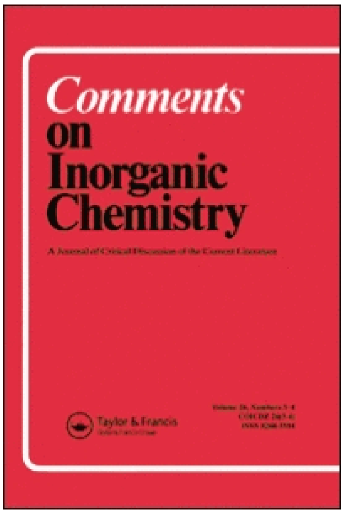

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Ruthenium Aqua Ions—Their Comparison to Ruthenium Ammines

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To cite this Article Bernhard, Paul , Lehmann, Hans and Ludi, Andreas(1983) 'Ruthenium Aqua Ions—Their Comparison to Ruthenium Ammines', Comments on Inorganic Chemistry, 2: 3, 145 — 156

To link to this Article: DOI: 10.1080/02603598308078114

URL: http://dx.doi.org/10.1080/02603598308078114

Ruthenium Aqua Ions—Their Comparison to Ruthenium Ammines

Similarities and contrasts in the descriptive chemistry of aqua and ammine complexes of ruthenium are discussed. The reactivities of the two classes of coordination compounds are compared; both show a remarkable tendency to form complexes with π-accepting ligands, including alkenes and alkynes. The exploitation of $Ru(H_2O)_6^{2+}$ as a versatile preparative reagent is demonstrated.

A simplified and concise survey of the chemical literature on ruthenium[1] for the past three decades reveals three classes of compounds where the overwhelming part of research activity has occurred. One of these prominent areas of research encompasses the rapidly expanding organoruthenium chemistry with its connections to studies in homogeneous and heterogeneous catalysis. The progress in the other two somewhat overlapping fields evolved quite separately from the expansion in metallorganic chemistry and deals with the synthesis and the elucidation of various physical and chemical properties of classical coordination compounds. There exist only rather rare cases where compounds have been investigated which represent conceptual links between Werner complexes and organoruthenium chemistry. Among classical coordination compounds of ruthenium the first development was initiated by the comprehensive studies of electron transfer processes by Henry Taube and his associates. A coherent descriptive chemistry of the ruthenium ammines in oxidation states two and three emerged as an important result of these investigations. Moreover, this area of ruthenium chemistry embraces synthetic, thermodynamic and spectroscopic studies of

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Comments Inorg. Chem.
1983, Vol. 2, Nos. 3–4, pp. 145–156
0260-3594/83/0204-0156/$18.50/0

Printed in the United States of America

a variety of ligand bridged mixed-valence complexes. Originally envisaged as study objects for the intermediates in electron transfer reactions, these binuclear mixed-valence complexes became an interesting and challenging class of compounds in their own right.[2] The third major part of research activity, finally, is focused on one single compound. Tris(bipyridine)ruthenium became an extremely popular (too popular?) complex as a sensitizer in the light-driven water splitting process.[1b]

The impressive revitalization of the classical coordination chemistry of ruthenium evidently has been confined largely to nitrogen containing ligands. Systematic studies in synthetic chemistry for these complexes have been carried out as well as a thorough elucidation and rationalization of their various properties. In contrast to the large body of information available for the ruthenium ammines, surprisingly few studies have been devoted to compounds with other ligating atoms.[1]

The common starting material for the preparative ruthenium chemist is commercially available hydrated trichloride, actually a rather poorly defined mixture. The use of this reagent in aqueous solution has its limitations owing to the high stability of mixed aqua–chloro complexes. Well established and efficient synthetic routes are used for the ammines[1a]:

$$\begin{tikzcd}
\text{“}RuCL_3 \cdot 3H_2O\text{”} \arrow[r, "Zn{,}NH_3aq", "NH_4Cl"'] & Ru(NH_3)_6^{2+} \arrow[r, "Cl_2", "H^+"'] & Ru(NH_3)_6^{3+} \arrow[d, "HCl"] \\
Ru(NH)_3)_5L^{2+} & Ru(NH_3)_5H_2O^{2+} \arrow[l, "L"'] & Ru(NH_3)_5Cl^{2+}\ . \arrow[l, "Zn/Hg"', "H^+"]
\end{tikzcd}$$

A few qualitative and rather crude approximations are used to rationalize a wealth of experimental data. They also serve as simple guidelines for the preparative coordination chemist to design the synthetic approach. For the specific case of the ruthenium ammines the following three predominant properties are used in this regard:

(i) The $Ru(NH_3)_6^{3+/2+}$ and $Ru(NH_3)_5L^{3+/2+}$ couples are well defined and stable low-spin $t_{2g}^5 - t_{2g}^6$ pairs. Since the electron transfer process involves only one σ-nonbonding t_{2g} electron it does not require an elaborate electronic rearrangement and the electron transfer is therefore reasonably fast. On the other hand, the substitution of an ammine ligand is usually very slow[3] for complexes with a t_{2g}^5 or t_{2g}^6 configuration. In combination with their extended range of reduction potentials (Table I)

TABLE I
Reduction potentials of $Ru(NH_3)_5L^{3+/2+}$; mV vs NHE

L	E	L	E
Cl^-	-42^a	acetylene	665^b
NH_3	50^a	ethylene	930^b
H_2O	66^a	N_2	1120^a
pyridine (py)	305^a	$S(CH_3)_3^+$	1250^c
pyrazine (pyz)	490^a	fumaric acid	1400^b

[a] H. S. Lim, D. J. Barclay and F. C. Anson, Inorg. Chem. **11**, 1460 (1972).
[b] Reference 7.
[c] C. A. Stein and H. Taube, J. Am. Chem. Soc. **100**, 336 (1978).

$Ru(NH_3)_5L^{3+/2+}$ species are thus very attractive partners for a wide spectrum of redox reactions.

(ii) The water molecule in $Ru(NH_3)_5H_2O^{2+}$ is more substitution labile than ammonia by orders of magnitude. This property makes the pentaamminemonoaqua ion the ideal starting reagent for the synthesis of a variety of complexes $Ru(NH_3)_5L^{2+}$. Synthetic chemistry within the ruthenium ammines is therefore primarily and selectively determined by this striking substitution lability of one single coordination site. Replacing ammonia ligands by other molecules requires considerable effort; the ruthenium ammines are not universal starting materials to synthesize complexes of the stoichiometry $Ru(NH_3)_xL_{6-x}^{n+}$.

(iii) The concept of π backbonding[4] is very important and useful for the discussion of the Ru(II)–L bond in $Ru(NH_3)_5L^{2+}$ species[5] emphasizing the behavior of Ru(II) as a σ acceptor and π donor. Good π-accepting ligands are N_2, CO, nitriles and the family of *N*-heterocycles like pyridine (py), pyrazine (pyz), pyridazine (paz) and their numerous derivatives. The π-donating capacity of Ru(II) is also demonstrated by the easy formation and remarkable stability of the $Ru(NH_3)_5$ complexes with the highly reactive quinone diimines.[6] More recently, alkenes and alkynes also were found to form stable and well-defined complexes with the $Ru(NH_3)_5$ moiety.[7] Whereas the UV-VIS spectrum of $Ru(NH_3)_6^{2+}$ exhibits weak ligand-field transitions, intense ($\varepsilon \sim 10^4$) bands are observed in this spectral range for the complexes with good π acceptors. These strong bands are assigned to allowed $M(t_{2g}) \rightarrow L(\pi^*)$ charge-transfer transitions. Further experimental manifestations of π back donation are enhanced basicities of suitable ligands like pyrazine upon coordination to Ru(II).[5] The extent of this Ru–L π interaction can be qualitatively gauged by the reduction potentials of the $Ru(NH_3)_5L^{3+/2+}$ couples. The metal center acquires more Ru(III) character in $Ru(II)(NH_3)_5L$ complexes with strong metal-to-ligand backbonding. Correspondingly, a shift to more positive reduction potentials is observed (Table I). We note the occurrence of alkenes and alkynes in this list of ligands which thus bridge the gap between classical coordination chemistry and organoruthenium chemistry.

Structural data also may serve to illustrate the simple π backbonding model. Table II presents relevant interatomic distances for a few selected complexes where crystallographic results are available for both oxidation states.[8,9] We notice the contraction of the Ru–*N*(heterocycle) distance for Ru(II) and the influence of the π-accepting ligand on the bond length in *trans* position. Both effects are also very clearly demonstrated by the results of an x-ray structure analysis of the Creutz–Taube complex and of its reduced and oxidized form.[10] Moreover, these data unambiguously show that the mixed-valence ion cannot be represented by a structure midway between the two extremes of this electron transfer series. The combined structural results for the II–II, II–III and III–III complex rather present strong evidence that the Creutz–Taube complex has a valence delocalized ground state.

Metal aqua ions play a dominant role in the aqueous solution chemistry of the compounds of the first-row transition elements. The species $M(H_2O)_6^{n+}$ are Brönsted acids; pK_a values cluster around 7 for $M(H_2O)_6^{2+}$ and around 2 for $M(H_2O)_6^{3+}$. The synthetic chemistry exploits the high substitution lability of the water ligands leading to a wide spectrum of compounds. In contrast, only a few mononuclear aqua ions have been described for the metals of the 4*d* and 5*d* series: Mo^{3+}, Ru^{2+}, Ru^{3+}, Rh^{3+}, Pd^{2+}, Ir^{3+} and Pt^{2+}. So far, these aqua ions do not represent important starting materials in the preparative chemistry of the corresponding metals. Owing to the notorious difficulty of growing crystals of the very soluble metal aqua ions the studies of the hydrated heavy transition metal cations have usually been confined to quite dilute solutions.

Early attempts to prepare ruthenium aqua ions were performed in chloride-containing media where mixed aqua–chloro complexes are the predominant species.[11] Mercer and Buckley[12] reduced a mixture of the mono and dichloro complexes at a mercury cathode. Subsequent ion exchange produced dilute solutions of $Ru(H_2O)_6^{2+}$. The reduction of

TABLE II

Average metal–ligand distances (Å) in mixed ammine–heterocycle complexes of Ru(II) and Ru(III)

	$Ru(NH_3)_5pyz$[a]		*cis*-$Ru(NH_3)_4isn_2$[b]		$(NH_3)_5Ru(pyz)Ru(NH_3)_5$[c]		
	II	III	II	III	II–II	II–III	III–III
Ru–NH_3 *trans*	2.166(7)	2.125(8)	2.167(6)	2.133(11)	2.149(3)	2.127(2)	2.090(1)
Ru–NH_3 *cis*	2.153(6)	2.106(6)	2.143(6)	2.118(5)	2.128(3)	2.125(3)	2.098(1)
Ru–N hetero	2.006(6)	2.076(8)	2.058(14)	2.099(6)	2.013(3)	2.014(4)	2.115(1)

[a] pyz = pyrazine, Ref. 8.
[b] isn = isonicotinamide, Ref. 9.
[c] Reference 10.

RuO_4 by metallic tin in 2 M HBF_4 followed by ion exchange gave approximately 10^{-2} M solutions of $Ru(H_2O)_6^{2+}$.[13] A slightly modified version of this procedure was recently used in our laboratory to prepare crystalline salts of the hexaaqua ions of both Ru(II) and Ru(III)[14]:

$$Ru \xrightarrow[\text{KOH melt}]{KMnO_4} RuO_4^-,\ RuO_4^{2-} \xrightarrow[O_2,\ H_2SO_4]{KMnO_4} RuO_4 \text{ in } H_2SiF_6\ ;$$

$$RuO_4 \xrightarrow[\text{ion exchange}]{Pb,\ H^+} Ru(H_2O)_6^{2+} \xrightarrow{O_2} Ru(H_2O)_6^{3+}.$$

The reduced $Ru(H_2O)_6^{2+}$ was eluted from the ion exchange column with 1 M *p*-toluene sulfonic acid (Htos). The isolation of solid products yields crystals of composition $Ru(H_2O)_6tos_2$ (pink) and $Ru(H_2O)_6tos_3 \cdot 3H_2O$ (yellow) both of which are surprisingly stable towards humidity and oxidation by atmospheric oxygen. Some properties of the two aqua ions are summarized in Table III.

For purposes of discussion the hexaaqua ions of Ru(II) and Ru(III) are compared with the corresponding aqua iron ions on the one hand and with the ruthenium ammines on the other hand. The vertical Ru–Fe comparison, however, is of limited value owing to the different spin multiplicities of the two metal ions. For iron the ground state configurations are $t_{2g}^4e_g^2$ [Fe(II)] and $t_{2g}^3e_g^2$ [Fe(III)] whereas the corresponding

TABLE III
Some properties of $RU(H_2O)_6^{n+}$

	$Ru(H_2O)_6^{2+}$	$RU(H_2O)_6^{3+}$	
UV-VIS bands, nm (ε)[a]	529(10.5) 386(14.4)	390(30.2)	
pK_a		2.90(5)[b]	2.4(2)[c]
r(Ru–O), Å[d]	2.122(16)	2.029(7)	
E°, V vs NHE[a,b,e,f]	0.205		

[a] Reference 20.
[b] Reference 16.
[c] Z. Harzion and G. Navon, Inorg. Chem. **19**, 2236 (1980).
[d] Reference 14.
[e] Reference 12.
[f] Reference 13.

TABLE IV
Metal–ligand distances and electron transfer kinetics for $RU(NH_3)_6^{3+/2+}$, $RU(H_2O)_6^{3+/2+}$ and $Fe(H_2O)_6^{3+/2+}$

	$Ru(NH_3)_6^{3+/2+}$ [a]	$Ru(H_2O)_6^{3+/2+}$ [b]	$Fe(H_2O)_6^{3+/2+}$ [a]
Δr(M-L), Å	0.04(1)	0.09(2)	0.14(2)
$\Delta G^{\ddagger}_{in}$, kcal mol^{-1}	0.9(5)	4.4(2.1)	8.4(3.2)
$\Delta G\ddagger$, kcal mol^{-1}	11.8(5)	15.3(2.1)	18.5(3.2)
log *k*, calc	4.2(3)	1.6(1.6)	−0.7(2.3)
log *k*, obs	3.6	1.8	0.6

[a] Reference 17.
[b] Reference 14.

Ru aqua ions possess the low-spin configurations t_{2g}^6 and t_{2g}^5. We just mention that many similarities in chemical behavior are observed for cationic $Ru(II)(NH_3)_5L^{2+}$ and anionic $Fe(II)(CN)_5L^{3-}$, both metal centers belonging to the low-spin configuration.[15]

In search for analogies and disparities between the aqua ions and the ammines of ruthenium we begin with a short survey of some crucial structural properties and their effect on the rate of the corresponding self-exchange reaction:

$$ML_6^{3+} + ML_6^{2+} \overset{k}{\rightleftharpoons} ML_6^{2+} + ML_6^{3+}.$$

The rate of the $Ru(H_2O)_6^{3+/2+}$ self-exchange process has been estimated by applying the Marcus cross relation to a number of redox reactions involving either $Ru(H_2O)_6^{2+}$ or $Ru(H_2O)_6^{3+}$.[16] For the three couples compared in Table IV we assume that the self-exchange reactions are adiabatic. We therefore can express the rate *k* as

$$k = \frac{k_B T}{h} \exp(-\Delta G\ddagger / RT).$$

We furthermore assume that the contributions to $\Delta G\ddagger$ dealing with the formation of the precursor complex and with the solvent reorganization are virtually the same for all of the three complexes owing to the identical charges and very similar geometries. We thus focus our attention on the inner-sphere barrier, in the classical limit given by

$$\Delta G^{\ddagger}_{\text{in}} = \frac{3f_2f_3(r_2 - r_3)^2}{f_2 + f_3} = \frac{3}{2}\bar{f}\,(\Delta r)^2.$$

The quantities r_2, r_3 and f_2, f_3 are the metal–ligand distances and breathing force constants, respectively, for the two reactants. For our calculations we use the reported force constants for $Ru(NH_3)_6^{3+/2+}$ and $Fe(H_2O)_6^{3+/2+}$.[17] For $Ru(H_2O)_6^{3+/2+}$ we adopt a value of 2.5(5) mdyn $Å^{-1}$ for the reduced force constant $\bar{f}$. One entry of Table IV merits special attention: The calculated rate constants have impressively large error bounds. The only error sources considered for these calculations are the standard deviations of the M–L distances as obtained from the least squares refinement of the corresponding crystal structures and the error in $\bar{f}$. Since $\Delta G^{\ddagger}_{\text{in}}$ depends on the square of Δr, the former error is much more important in the error propagation than the uncertainty in $\bar{f}$. Even for very careful and precise crystallographic studies the error in Δr is on the order of 0.005 to 0.01 Å, the standard deviation of the interatomic distances actually representing a lower limit for realistic fluctuations in M–L distances. Moreover, deviations of such distances for species in solution from the values in crystals have been discussed recently for a number of transition metal aqua ions.[18] Calculated rate constants for electron transfer processes thus really reflect orders of magnitude and trends within a series of redox pairs rather than exact numbers for a particular couple. This inherent uncertainty may overshadow the level of approximation.

A crucial property for the application of the aqua and ammine complexes in ligand substitution processes and hence in preparative coordination chemistry is the lability of the ligands H_2O and NH_3. Table V presents a summary of these labilities expressed as rate constants for

TABLE V

Substitution labilities of Ru–NH_3 and Ru–H_2O bonds (k, s^{-1}; 25°C)

	Ru(II)	Ru(III)
$Ru(NH_3)_6 + H_2O$[a]	1.5×10^{-6}	1.4×10^{-10}
$Ru(NH_3)_5H_2O + H_2O$[a]	3	5×10^{-4}
$Ru(H_2O)_6 + H_2O$[b]	5×10^{-2}	4×10^{-6}

[a] Reference 3.
[b] Reference 19.

the pseudo-first-order substitution process. Preliminary results of an ^{17}O-NMR study of the ruthenium aqua ions are included.[19] As expected, both aqua ions are quite substitution inert, intermediate between the labile water molecule in $Ru(NH_3)_5H_2O^{2+}$ and the very robust $Ru(NH_3)_6^{3+}$. The difference of four orders of magnitude in the lability of the two oxidation states is remarkably well maintained for the complexes considered in Table V. The not too slow exchange rate of $Ru(H_2O)_6^{2+}$ coupled with the rather wide accessible pH range renders this ion a potential candidate for the study of a large number of substitution reactions and therefore a versatile starting reagent in preparative coordination chemistry.

Keeping the synthetic aspects in mind, we stress the point that $Ru(NH_3)_5H_2O^{2+}$ is a strongly selective reagent of very high specificity capable of producing in a straightforward way a wide variety of $Ru(NH_3)_5L^{2+}$ complexes in good yield. Special efforts also have to be made to substitute ammonia molecules in a defined sense. A significant share of the classical coordination chemistry of ruthenium thus originates from the systematic utilization of this unique labile water ligand.[1,3,5–7] $Ru(H_2O)_6^{2+}$ on the other hand is a general purpose reagent. There does not exist any singular preference for one specific coordination site. The stoichiometry of the final product of a substitution reaction is largely governed by the concentration of the substituting ligand. In perfect analogy again to $Ru(NH_3)_5H_2O^{2+}$ the π-accepting ligands are important and produce well defined substitution products. Using the common *N*-heterocycles (py, pyz, paz, etc.) the reaction proceeds depending on the chosen concentration ratios:

$$Ru(H_2O)_6^{2+} \rightarrow Ru(H_2O)_4L_2^{2+} \rightarrow Ru(H_2O)_2L_4^{2} \rightarrow RuL_6^{2+}.$$

We notice in particular the facile formation of the 4:2 complexes illustrating that water is the better leaving group than ammonia. Since only one absorption band is observed for these species we assume *trans* geometry.

The UV-VIS spectrum of $Ru(H_2O)_6^{2+}$ and $Ru(H_2O)_6^{3+}$ contains weak bands corresponding to ligand field transitions of low-spin d^6 and d^5 complexes (Table III). Intense bands ($\varepsilon \sim 10^4$) are observed for complexes $Ru(H_2O)_xL_{6-x}^{2+}$, L being a π-accepting ligand. This property again mimics the behavior of $Ru(NH_3)_5L^{2+}$ (Figure 1). Table VI presents the positions and the intensities for these intense bands which are attributed

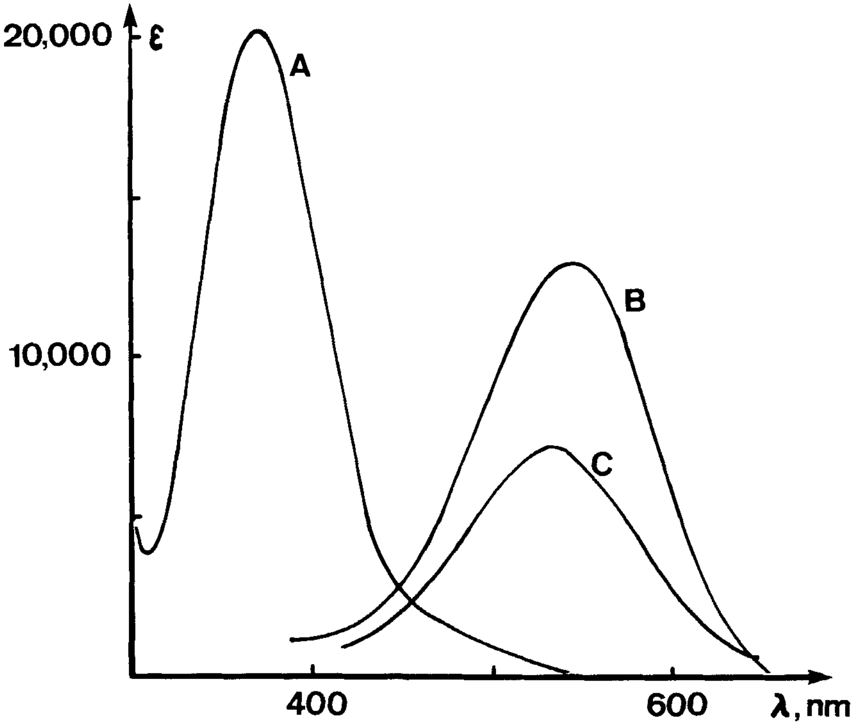

FIGURE 1 Charge transfer absorption of $Ru(pyz)_6^{2+}$ (A), $Ru(NH_3)_5(Mepyz)^{3+}$ (B) and $Ru(H_2O)_5(Mepyz)^{3+}$ (C).

TABLE VI

Charge transfer bands of complexes $Ru(II)(H_2O)_xL_{6-x}^{n+}$ (20) (abbreviations cf. Figure 2)

Complex	λ_{max} (nm)	ε_{max}	E_0, V vs NHE
$Ru(H_2O)_5(Mepyr)^{3+}$	527	7 100	0.80
$Ru(H_2O)_4py_2^{2+}$	372	9 500	0.42
$Ru(H_2O)_2py_4^{2+}$	353	16 200	0.73
$Ru\ py_6^{2+}$	345	24 000	1.27
$Ru(H_2O)_4pyz_2^{2+}$	436	13 300	0.44
$Ru\ pyz_6^{2+}$	369	20 400	1.48
$Ru\ paz_6^{2+}$	381	33 000	1.35
$Ru(DMF)_6^{2+}$	315	12 000	0.05
$Ru(AN)_5H_2O^{2+}$	327	1 640	0.70

to a t_{2g} → π* charge-transfer transition together with the reduction potentials for a selection of compounds obtained from $Ru(H_2O)_6^{2+}$.

$Ru(H_2O)_6^{2+}$ thus acts as a versatile starting reagent in aqueous or nonaqueous solutions (Figure 2). The availability of solid salts of this aqua ion opens new and efficient synthetic routes to a remarkable variety of novel compounds. As one specific example we mention the complexes RuL_6^{2+} (L = py, pyz, paz) which are obtained in a very facile and smooth way.[20] So far only the hexakispyridine complex has been prepared requiring quite elaborate synthetic procedures.[21] A second remark concerns the reaction of $Ru(H_2O)_6^{2+}$ with unsaturated organic molecules mirroring the formation of complexes of the $Ru(NH_3)_5$ moiety with the same ligands. The easy and efficient preparation[22] of ruthenocene, $Ru(H_2O)_3$-benzene^{2+} and $Ru(H_2O)_4COD^{2+}$ from $Ru(H_2O)_6^{2+}$ and cyclopentadiene, cyclohexadiene and 1,5-cyclooctadiene, respectively, serves to illustrate novel opportunities in preparative chemistry and new connections between classical and metallorganic chemistry.

We are convinced that these conceptual links merit further attention and that they eventually will prove quite fruitful for the future development of the descriptive ruthenium chemistry. We conclude our Comment by expressing our firm belief that quite a few new and rewarding entries will enrich the scheme of Figure 2 during the next few years.

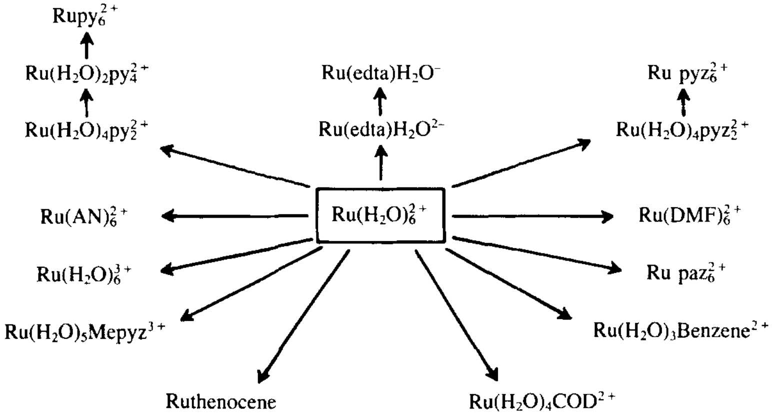

FIGURE 2 Reactions of $Ru(H_2O)_6^{2+}$ (edta = ethylenediamine tetraacetate; DMF = dimethylformamide; COD = 1,5-cyclooctadiene; $Mepyz^+$ = N-methylpyrazinium; AN = acetonitrile).

Acknowledgment

We gratefully acknowledge the support of our research by the Swiss National Science Foundation (Grant No. 2.209-0.81) and by the Entwicklungsfonds Seltene Metalle.

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