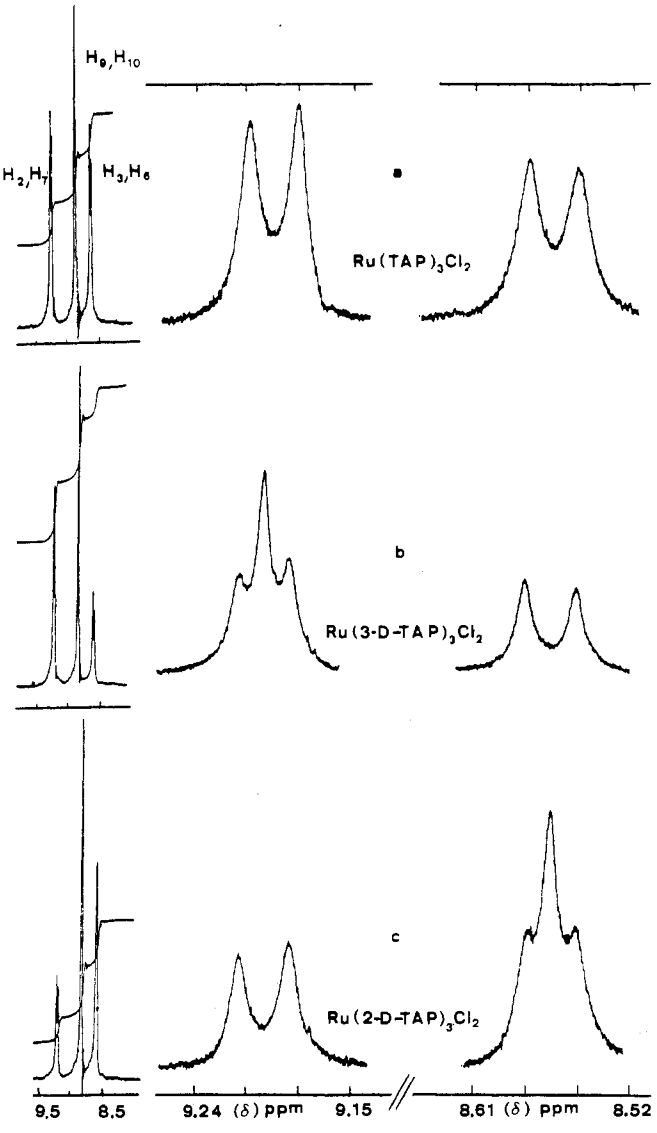

Figure 1. ^1H NMR spectra of $Ru(TAP)_3^{2+}$ (a), Ru(TAP-*3-d*)$_3^{2+}$ (b), and Ru(TAP-*2-d*)$_3^{2+}$ (c) in D_2O. To the left is given an overview of the spectra in the 8.5–9.5 ppm range showing the integration, and to the right, an expansion of the signals corresponding to the 2-protons (8.52–8.61 ppm) and 3-protons (9.15–9.24 ppm). A JEOL 100-MHz spectrometer was used.

ring of one of the other TAP molecules.

Spectroscopic Properties

The absorption spectrum of the $Ru(TAP)_3^{2+}$ ion consists of three maxima at 435 nm ($\epsilon = 1.6 \times 10^4$), 407 nm ($\epsilon = 1.7 \times 10^4$), and 270 nm ($\epsilon = 3.2 \times 10^4$ dm^3 mol^{-1} cm^{-1}) in acetonitrile; it is quite similar in water and aqueous acid (pH 0) (Figure 2). In comparison with $Ru(phen)_3^{2+}$ (λ_{max} = 450 and 425 nm),[14] there is a very small hypsochromic shift.

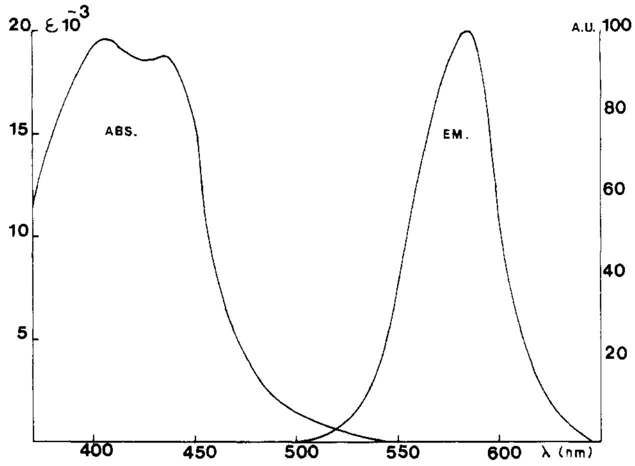

Figure 2. Absorption and emission spectra of $Ru(TAP)_3(PF_6)_2$ (5×10^{-5} M) in water at 293 K.

$Ru(TAP)_3^{2+}$ shows room-temperature emission from the CT state, characteristic of Ru complexes bonded to α-diimine. The corrected emission of $Ru(TAP)_3^{2+}$ in CH_3CN or H_2O is centered around 580 nm (Figure 2) and has a lifetime of 200 ns in H_2O, of the same order of magnitude as for the $Ru(phen)_3^{2+}$ complex.[15] The luminescence decay is measured with a 56DUVP photomultiplier perpendicularly to the excitation light at 337 nm of a Jobin-Yvon nitrogen laser. The emission is only very slightly quenched in a solution saturated with oxygen. In acidic solution (HCl or H_2SO_4, pH 0), no luminescence is observed as with $Ru(bpz)_3^{2+}$,[6] indicating probably a protonation of the excited state, and the complex is photochemically stable, contrary to the case of $Ru(bpy)_3^{2+}$.[16] However, in neutral aqueous solution, it is not stable over a long illumination time. In 0.1 M aqueous NaOH, the complex is thermally unstable and decomposes to a brownish solution, probably because of the high sensitivity of coordinated TAP toward nucleophiles, similar to what is observed with $Fe(bpz)_3^{2+}$.[17,18]

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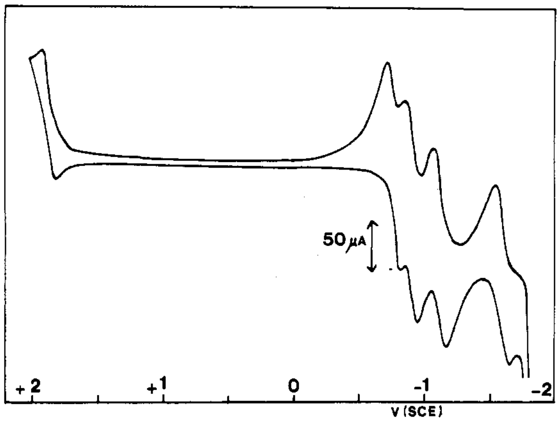

Figure 3. Cyclic voltammogram of $Ru(TAP)_3(PF_6)_2$ (10^{-3} M) in CH_3CN (0.1 M) in *n*-Bu_4ClO_4 (scan rate 180 mV/s).

Electrochemistry

The electrochemical measurements were performed on the chloride and the hexafluorophosphate salt of the complex. This latter was obtained from the chloride as described for the corresponding bipyrazine complex.[6] Table I gives the oxidation and reduction potentials vs. SCE of the free ligand and the complex in DMF and CH_3CN. The reduction potentials in DMF (0.1 M Bu_4NI) are measured at a dropping-mercury electrode by polarography or by cyclic voltammetry with scan rates ranging from 0.5 to 1.5 V s^{-1}, with a mercury pool as reference and counterelectrode (−0.55 V vs. SCE). In acetonitrile (0.1 M Bu_4NClO_4), a platinum wire is used and the SCE is connected through a double bridge. The scan rate is 0.2 or 0.25 V s^{-1}.

As shown in Table I, the free ligand is reduced only at −1.5 V, with a one-electron reversible wave, followed by an irreversible wave at −2.1 V, whereas the first reduction of the complex occurs already at −0.76 V. $Ru(TAP)_3^{2+}$ shows actually three successive one-electron reversible reduction waves, followed by a fourth quasi-reversible one in cyclic voltammetry ($\Delta E_p \approx 100$ mV) (Figure 3), this fourth wave being irreversible in polarography. The three first-reduction waves are slightly better defined in CH_3CN than in DMF.

The oxidation potential of $Ru(TAP)_3^{2+}$ in CH_3CN was difficult to measure because it occurs ($\sim$+1.93 V) at the limit of the potential region that can be examined with the Pt/CH_3CN system.

As could be expected for the complexes, the two additional nitrogen atoms in TAP induce a fairly strong anodic shift of the first-reduction wave compared to those of bipyridine or 1,10-phenanthroline and make it very similar to the case of $Ru(bpz)_3^{2+}$ (Table I).

Conclusions

The data collected here lead to the conclusion that the $Ru(TAP)_3^{2+}$ and $Ru(bpz)_3^{2+}$ complexes have similar properties, with one exception for the excited-state lifetime, and both differ from the corresponding bpy[15,19,20,22] and phen[15,19] complexes. The MLCT excited state of $Ru(TAP)_3^{2+}$ should thus behave as a weak reducing reagent ($\sim$−0.2 V vs. SCE) but as a strong oxidant ($\sim$+1.4 V), and analogously to what was shown by Crutchley and Lever for the bipyrazine complex, it should be thermodynamically able to oxidize water. The good photostability of $Ru(TAP)_3^{2+}$ in aqueous acid would allow us to use it for the water-splitting reaction in acid medium; its moderate photostability in neutral water, as compared to the case of $Ru(bpy)_3^{2+}$, precludes its use, however, as an ideal photosensitizer in neutral aqueous medium.

Registry No. $Ru(TAP)_3Cl_2$, 88181-59-3; $Ru(TAP)_3(PF_6)_2$, 88181-61-7; $Ru(Me_2SO)_4Cl_2$, 11070-19-2; D, 7782-39-0.

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Mixed Isocyanide–Halide Complexes of Osmium(II) and Osmium(III)

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We have been engaged in a systematic study of the synthetic, structural, and reaction chemistry of homoleptic isocyanide complexes of the early transition series, especially those of chromium, molybdenum, tungsten, and rhenium.[1] In view of the tremendous stability and ease of preparation of the 18-electron rhenium(I) cations $[Re(CNR)_6]^+$ (with both alkyl and aryl isocyanide ligands), we wondered whether a similar chemistry might not exist for the isoelectronic osmium(II) cations $[Os(CNR)_6]^{2+}$. The hexakis(alkyl isocyanide)- and hexakis(aryl isocyanide)iron(II) and -ruthenium(II) compounds are uncommon and their chemistry has been little explored,[2-5] while for osmium there is but a single report describing the syntheses of $[Os(CNMe)_6](ClO_4)_2$ and *trans*-$Os(CNMe)_4Br_2$.[8]

Following our recent isolation of several osmium(VI) complexes of the type *trans*-$OsO_2X_2(PR_3)_2$,[9,10] we have been investigating their chemical reactivity toward a variety of bridging ligands.[10-12] In the course of this work, we discovered that these osmyl derivatives could be converted into the diosmium(IV) complexes $Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR_3)_2$[11,12] upon reaction with carboxylic acid–anhydride mixtures. We have now found that the reactions of alkyl isocyanide ligands with *trans*-$OsO_2X_2(PPh_3)_2$ and $Os_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2X_4(PPh_3)_2$

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