Synthesis and Properties of Substituted Ruthenium Aqua Complexes

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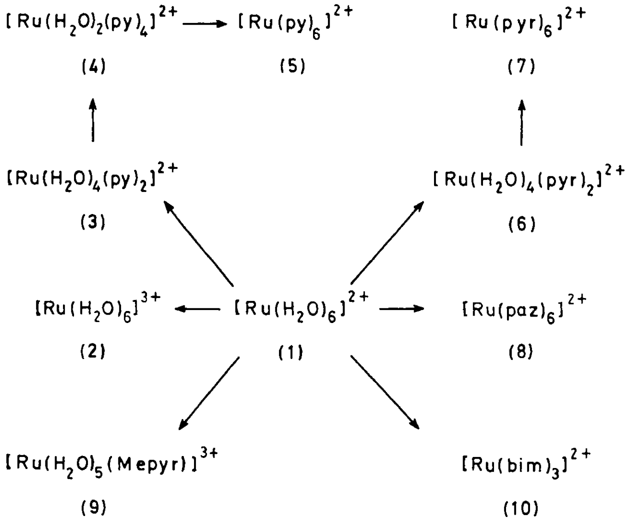
Summary $[Ru(H_2O)_6]^{2+}$ is a versatile reagent for the facile synthesis of a variety of complexes $[Ru(H_2O)_nL_{6-n}]^{2+}$ (L = heterocyclic *N*-donor) whose spectroscopic and electrochemical properties are described.

There exist only a few studies on ruthenium aqua ions[1] in contrast with the vast amount of data for complexes with nitrogen donors.[2] In particular, ruthenium aqua ions have not been employed so far as reagents in preparative chemistry. In order to isolate a solid salt of $[Ru(H_2O)_6]^{2+}$, we have modified the original preparative procedure[1b] by using Pb instead of Sn as reducing agent, the resulting Pb^{2+} being removed by Na_2SO_4. This solution was loaded on to a Dowex 50 W column, and $[Ru(H_2O)_6]^{2+}$ was eluted with 1 M toluene-*p*-sulphonic acid (H tos). Rotatory evaporation of the resulting solution under reduced pressure at 35 °C produced pink crystals of $[Ru(H_2O)_6][tos]_2$.[3] All operations were carried out under argon. The availability of a solid salt of the aqua ion opens facile and efficient synthetic routes to a variety of ruthenium complexes, the nitrogen heterocycles playing a dominant role as substituting ligands. Complexes $[Ru(H_2O)_nL_{6-n}]^{2+}$ (*cf.* Scheme) were obtained by the reaction under argon at 50 °C of *ca.* 0·1 M aqueous



Scheme. Syntheses of $[Ru(H_2O)_nL_{6-n}]^{2+}$ from $[Ru(H_2O)_6]^{2+}$ (py = pyridine; pyr = pyrazine; paz = pyridazine; Mepyr = *N*-methylpyrazinium; bim = 2,2′-bi-imidazole).

$[Ru(H_2O)_6][tos]_2$ with the appropriate ligand L in stoicheiometric ratio or in tenfold excess for the preparation of $[RuL_6]^{2+}$. Ethanol was added if necessary to produce a homogeneous reaction mixture. The complexes were precipitated as crystalline solids by adding tos^-, BF_4^-, or $S_2O_6^{2-}$. Elemental analyses were in excellent agreement with the given stoicheiometries.

The dominant spectroscopic feature of the complexes with mixed water–*N*-heterocyclic ligands (*cf.* Table) is an intense absorption band in the visible region assigned to a $t_{2g} \rightarrow \pi^*$ charge transfer. The disubstituted complexes are very readily formed, probably because water is a better leaving group than ammonia. We assume *trans*-geometry for the 4:2 composition since only one charge-transfer band is observed. Moreover, the use of $[Ru(H_2O)_6]^{2+}$ as reagent affords a very easy access to the $[RuL_6]^{2+}$ species (L = py, pyr, or paz). Only the hexakispyridine complex had previously been described with a rather difficult procedure for its preparation.[4] The formal reduction potentials listed in the Table are estimated from cyclic voltammograms. For all the compounds $[Ru(H_2O)_nL_{6-n}]^{2+}$ the potentials are considerably more positive compared with $[Ru(H_2O)_6]^{2+}$, thus demonstrating the stabilization of two-valent ruthenium by π-acids.

TABLE. Absorption spectra and formal reduction potentials $[Ru^{III} + e \rightarrow Ru^{II}]$ for $[Ru(H_2O)_nL_{6-n}]^{2+}$ complexes.

Complex	λ_{max}/nm (ϵ_{max})	*E*/V (*vs.* N.H.E.)[a]
(**1**)	529 (10·5); 386 (14·4)[b]	0·205[b]
(**2**)	390 (30·2)[b]	
(**3**)	372 (9,500); 240 (8,500)[c]	0·42[b]
(**4**)	353 (16,200); 240 (13,800)[c]	0·73[b]
(**5**)	345 (24,000); 243 (26,900)[d]	1·27[e]
(**6**)	436 (13,300); 250 (13,300)[c]	0·44[f]
(**7**)	369 (20,400); 250 (27,800)[c]	1·48[e]
(**8**)	381 (33,000); 233 (14,100)[c]	1·35[e]
(**9**)	527 (7,100); 267 (7,600)[c]	0·80[b]
(**10**)	396 (10,700); 279 (40,000)[c]	0·44[e]

[a] N.H.E. = normal hydrogen electrode. Calibration potentials: 0·05 V for $Ru(NH_3)_6^{3+/2+}$ (H. S. Lim, D. J. Barcley, and F. C. Anson, *Inorg. Chem.*, 1972, **11**, 1460); 1·05 V for $Fe(bpy)_3^{3+/2+}$ (bpy = 2,2′-bipyridine: C. T. Lin, W. Böttcher, M. Chou, and N. Sutin, *J. Am. Chem. Soc.*, 1976, **98**, 6536). [b] 0·5 M H_2SO_4. [c] H_2O. [d] MeCN. [e] MeCN, 0·1 M $[Bu_4N][PF_6]$. [f] H_2O, 0·1 M $[NH_4][PF_6]$.

We thank Dr. H. Wagner, CIBA-GEIGY, for the elemental analyses. This work was supported by the Swiss National Science Foundation.

(*Received*, *7th August* 1981; *Com.* 964.)

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[2] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., Wiley–Interscience, New York, 1980, p. 920.

[3] The crystal structure of $[Ru(H_2O)_6][tos]_2$ has been reported by P. Bernhard *et al.*, Proceedings of the International Conference on the Chemistry of the Platinum Group Metals, Bristol, 1981, C16.

[4] J. L. Templeton, *J. Am. Chem. Soc.*, 1979, **101**, 4906.