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ISOMER SHIFTS AND CHEMICAL BONDING IN RUTHENIUM COMPLEXES *

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ABSTRACT

Isomer shifts of the recoilless 90 keV γ-rays of ^{99}Ru were observed in a number of octahedrally coordinated complexes of ruthenium and reveal the influence of different ligands on the electron density at the ruthenium nuclei. For a given oxidation state the observed shifts are correlated with the spectrochemical series; the backbonding properties of ligands like CN^- and NO^+ cause a considerable increase of the electron density. This behaviour is largely similar to that found for compounds of iron and some 5d elements.

1. INTRODUCTION

Recent investigations [1, 2] of the isomer shifts of the recoilless 90 keV γ-rays of ^{99}Ru in the majority of the studied chemical compounds revealed a monotonic increase of the observed shifts with the oxidation state of the metal. This has been attributed to the shielding effect which the 4d electrons exert on the closed-

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shell s electrons. Since the number of the d electrons decreases from $4d^6$ in divalent to $4d^0$ in octavalent ruthenium one expects the electron density D at the sites of the Ru nuclei to increase with the oxidation state. The observation that at the same time the isomer shift energy

$$S = (2\pi/3)\ Z\ e^2\ \delta\langle r^2\rangle\ D$$

also increases implies that the change $\delta\langle r^2\rangle$ of the mean square nuclear charge radius must be positive [1, 3]. The considerable spread of the shifts for compounds of the same formal oxidation state but with different ligands, however, reflects the importance of additional effects of chemical bonding, without a thorough understanding of which the observed details cannot satisfactorily be explained. Such are, for instance, the 5s, 5p and additional 4d populations arising from σ bond covalency and changes of the effective number of 4d electrons due to π bonding. Drastic effects of the latter kind have been observed in complexes containing ligands with low-lying empty π^* orbitals. In such compounds backbonding with metal d orbitals may lead to an increase of the electron density by an amount corresponding to more than two oxidation states [1, 5, 6].

Since both σ and π bonding strongly depend on the nature of the ligands, one can hope to gain some insight into these mechanisms by a systematic variation of one or several ligands in otherwise similar complexes. In the present paper we report such data for hexacoordinated complexes of divalent and trivalent ruthenium and some other recent Ru isomer shift results, which are of interest in this context.

2. EXPERIMENTS AND RESULTS

Experimental details and the evaluation of the data have been described previously [1]. A source of ^{99}Rh in a 150 mg/cm^2 foil of natural Ru metal was used in

all experiments and both the source and the absorbers were cooled to 4.2 K in a liquid helium cryostat. Some of the transmission spectra are reproduced in Fig. 1. The results obtained for the different absorber substances are compiled in the table. The isomer shifts S are given with respect to Ru metal. The quadrupole splittings $\Delta E_Q = (eQV_{zz}/2)(1 + \eta^2/3)^{1/2}$, the sign of which cannot be derived from the nuclear gamma resonance spectra, are those of the 90 keV state with spin $I = 3/2^+$. As in the previous nuclear gamma resonance work on ruthenium [1, 2, 4] the quadrupole splitting of the $I = 5/2^+$ groundstate could not be resolved in any of the compounds studied, nor was a magnetic hyperfine splitting observed in any of them at 4.2 K.

3. DISCUSSION

The isomer shift data given in the table as well as some relevant previous results [1] are plotted in Fig. 2 where, for the sake of clarity, the different types of compounds are arranged in separate columns. Even though for most of these compounds no x-ray structure data are available, their chemical formulae suggest an octahedral or distorted octahedral arrangement of the ligands. This is true even for RuF_5 which consists of tetrameric Ru_4F_{20} clusters made up of bridged fluorine octahedra [7].

The behaviour of the hexahalogen complexes of ruthenium is very similar to that of the isoelectronic iridium compounds [5]. Obviously this group of compounds exhibit the lowest electron densities which are at all observed for any given formal oxidation state of the metal. The absorption lines of the hexammine complexes of trivalent ruthenium are shifted to higher velocities by an amount corresponding to about one half of the difference between adjacent oxidation states of the hexahalides. This is probable due to a higher degree of σ bond covalency,

since ammonia is expected to be neither a π donor nor a π acceptor [8, 9] and electronic coupling effects should proceed via σ bonds only. A more drastic shift to higher electron densities occurs whenever a polyatomic ligand with backdonation properties is introduced into a complex of ligands which do not themselves possess empty π^* orbitals adequate for backbonding . Most striking in this context is the nitrosyl group, which forms bonds of high stability in many Ru(II) complexes [10,11]. Compared to those of $[Ru(NH_3)_6]^{2+}$ the resonance lines of $[Ru(NH_3)_5NO]^{3+}$ and $[RuCl_5NO]^{2-}$ are shifted towards higher velocities by an amount which corresponds to nearly two oxidation states in the hexahalide scale and may formally be identified with a reduction of the number of 4d electrons by slightly less than two units. The outstanding properties of the Ru-NO bond can be attributed to the large overlap between the filled metal $4d_{xz}$ and $4d_{yz}$ orbitals and the empty π^* orbitals of the nitrosyl group, which is the essential feature of the molecular orbital scheme for $[MX_5NO]^-$ type complexes [12, 14]. The formation of these antibonding π-type molecular orbitals with the nitrosyl ligand results in the backdonation of d electrons to the ligand and leads to a higher s electron density at the nuclear site since the s electrons of the metal become less strongly shielded. Moreover, the expansion of the d electrons to the ligand is expected to go along with an enhancement of the σ bonding strength. In this way electrons occupying the σ bonding orbitals are shifted from the ligands to the metal and the principle of electroneutrality is, at least partially, obeyed. Such a process may again increase the electron density at the nucleus, since the s character of the σ bonding orbitals presumably outweighs the shielding power of their d and p contributions [15]. In analogy to what has been observed for the iron case the nitrosyl group exhibits the strongest backbonding capability in ruthenium complexes [16].

From the isomer shifts in the series

$$\left[Ru^{II}(CN)_5NO_2\right]^{4-} < \left[Ru^{II}(CN)_6\right]^{4-} < \left[Ru^{II}(CN)_5NO\right]^{2-} \quad \text{and}$$

$$\left[Ru^{II}(NH_3)_6\right]^{2+} < \left[Ru^{II}(NH_3)_5N_2\right]^{2-} < \left[Ru^{II}(NH_3)_5NO\right]^{3+}$$

of compounds in which only one ligand varies, the following order for the back-donation power of the ligands can be established:

$$NO_2^- < CN^- < NO^+ \quad \text{and}$$

$$NH_3 < N_2 << NO^+$$

While NH_3 is neither a π donor nor a π acceptor [8, 9], the π^* antibonding tendency of the N_2 ligand has been the object of some discussion [17, 18]. The isomer shift values for the $\left[Ru^{II}(NH_3)_5N_2\right]^{2+}$ complexes as compared to those of the hexammine compounds of Ru(II) are in agreement with the notion that N_2 possesses some π^* antibonding capability.

For the isomer shifts in compounds with two substituted ligands one can write the sequence,

$$\left[Ru^{II}(NH_3)_6\right]^{2+} < \left[Ru^{II}(NH_3)_4pyr_2\right]^{2+} < \left[Ru^{II}(NH_3)_4(HSO_3)_2\right] <$$

$$\left[Ru^{II}(NH_3)_4 \begin{matrix} Cl \\ SO_2 \end{matrix}\right]^{+} << \left[Ru^{II}(NH_3)_4 \begin{matrix} OH \\ NO \end{matrix}\right]^{2+}$$

which again demonstrates the backbonding power of the NO^+ ligand.

In $[MX_5\ NO]$-type complexes the five X-ligands are less important for the molecular orbital bonding scheme [12, 14] than the nitrosyl group, but they are by no means negligible. This is demonstrated by the juxtaposition of the isomer shift series

$$\left[Ru^{II}Cl_5NO\right]^{2-} < \left[Ru^{II}(NH_3)_5NO\right]^{3+} < \left[Ru^{II}(CN)_5NO\right]^{2-} \quad \text{and}$$

$$\left[Ru^{II}(NH_3)_6\right]^{2+} << \left[Ru^{II}(CN)_6\right]^{4-}$$

which shows, that the strong backdonation properties of the CN^- ligands as compared to the "innocent" NH_3 provoke less change of the electron density when a nitrosyl group is present than they do between $\left[Ru^{II}(NH_3)_6\right]^{2+}$ and $\left[Ru^{II}(CN)_6\right]^{4-}$. This indicates, that a saturation value is reached, when a shift formally corresponding to about 2.5 oxidation states has been induced. The $\left[Ru^{II}(CN)_5NO\right]^{2-}$ complex exhibits the highest isomer shift value observed for divalent ruthenium compounds, in striking analogy to the iron case [16].

From the sequence

$$\left[Ru^{III}(NH_3)_6\right]^{3+} \approx \left[Ru^{III}(NH_3)_5H_2O\right]^{3+} \approx$$

$$\left[Ru^{III}(NH_3)_4Cl_2\right]^{+} < \left[Ru^{III}(NH_3)_4 \begin{matrix} Cl \\ OH \end{matrix}\right]^{+}$$

of isomer shifts in ammine complexes one may infer a slight backbonding tendency of the OH^- group [19, 20]. The interpretation of such small effects in terms of π^* antibonding may, however, already stress this model too much.

It is interesting to note that the sequences

$$\left[Ru^{II}Cl_5NO\right]^{2-} < \left[Ru^{II}(NH_3)_5NO\right]^{3+} < \left[Ru^{II}(CN)_5NO\right]^{2-} ,$$

$$\left[Ru^{II}(NH_3)_6\right]^{2+} << \left[Ru^{II}(CN)_6\right]^{4-} \quad \text{and}$$

$$\left[Ru^{III}F_6\right]^{3-} < \left[Ru^{III}(NCS)_6\right]^{3-} \approx \left[Ru^{III}(NH_3)_6\right]^{3+}$$

for the isomer shifts correspond to the order of the ligands in the spectrochemical

series [20] if the thiocyanate group is nitrogen bonded to the ruthenium atom, which has been inferred from infrared spectroscopy data [21].

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TABLE

Isomer shift S relative to ruthenium metal, half linewidth at half maximum W/2, and electric quadrupole splitting ΔE_Q of the 90 keV state of ^{99}Ru obtained from absorbers of various ruthenium compounds. In the last column references as to the suppliers or preparation of the samples are given.

Compound	S [mm/s]	ΔE_Q [mm/s]	W/2 [mm/s]	Ref.
$Ru^{V}F_5$	+ 0.15 ± 0.01	0.56 ± 0.01	0.18 ± 0.02	(a)
$[Ru^{III}(NH_3)_6]Br_3$	- 0.50 ± 0.06	-	0.37 ± 0.1	(b)
$[Ru^{III}(NH_3)_5Br]Br_2$	- 0.53 ± 0.02	-	0.30 ± 0.02	(b)
$[Ru^{III}(NH_3)_5H_2O](NO_3)_3$	- 0.50 ± 0.07	0.49 ± 0.05	0.32 ± 0.08	(c)
$[Ru^{III}(NH_3)_4Cl_2]Cl.H_2O$	- 0.51 ± 0.01	0.58 ± 0.01	0.15 ± 0.01	(d)
$[Ru^{III}(NH_3)_4Cl_2]JCl_2$	- 0.56 ± 0.02	0.57 ± 0.02	0.17 ± 0.02	(d)
$K_2[Ru^{III}Cl_5H_2O]$	- 0.71 ± 0.02	0.32 ± 0.02	0.17 ± 0.03	(e)
$K_3[Ru^{III}F_6]$	- 0.84 ± 0.01	-	0.24 ± 0.01	(f)
$[Ru^{II}(NH_3)_6]Cl_2$	- 0.92 ± 0.01	-	0.13 ± 0.01	(b)
$[Ru^{II}(NH_3)_6]J_2$	- 0.93 ± 0.03	-	0.13 ± 0.04	(b)
$[Ru^{II}(NH_3)_6](BF_4)_2$	- 0.92 ± 0.01	-	0.14 ± 0.01	(b)
$[Ru^{II}(NH_3)_5N_2]Br_2$	- 0.80 ± 0.02	0.26 ± 0.02	0.14 ± 0.02	(g)
$[Ru^{II}(NH_3)_5N_2]J_2$	- 0.82 ± 0.02	0.25 ± 0.03	0.10 ± 0.02	(g)
$[Ru^{II}(NH_3)_5NO]Cl_3.H_2O$	- 0.19 ± 0.01	0.39 ± 0.01	0.14 ± 0.01	(h)
$[Ru^{II}(NH_3)_5NO]Br_3.H_2O$	- 0.22 ± 0.02	0.37 ± 0.02	0.14 ± 0.02	(h)
$[Ru^{II}(NH_3)_5NO]SO_4(S_2O_8)_{1/2}$	- 0.20 ± 0.01	0.38 ± 0.01	0.13 ± 0.01	(h)
$[Ru^{II}(NH_3)_4 \begin{smallmatrix} Cl \\ SO_2 \end{smallmatrix}]Cl$	- 0.50 ± 0.01	0.56 ± 0.01	0.15 ± 0.02	(d)
$[Ru^{II}(NH_3)_4 \begin{smallmatrix} NO \\ OH \end{smallmatrix}]Cl_2$	- 0.16 ± 0.02	0.25 ± 0.02	0.14 ± 0.02	(h)
$[Ru^{II}(NH_3)_4 \begin{smallmatrix} NO \\ OH \end{smallmatrix}]Br_2$	- 0.15 ± 0.03	0.28 ± 0.03	0.15 ± 0.03	(h)
$K_2[Ru^{II}Cl_5NO]$	- 0.36 ± 0.03	0.18 ± 0.02	0.14 ± 0.03	(i)
$K_4[Ru^{II}(CN)_5NO_2]$	- 0.34 ± 0.02	0.20 ± 0.02	0.15 ± 0.02	(k)
$K_2[Ru^{II}(CN)_5NO].2H_2O$	- 0.08 ± 0.01	0.39 ± 0.01	0.18 ± 0.01	(l)
$[Ru^{II}(NH_3)_4(pyr)_2]J_2$	- 0.71 ± 0.06	0.46 ± 0.06	0.20 ± 0.1	(g)

References given in the Table:

(a) Holloway, J. H., Peacock, R. D., Small, R. W. H.: J. Chem. Soc., 644 (1964). The sample was kindly provided by Prof. Peacock, Department of Chemistry - The University, Leicester, England.

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* * *

Figure Captions:

Fig. 1 - Relative transmission $N(v)/N(\infty)$ of the 90 keV γ-rays of ^{99}Ru through absorbers of various ruthenium compounds versus the Doppler velocity v. Both the absorbers and the source of ^{99}Rh in Ru were cooled to 4.2 K. The small peak near v = 0 mm/s in the K_3RuF_6 spectrum is probably due to impurities.

Fig. 2 - Plot of the present and some previous [1] ruthenium isomer shift data. The data from ref. [1] are marked with an asterisk.

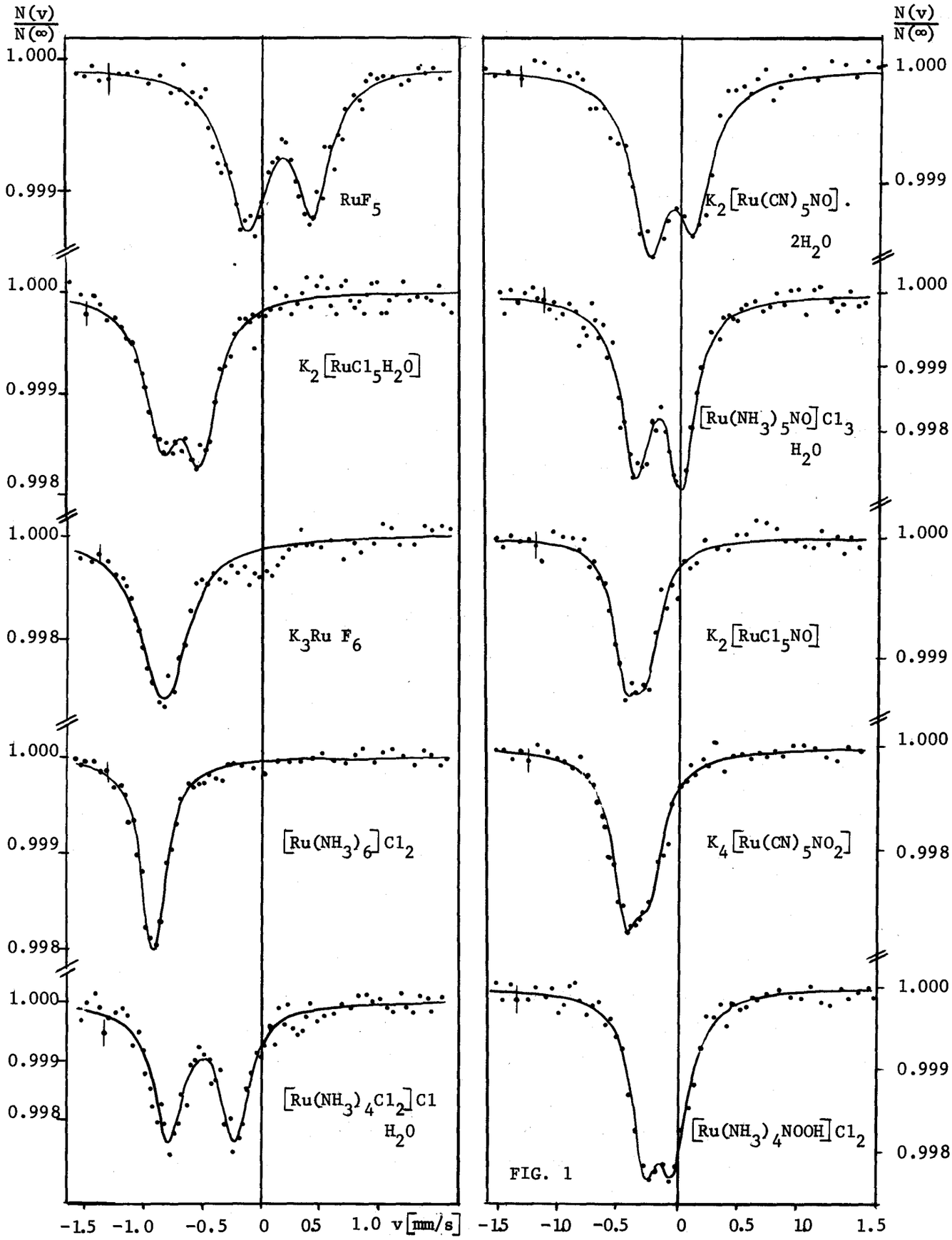
N(v)/N(∞)
1.000
0.999
0.998
RuF5
K2[RuCl5H2O]
K3Ru F6
[Ru(NH3)6]Cl2
[Ru(NH3)4Cl2]Cl H2O
K2[Ru(CN)5NO]. 2H2O
[Ru(NH3)5NO]Cl3 H2O
K2[RuCl5NO]
K4[Ru(CN)5NO2]
[Ru(NH3)4NOOH]Cl2
-1.5 -1.0 -0.5 0 0.5 1.0 v[mm/s]
-1.5 -1.0 -0.5 0 0.5 1.0 1.5

FIG. 1

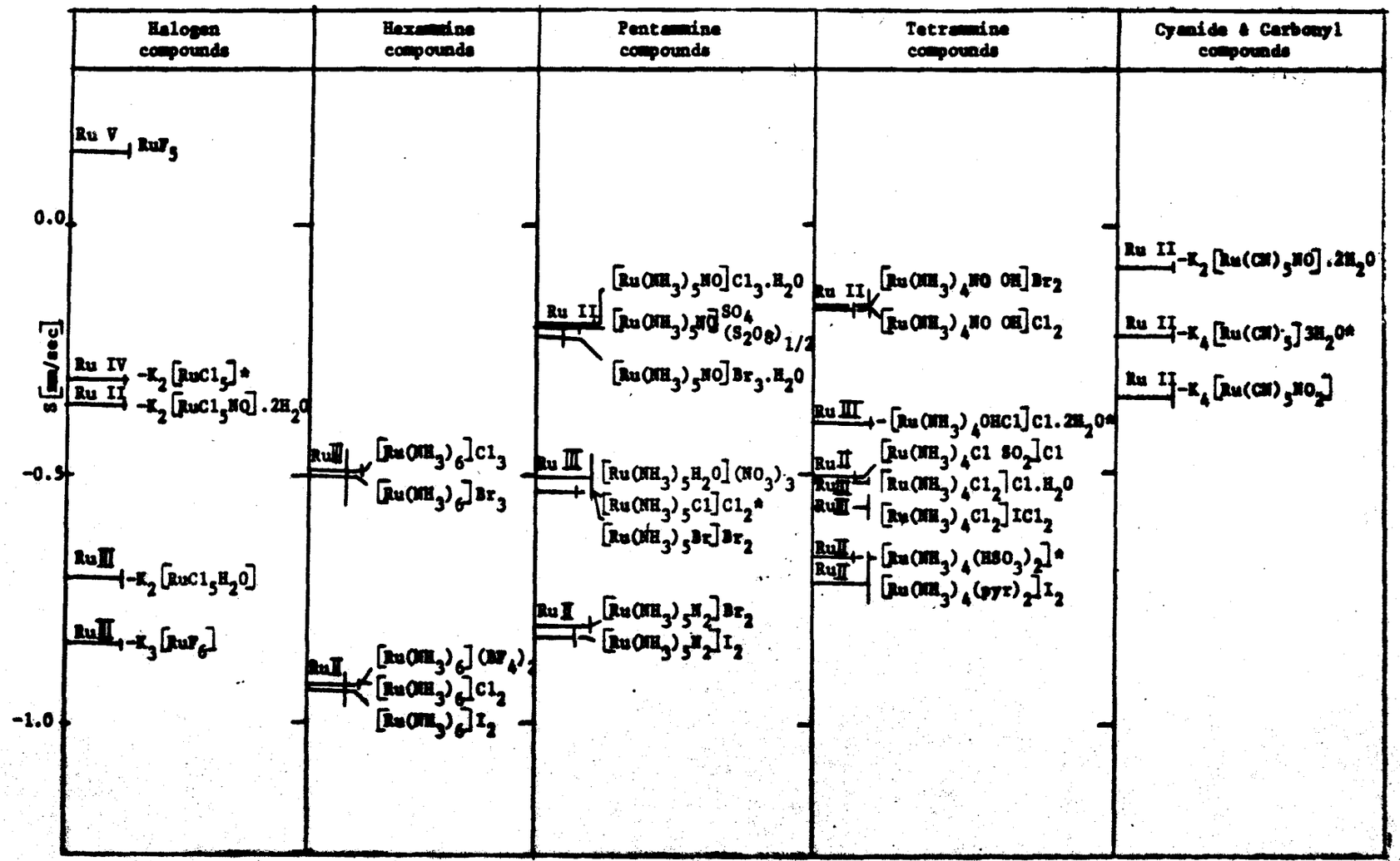
Halogen compounds
Hexammine compounds
Pentammine compounds
Tetrammine compounds
Cyanide & Carbonyl compounds
s [mv/sec]
0.0
-0.5
-1.0
Ru V
RuF_5
Ru IV
$-K_2[RuCl_5]$*
Ru II
$-K_2[RuCl_5NO].2H_2O$
RuIII
$-K_2[RuCl_5H_2O]$
RuIII
$-K_3[RuF_6]$
RuIII
$[Ru(NH_3)_6]Cl_3$
$[Ru(NH_3)_6]Br_3$
RuII
$[Ru(NH_3)_6](BF_4)_2$
$[Ru(NH_3)_6]Cl_2$
$[Ru(NH_3)_6]I_2$
Ru II
$[Ru(NH_3)_5NO]Cl_3.H_2O$
$[Ru(NH_3)_5NO]^{SO_4}_{(S_2O_8)_{1/2}}$
$[Ru(NH_3)_5NO]Br_3.H_2O$
Ru III
$[Ru(NH_3)_5H_2O](NO_3)_3$
$[Ru(NH_3)_5Cl]Cl_2$*
$[Ru(NH_3)_5Br]Br_2$
Ru II
$[Ru(NH_3)_5N_2]Br_2$
$[Ru(NH_3)_5N_2]I_2$
Ru II
$[Ru(NH_3)_4NO\ OH]Br_2$
$[Ru(NH_3)_4NO\ OH]Cl_2$
RuIII
$-[Ru(NH_3)_4OHCl]Cl.2H_2O$*
RuII
$[Ru(NH_3)_4Cl\ SO_2]Cl$
RuIII
$[Ru(NH_3)_4Cl_2]Cl.H_2O$
RuIII
$[Ru(NH_3)_4Cl_2]ICl_2$
RuII
$[Ru(NH_3)_4(HSO_3)_2]$*
RuII
$[Ru(NH_3)_4(pyr)_2]I_2$
Ru II
$-K_2[Ru(CN)_5NO].2H_2O$
Ru II
$-K_4[Ru(CN)_5]3H_2O$*
Ru II
$-K_4[Ru(CN)_5NO_2]$

FIG. 2

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