Contribution from the Laboratory of Chemical and Biological Dynamics,
Katholieke Universiteit Leuven, Leuven, Belgium

Formation and Properties of a Stable Heterobinuclear Complex Containing Ruthenium and Vanadium

HUMBERT DE SMEDT, ANDRE PERSOONS,* and LEO DE MAEYER

Received March 2, 1973

The reaction of $Ru(NH_3)_5H_2O^{2+}$ or $Ru(NH_3)_6{}^{2+}$ with VO^{2+} yields a stable, dark green binuclear complex. This complex is also obtained from the reaction of $Ru(NH_3)_5Cl^{2+}$ with $V(H_2O)_6{}^{3+}$. Analytical data are reported indicating that the structure of the complex is $[(NH_3)_5RuOV(H_2O)_n]^{4+}$. Uv, ir, and esr spectra are also presented. Results of a thorough kinetic investigation of different reactions leading to the formation of the complex are reported and discussed. In the reactions of VO^{2+} with $Ru(NH_3)_5H_2O^{2+}$ the vanadyl acts as a ligand replacing the H_2O molecule in the inner coordination sphere of Ru(II). The reaction of VO^{2+} with $Ru(NH_3)_6{}^{2+}$ involves $Ru(NH_3)_5H_2O^{2+}$ formed in a rate-determining acid-catalyzed hydrolysis of the hexaammine. It is shown that the reaction between $Ru(NH_3)_5Cl^{2+}$ and $V(H_2O)_6{}^{3+}$ ultimately results in the formation of the complex ion *via* $Ru(NH_3)_5H_2O^{2+}$ and VO^{2+}, formed in a preceding redox electron-transfer process in which VO^+ (or $V(OH)_2{}^+$) is the reducing species. The bonding in $(NH_3)_5RuOV(H_2O)_n{}^{4+}$ is discussed in relation to other complexes of Ru(II), and similarities to the bonding of molecular nitrogen in $Ru(NH_3)_5N_2{}^{2+}$ are pointed out.

Introduction

Research on nitrogen activation has been promoted considerably by the recent discovery of several complexes containing molecular nitrogen as a ligand.[1] The mechanism and conditions for the transfer of electrons from a metal ion to nitrogen is recognized as a fundamental problem in nitrogen activation. We therefore undertook an extensive study of the oxidation-reduction chemistry of the aquopentaammineruthenium(II) which is known to react spontaneously with molecular nitrogen. In an attempt to oxidize $Ru(NH_3)_5H_2O^{2+}$ with vanadyl we obtained a stable binuclear complex of ruthenium and vanadium with oxygen as a bridging ligand instead of the expected ruthenium(III) complex. Homobinuclear complexes are known or proposed in the hydrolysis of tervalent aquo ions such as Cr(III), Fe(III), and V(III).[2] Much rarer, however, are heterobinuclear complexes; they are sometimes postulated as kinetic intermediates, *e.g.*, in the reactions of Cr(II) with U(VI),[3] Np(VI),[4] V(III),[5] and VO^{2+}.[6] In some instances heterobinuclear complexes have been isolated, but they dissociate readily. In contrast, aquovanadylpentaammineruthenium(II) is very stable in solution; it is not a kinetic intermediate and it has been isolated in crystalline form. The kinetics of formation of this complex as well as its relevant physical and chemical properties are presented here.

Experimental Section

Reagents and Analyses. Ruthenium complexes were prepared according to procedures given by Taube.[7] $Ru(NH_3)_6Cl_3$ (Johnson-Matthey and Co. Ltd., London) was recrystallized twice from hot 0.1 *M* HCl. $[Ru(NH_3)_5Cl]Cl_2$ was prepared as described by Gleu and Rehm.[8] Solutions of Ru(II) were prepared either by electrolytic reduction or by treatment of the corresponding Ru(III) solutions with amalgamated Zn. Total Ru content was determined by taking an aliquot, making it basic (0.2-0.4 *M* NaOH), oxidizing with peroxodisulfate, and measuring the absorption at 415 nm (isosbestic point), using an extinction coefficient of 1045 M^{-1} cm^{-1}.[9] The proportion of Ru(II) in the solution was measured by adding an aliquot to a deaerated Fe(III) solution and determining the Fe(II) as the *o*-phenanthroline complex.[10]

Stock $VOCl_2$ solutions were prepared from $VOSO_4$ and $BaCl_2$ (Merck, AR). The VO^{2+} content of the stock solutions was determined by adding an excess of EDTA, and, after raising the pH to 10 with NH_3-NH_4Cl buffer and adding ascorbic acid to avoid oxidation of vanadyl, the remaining EDTA was titrated with Mg^{2+} to an end point indicated by Eriochrome Black T.[11]

Hydrogen ion concentrations were calculated from pH values measured with a Radiometer PHM 26 pH meter calibrated with HCl solutions of known concentration at the temperature and ionic strength used in the corresponding experiments. All manipulations with air-sensitive compounds were carried out in an argon atmosphere using well-known standard techniques.[12] For the manipulation of solid compounds a glove box ("Dri-lab," Vacuum/Atmospheres Corp.) filled with dry argon was occasionally used.

Water for making the solutions was distilled twice, the second time from alkaline permanganate, and deaerated with argon. Traces of oxygen present in the argon were removed by passing the argon through scrubbing towers containing Cr(II) derived from a Cr(III) solution by reducing with amalgamated Zn.

Kinetic Studies. Spectrophotometric monitoring of reaction progress was used. The absorbance changes at 378 nm (absorption maximum of the binuclear complex) were measured with a Pye Unicam SP 800 B spectrophotometer equipped with a thermostated cell holder. A typical experiment involved filling the two compartments of a specially designed split cell with syringes, thermostating, and finally mixing the reagent solutions by shaking the cell. For slow reactions, samples were withdrawn from a thermostated reaction vessel and the absorbance was measured with a Zeiss Elko II photometer.

Instrumentation. Infrared spectra from crystalline complexes in a KBr disk were recorded on a Perkin-Elmer 521 grating spectrophotometer. Ultraviolet and visible spectra were obtained with the Pye Unicam SP 800 B or a Cary 14 spectrophotometer.

Esr spectra were run on an esr spectrometer developed and constructed by Dr. Witters in the Department of Physics, Katholieke Universiteit Leuven.

A Wenking potentiostat (G. Bank, Gottingen) was used for electrolytic preparations.

Results

Complex Formation and Spectral Data. The reaction of VO^{2+} with $Ru(NH_3)_5H_2O^{2+}$ proceeds to the formation of a green binuclear complex, $(NH_3)_5RuOV(H_2O)_n{}^{4+}$ (hereafter

---

* To whom correspondence should be addressed at the Laboratory of Chemical and Biological Dynamics, Institut Natuurkunde, B-3030 Heverlee, Belgium.

(1) A. D. Allen and C. W. Senoff, *Chem. Commun.*, 24, 621 (1965); A. D. Allen, F. Bottomley, R. O. Harris, U. P. Reinsalu, and C. W. Senoff, *J. Amer. Chem. Soc.*, 89, 5595 (1967).

(2) T. W. Newton and F. B. Baker, *Inorg. Chem.*, 3, 569 (1964).

(3) T. W. Newton and F. B. Baker, *Inorg. Chem.*, 1, 368 (1962).

(4) J. C. Sullivan, *Inorg. Chem.*, 3, 315 (1964).

(5) J. H. Espenson, *Inorg. Chem.*, 4, 1025 (1965).

(6) J. H. Espenson, *Inorg. Chem.*, 4, 1533 (1965).

(7) T. J. Meyer and H. Taube, *Inorg. Chem.*, 7, 2369 (1968).

(8) K. Gleu and K. Rehm, *Z. Anorg. Allg. Chem.*, 227, 237 (1936); K. Gleu, W. Breuel, and K. Rehm, *ibid.*, 235, 201 (1938).

(9) J. L. Woodhead and J. H. Fletcher, *J. Chem. Soc.*, 5039 (1961).

(10) A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis—Theory and Practice," 2nd ed, Longmans, Green and Co., London, 1951, pp 646-647; W. B. Fortune and M. G. Mellor, *Ind. Eng. Chem., Anal. Ed.*, 10, 60 (1938).

(11) K. Kustin and R. Pizer, *Inorg. Chem.*, 9, 1536 (1970).

(12) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

denoted $RuOV^{4+}$) which is characterized by a strong absorption maximum at 378 nm ($\epsilon \simeq 13{,}000\ M^{-1}\ cm^{-1}$) and a somewhat weaker absorption at 625 nm ($\epsilon \simeq 2000\ M^{-1}\ cm^{-1}$) (Figure 1). $RuOV^{4+}$ may also be formed from $Ru(NH_3)_5H_2O^{3+}$ and $V(H_2O)_6{}^{3+}$; the complex therefore is not a kinetic intermediate in the redox reaction between Ru(II) and vanadyl. The binuclear complex is also obtained starting from $Ru(NH_3)_6{}^{2+}$, presumably after hydrolysis of the hexaammine.

The stability of $RuOV^{4+}$ toward dissociation is very high. An ultraviolet absorption spectrum of a 10^{-4} M solution of $RuOV^{4+}$ saturated with nitrogen shows no absorption due to $Ru(NH_3)_5N_2{}^{2+}$. A lower bound for the stability constant of $RuOV^{4+}$ of the order of 10^7 M is calculated, assuming that the ruthenium(II)-nitrogen complex may be detected at a concentration as low as 10^{-5} M(ϵ_{221} 16,500 M^{-1} cm^{-1})[13] and using the known solubility of nitrogen in water (6.2×10^{-4} M at 25°)[14] and the stability constant of $Ru(NH_3)_5N_2{}^{2+}$ ($K = 3 \times 10^4$ M).[15] We succeeded also in isolating the binuclear complex as small dark green crystals. For that purpose equimolar solutions of $VOSO_4$ and $Ru(NH_3)_5H_2O^{2+}$ were mixed, and after reaction had gone to completion (0.5 hr), the solution was concentrated by vacuum evaporation. A small deposit of $Ru(NH_3)_5Cl_3$ was filtered off. The filtrate was diluted with ethanol, and a green crystalline precipitate formed. The very fine crystals were recrystallized from a 1:1 mixture of ethanol and water and dried in an argon atmosphere. All manipulations were carried out under rigorous exclusion of air. In this preparation the pH of all solutions was always maintained below 3 to avoid hydrolysis.

The products formed on oxidation of $RuOV^{4+}$ are vanadyl and, depending on pH, $Ru(NH_3)_5OH^{2+}$ (pH >4) or $Ru(NH_3)_5H_2O^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ (pH <4). These oxidations were used to determine the stoichiometric composition of the complex. For this purpose, a small quantity of the crystalline complex was dissolved in water and oxidized by air or oxygen. The course of a typical reaction is illustrated in Figure 2, where the oxidation was carried out at pH 5. The characteristic absorption of $RuOV^{4+}$ at 378 nm disappears concomitant with the formation of a broad absorption band at 295 nm due to $Ru(NH_3)_5OH^{2+}$. On lowering the pH of the oxidized solution the absorption at 295 nm immediately disappears and peaks appear at 268 nm ($Ru(NH_3)_5H_2O^{3+}$) and at 328 nm ($Ru(NH_3)_5Cl^{2+}$). The aquo complex slowly converts to the chloro complex with an isosbestic point at 288 nm.[16] The ruthenium content of the complex was determined from the absorbance of an oxidized solution at 328 nm after all the Ru(III) had been converted to $Ru(NH_3)_5Cl^{2+}$ (ϵ 1930 M^{-1} cm^{-1} [17]) by excess chloride; a small absorption by VO^{2+} was taken into account. The vanadium content of the complex was determined from absorbance measurements at 750 nm (ϵ 17 M^{-1} cm^{-1} [18]). The 1:1 ratio of ruthenium to vanadium in the complex is clearly shown from an analysis of the crystalline complex for which we tentatively assume the composition $[Ru(NH_3)_5OV(H_2O)_4SO_4]SO_4$ because crystals only form in the presence of sulfate anions. *Anal.* Calcd for $[Ru(NH_3)_5OV(H_2O)_4SO_4]SO_4$ (mol wt 517): Ru, 19.56; V, 9.86. Found: Ru, 19.8; V, 9.75.

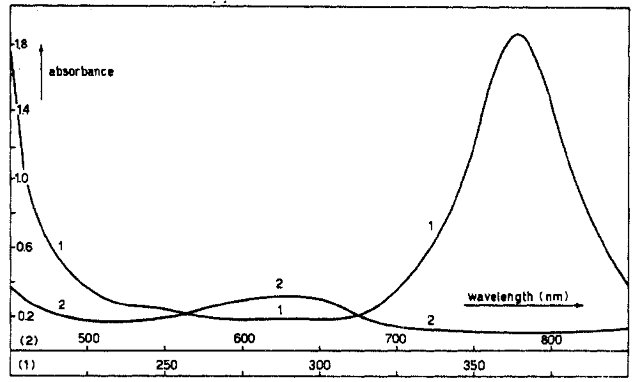


Figure 1. Absorption spectrum of 1.4×10^{-4} M $RuOV^{4+}$ (10-mm cells) in 0.1 M HCl: 1, lower wavelength scale; 2, upper wavelength scale.

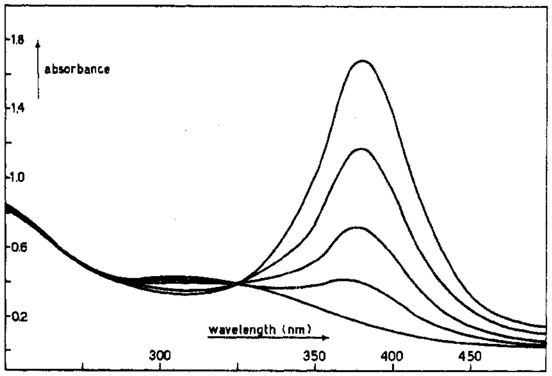


Figure 2. Oxidation of $RuOV^{4+}$ by air at pH 5. The absorption of the complex (379 nm) disappears with the simultaneous formation of the absorption band of $Ru(NH_3)_5OH^{2+}$ at 295 nm.

The proposed structure of $RuOV^{4+}$ is further supported by the infrared spectrum presented in Figure 3. The proposed assignment of the different spectral regions is given in Table I. The characteristic infrared absorptions of ammonia coordinated to ruthenium, as in $[Ru(NH_3)_5Cl]Cl_2$,[19] are clearly seen. The absorption found at 975 cm^{-1} is ascribed to the V=O stretching frequency which is displaced 30 cm^{-1} to a lower wave number as compared with vanadyl.[20] This lowering of the stretching frequency may be correlated with a decrease of the V–O multiple bond character, analogous to the case of dinitrogen or organonitriles coordinated to Ru(II).[1,21]

Formally, the complex may still be written as $Ru^{II}OV^{IV}$ or as $Ru^{III}OV^{III}$. This is properly a question of the localization of the unpaired electron. We attempted to obtain an answer from a measurement of the esr spectrum taken from a crystalline powder at room temperature. A strong resonance absorption was detected with a maximum corresponding to a g value of 1.98, this being very close to the g value of vanadyl sulfate, $g = 1.99$.[22] The line width for $RuOV^{4+}$, however, is 300 G as compared with the value of 150 G for vanadyl sulfate. To obtain a conclusive answer to this

[13] I. J. Itzkovitch and J. A. Page, *Can. J. Chem.*, 46, 2743 (1968).

[14] "Solubilities of Inorganic and Organic Compounds," Vol. 1, H. Stephen and T. Stephen, Ed., Part 1, Pergamon Press, New York, N. Y., 1963, p 85.

[15] J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, 92, 6170 (1970).

[16] J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 3, 827 (1964).

[17] H. Hartmann and C. Buschbeck, *Z. Phys. Chem.* (*Frankfurt am Main*), 8, 120 (1957).

[18] S. C. Furman and C. S. Garner, *J. Amer. Chem. Soc.*, 72, 1785 (1950).

[19] M. B. Fairey and R. J. Erving, *Spectrochim. Acta*, 22, 359 (1966).

[20] J. C. Evans, *Inorg. Chem.*, 2, 372 (1963).

[21] P. C. Ford and R. E. Clarke, *Chem. Commun.*, 1109 (1968); R. E. Clarke and P. C. Ford, *Inorg. Chem.*, 9, 227 (1970).

[22] N. B. Palma-Vittorelli, M. V. Palma, and D. Palumbo, *Nuovo Cimento*, 3, 718 (1956).

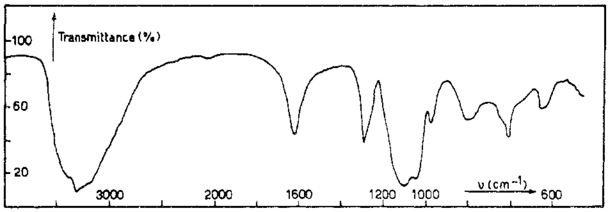


Figure 3. Infrared spectrum of $(RuOV)(SO_4)_2$ in a KBr disk (1 mg of complex in 200 mg of KBr).

Table I. Infrared Spectral Regions

Freq, cm^{-1}	Assignment
3500-3100	N-H str and O-H str—not resolved
1630	NH_3 degen def
1300	NH_3 sym def
1170	SO_4^{2-} complexed
1120-1100	SO_4^{2-} free and complexed
1045	SO_4^{2-} complexed
975	V=O str
800	NH_3 rotation
800-600	H_2O absorption
620	SO_4^{2-} free and complexed
450	Ru-N str

problem it will be necessary to study the hyperfine structure of esr spectra taken on matrix-isolated molecules.

Kinetics. 1. $RuOV^{4+}$ is formed from VO^{2+} and $Ru(NH_3)_5H_2O^{2+}$ according to a second-order rate law

$$d[RuOV^{4+}]/dt = k_2[Ru(NH_3)_5H_2O^{2+}][VO^{2+}]$$

with k_2 independent of $[H^+]$ when pH <3. Reactions were always carried out under pseudo-first-order conditions, by using vanadyl in large excess. The data in Table II include the observed first-order rate constants (to 90% conversion) and the second-order rate constants obtained as the slope of $k_{1,\text{obsd}}$ *vs.* $[VO^{2+}]$. First-order kinetics in VO^{2+} are apparent from Figure 4, where the large influence of ionic strength may also be noted, as expected for a reaction between two positively charged ions.

From the data in Table II, the activation parameters were obtained. Calculations yield $\Delta H^{\ddagger} = 14 \pm 2$ kcal mol^{-1} ($I = 0.11\ M$), $\Delta H^{\ddagger} = 13.5 \pm 0.5$ kcal mol^{-1} ($I = 1\ M$), $\Delta S^{\ddagger} = -16.7 \pm 5.0$ cal mol^{-1} deg^{-1} ($I = 0.11\ M$), and $\Delta S^{\ddagger} = -16.3 \pm 2.0$ cal mol^{-1} deg^{-1} ($I = 1\ M$). At 25° and an ionic strength of 1 *M*, the value of k_2 is $(2.47 \pm 0.04) \times 10^{-1}\ M^{-1}\ sec^{-1}$; at ionic strength of 0.11 *M* k_2 is $(8.9 \pm 0.1) \times 10^{-2}\ M^{-1}\ sec^{-1}$.

2. The $RuOV^{4+}$ complex is formed also in the reaction between $Ru(NH_3)_6^{2+}$ and VO^{2+}. In contrast to the previous reaction, the rate is linearly dependent on $[H^+]$, as shown in Figure 5, and independent of $[VO^{2+}]$

$$d[RuOV^{4+}]/dt = k_2[Ru(NH_3)_6^{2+}][H^+]$$

Rate data for this reaction are collected in Table III. The mean value of k_2 is $(2.12 \pm 0.1) \times 10^{-3}\ M^{-1}\ sec^{-1}$.

Table II. Rate Data for the Formation of $RuOV^{4+}$ from $Ru(NH_3)_5H_2O^{2+}$ and VO^{2+}[a]

Temp, °C	*I*(chloride), *M*	$10^2 \times [VO^{2+}]$, *M*	$10^4 \times k_{1,\text{obsd}}$, sec^{-1}	$10^2 k_2$, M^{-1} sec^{-1}
6	1.00	0.31	1.6	5.2 ± 0.2
6	1.00	2.03	10.6	
11	1.00	0.27	2.1	
11	1.00	0.51	4.3	8.1 ± 0.3
11	1.00	2.00	16.1	
20	0.11	0.24	1.5	
20	0.11	0.41	2.8	6.5 ± 0.5
20	0.11	2.35	14.8	
20	1.00	0.26	4.5	17.1 ± 0.3
20	1.00	1.97	33.1	
25	0.11	0.21	4.9	
25	0.11	0.62	5.5	8.9 ± 0.1
25	0.11	1.15	10.3	
25	0.11	2.39	21.8	
25	1.00	0.31	7.7[b]	24.7 ± 0.4
25	1.00	0.57	13.7[c]	
25	1.00	2.13	52.4	
30	0.11	0.31	4.4	
30	0.11	1.22	18.7	14.2 ± 1.0
30	0.11	2.37	31.0	
30	1.00	0.32	11.6[b]	
30	1.00	1.16	41.3	35.8 ± 0.6
30	1.00	2.24	81.4	
35	0.11	0.41	8.4	
35	0.11	0.62	12.3	20.2 ± 0.2
35	0.11	1.23	25.0	

[a] $[Ru(NH_3)_5H_2O^{2+}]_0 = 10^{-4}\ M$. pH is 1.38 for solutions with $I = 0.11\ M$ and 1.5 for solutions with $I = 1.00\ M$ unless otherwise stated. [b] pH 2. [c] pH 0.9.

Table III. Rate Data for the Formation of $RuOV^{4+}$ from $Ru(NH_3)_6^{2+}$ and VO^{2+}[a]

$10^2 \times [H^+]$, *M*	$10^2 \times [VO^{2+}]$, *M*	$10^4 \times k_{1,\text{obsd}}$, sec^{-1}	$10^3 \times k_{1,\text{obsd}}/[H^+]$, M^{-1} sec^{-1}
3.5	0.88	0.76	2.13
8.8	0.88	1.83	2.08
10	2.5	2.05	2.05
17.6	0.88	4.04	2.29
26.2	1.74	5.52	2.11
35.2	3.52	7.47	2.12

[a] $[Ru(NH_3)_6^{2+}]_0 = 1.2 \times 10^{-4}\ M$, 25°, $I = 1\ M$ (NaCl).

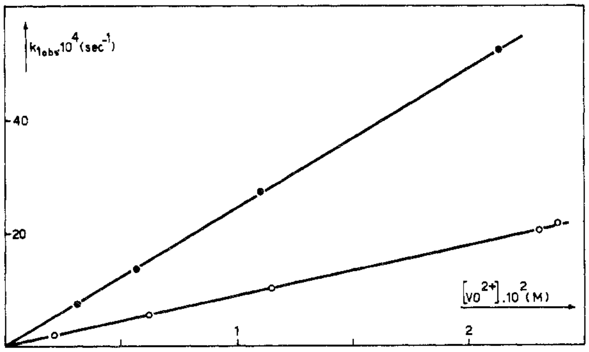


Figure 4. Dependence of vanadyl concentration of the observed pseudo-first-order rate constant for the reaction between vanadyl and $Ru(NH_3)_5H_2O^{2+}$ at 25°: ●, $I = 1\ M$ (NaCl); ○, $I = 0.11\ M$ (NaCl).

3. Kinetics of the $RuOV^{4+}$ formation from Ru(III) and V(III) were studied using $Ru(NH_3)_5Cl^{2+}$ and $V(H_2O)_6^{3+}$ in 1 *M* NaCl. We used $Ru(NH_3)_5Cl^{2+}$ and a high chloride concentration because it was observed that the water in $Ru(NH_3)_5H_2O^{3+}$ underwent a fast exchange with Cl^- in the presence of V(III). In the reaction between Ru(III) and V(III) the appearance of $RuOV^{4+}$ is characterized by an induction period which, however, can be removed by adding an excess of vanadyl to the initial reaction mixture. For the reaction between $Ru(NH_3)_5Cl^{2+}$ and $V(H_2O)_6^{3+}$ in the presence of a sufficient excess of VO^{2+} we obtained the rate law

$$d[RuOV^{4+}]/dt = k_{\text{exptl}}[Ru(NH_3)_5Cl^{2+}][V(III)]$$

where k_{exptl} is still a function of $[H^+]$, as can be seen from

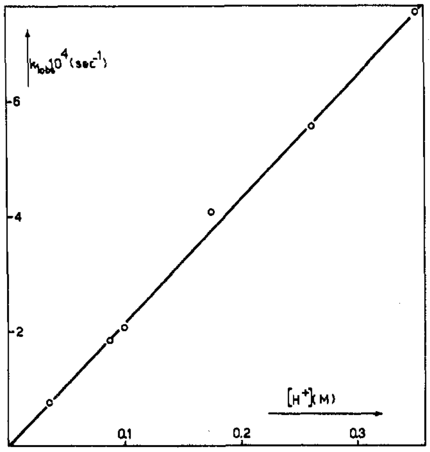


Figure 5. Dependence on $[H^+]$ of the observed first-order rate constant for the formation reaction of $RuOV^{4+}$ from $Ru(NH_3)_6{}^{2+}$ and VO^{2+} at 25° and $I = 1\ M$ (NaCl).

Figure 6. Rate data for the reaction carried out under pseudo-first-order conditions (excess of V(III) and VO^{2+}) are summarized in Table IV. Table V gives the results of rate measurements as a function of $[H^+]$. From the results in Table V k_{exptl} is seen to depend inversely on the square of $[H^+]$, at least for pH <2. At pH >2 the dependence on $[H^+]$ becomes more complex and can be written as

$$k_{\text{exptl}} = k/[H^+]([H^+] + K_1)$$

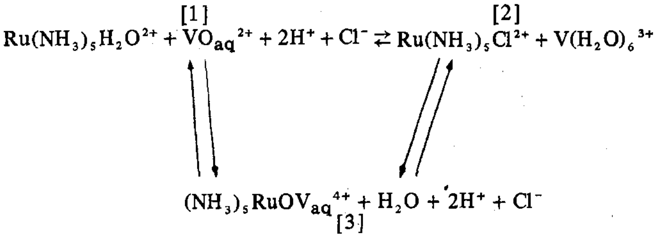
By fitting the data to this expression with different values of K_1 (Figure 7) an approximate value of $10^{-3}\ M$ for K_1 is obtained. The mean value of k is $(3.5 \pm 0.4) \times 10^{-7}\ M^{-1}$ sec^{-1}.

When the reaction between $Ru(NH_3)_5Cl^{2+}$ and V(III) is carried out in a solution saturated with nitrogen ($\simeq 6.2 \times 10^{-4}\ M$ at 25°) and without addition of vanadyl, the main product is $Ru(NH_3)_5N_2{}^{2+}$, together with a small amount of $RuOV^{4+}$. This is clearly seen from the time course of the spectral changes observed for the reaction. Concomitant with a slight increase in absorbance at 378 nm (due to $RuOV^{4+}$) an important increase in absorbance at 221 nm is noted which is characteristic for $Ru(NH_3)_5N_2{}^{2+}$.

Discussion

Kinetics. The formation of $RuOV^{4+}$ from either Ru(II) and VO^{2+} or Ru(III) and V(III) may be summarized by Scheme I. A detailed analysis of our results will show that

Scheme I



$$\underset{[1]}{Ru(NH_3)_5H_2O^{2+} + VO_{aq}{}^{2+}} + 2H^+ + Cl^- \rightleftarrows \underset{[2]}{Ru(NH_3)_5Cl^{2+} + V(H_2O)_6{}^{3+}}$$

$$\underset{[3]}{(NH_3)_5RuOV_{aq}{}^{4+}} + H_2O + 2H^+ + Cl^-$$

reactions [3] ⇄ [2] do not take place directly; instead the sequence [3] ⇄ [1] ⇄ [2] provides the faster pathway for establishing the equilibrium between [3] and [2].

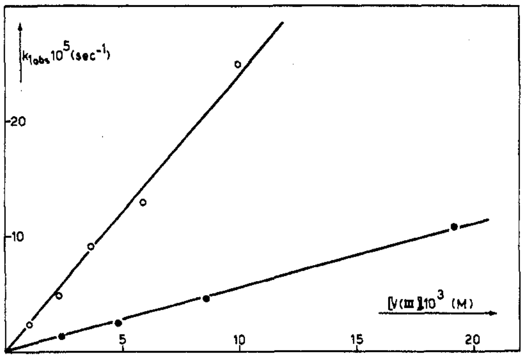


Figure 6. Dependence on the analytical V(III) concentration of the observed first-order rate constant for the reaction between Ru(III) and V(III) at two different hydrogen ion concentrations at 30° and $I = 1\ M$ (NaCl): ●, $[H^+] = 7.64 \times 10^{-3}\ M$; ○, $[H^+] = 3.62 \times 10^{-3}\ M$.

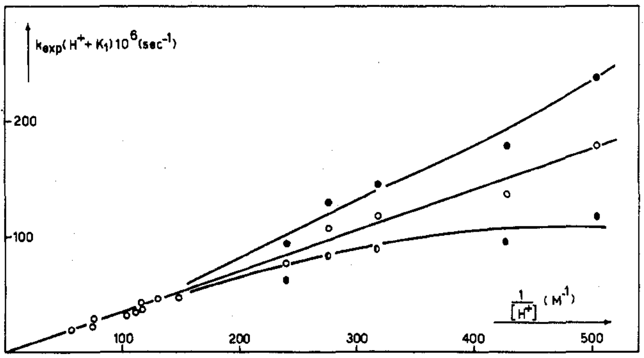


Figure 7. Dependence on hydrogen ion concentration of the second-order rate constant k_{exptl} for the reaction between Ru(III) and V(III) (see Table V) in the presence of an excess of VO^{2+} at 30° and $I = 1\ M$ (NaCl). In the figure $k_{\text{exptl}}([H^+] + K_1)$ is fitted against $[H^+]^{-1}$ for different values of K_1, with $K_1 = 1 \times 10^{-3}\ M$ giving the best fit: ●, $K_1 = 2 \times 10^{-3}\ M$; ○, $K_1 = 1 \times 10^{-3}\ M$; ◐, $K_1 = 0$.

Table IV. Rate Data for the Formation of $RuOV^{4+}$ from $Ru(NH_3)_5Cl^{2+}$ and V(III)[a]

$10^3[H^+]$, M	$10^3 \times$ [V(III)],[b] M	$10^5 \times k_{1,\text{obsd}}$, sec^{-1}	$10^3 \times k_{\text{exptl}} = 10^3 \times k'_{1,\text{obsd}}/$[V(III)], M^{-1} sec^{-1}
3.62	10.0	25.0	25.0
3.62	6.0	12.9	21.5
3.62	3.7	9.0	24.3
3.62	2.3	4.9	21.3
3.62	1.0	2.4	24.0
7.64	19.2	10.8	5.6
7.64	8.6	4.5	5.3
7.64	4.8	2.5	5.2
7.64	2.4	1.3	5.4

[a] At 30°, $I = 1\ M$ (NaCl), $[VO^{2+}]_0 = 2 \times 10^{-2}\ M$, and $[Ru(NH_3)_5Cl^{2+}]_0 = 10^{-4}\ M$. [b] [V(III)] is the total analytical concentration of V(III) irrespective of hydrolysis.

A comparison of our kinetic data for reaction [1] → [3] (rate constants and activation parameters) with other ligand substitution reactions of $Ru(NH_3)_5H_2O^{2+}$ involving N_2, N_2O, pyridine, etc.,[23] clearly shows that the second-order reaction between $Ru(NH_3)_5H_2O^{2+}$ and VO^{2+} constitutes a similar ligand-exchange process, where VO^{2+} must be considered as an incoming ligand replacing the coordinated water molecule in a substitution process with a predominant SN1 character; in accordance with this mechanism there is no influence of the H^+ concentration (1 < pH < 2). Moreover the effect of ionic strength is as expected for a reaction between two positively charged ions.

The observed kinetics of the reaction between $Ru(NH_3)_6{}^{2+}$ and VO^{2+} are in agreement with the interpretation that $Ru(NH_3)_5H_2O^{2+}$, formed in a rate-determining, preceding,

---

[23] R. J. Allen and P. C. Ford, *Inorg. Chem.*, 11, 679 (1972).

Table V. Influence of [H^+] on the Rate of Formation of $RuOV^{4+}$ from $Ru(NH_3)_5Cl^{2+}$ and V(III)[a]

$10^3[H^+]$, *M*	10^3[V(III)], *M*	10^3k_{exptl}, M^{-1} sec^{-1}
17.50	8.9	1.1
13.30	4.1	1.5
9.60	3.9	3.0
9.00	4.1	3.4
8.60	7.7	4.5
7.64	*b*	5.4
6.73	10.4	6.1
4.16	4.1	15.2
3.62	*b*	23.3
3.15	3.9	28.6
2.34	2.3	41.3
1.98	4.9	60.0

[a] At 30°, $I = 1$ *M* (NaCl), $[VO^{2+}]_0 = 2 \times 10^{-2}$ *M*, and $[Ru(NH_3)_5Cl^{2+}]_0 = 10^{-4}$ *M*. [b] See Table IV.

and acid-catalyzed NH_3 displacement, undergoes further substitution in the presence of VO^{2+} to form $RuOV^{4+}$. For this acid-catalyzed substitution of the first ammonia molecule Taube[24] reported a bimolecular rate constant of 1.24×10^{-3} M^{-1} sec^{-1}.

This rate constant was obtained at 25° in 1 *M* *p*-toluenesulfonate. According to our interpretation this rate constant should be in agreement with the value of 2.12×10^{-3} M^{-1} sec^{-1}, obtained for the rate-determining step in the $RuOV^{4+}$ complex formation from $Ru(NH_3)_6{}^{2+}$. The slightly higher rate obtained in our case at 25° in 1 *M* NaCl may be due to a medium effect. Taube also noted an enhanced rate when chloride was used, instead of *p*-toluenesulfonate, for making up the ionic strength.

The formation of the binuclear complex from Ru(III) and V(III) is a quite interesting reaction with a relatively complicated mechanism, as was already mentioned in the description of the experimental results. In principle, this reaction could be conceived as a direct ligand exchange on either of the two ions. From the rates measured, a ligand substitution on Ru(III) can be ruled out because ligand exchange on Ru(III) is a very slow process.[16] On the other hand ligand substitution in the coordination sphere of V(III) is fast[25] and one could have a direct formation of $RuOV^{4+}$ from $Ru(NH_3)_5OH^{2+}$ and $V(H_2O)_6{}^{3+}$ with OH^- as a bridging group.

The reaction conditions used (1 *M* chloride and pH <3) make the presence of $Ru(NH_3)_5OH^{2+}$ very unlikely as may be concluded from the value of the equilibrium constant for the hydrolysis of $Ru(NH_3)_5Cl^{2+}$.[16] We therefore exclude a direct formation of $RuOV^{4+}$ from Ru(III) and V(III) and favor a consecutive reaction path where $Ru(NH_3)_5H_2O^{2+}$ and VO^{2+} appear as intermediates, formed in an outer-sphere redox reaction between $Ru(NH_3)_5Cl^{2+}$ and V(III)

$$Ru(NH_3)_5Cl^{2+} + V(III) \underset{H_2O}{\overset{H^+}{\rightleftharpoons}} Ru(NH_3)_5H_2O^{2+} + Cl^- + VO^{2+}$$

$$Ru(NH_3)_5H_2O^{2+} + VO^{2+} \rightarrow RuOV^{4+} + H_2O$$

This consecutive mechanism explains the induction period observed for the appearance of $RuOV^{4+}$ and also the suppression of this induction period on adding an excess of VO^{2+}. In the presence of this excess of VO^{2+} the electron-transfer reaction between V(III) and Ru(III) becomes the rate-determining step in the formation of the complex.

The fast exchange of the aquo ligand by chloride in $Ru(NH_3)_5H_2O^{3+}$ observed in the presence of V(III) is another indication of the intervention of Ru(II) in the reaction path. Normally, ligand substitution on Ru(III) is extremely slow and one might anticipate that $Ru(NH_3)_5H_2O^{3+}$ should remain stable toward ligand exchange under the conditions used. The addition of V(III), however, to a solution of $Ru(NH_3)_5H_2O^{3+}$ induces ligand exchange, and after 20 min at room temperature the equilibrium

$$Ru(NH_3)_5H_2O^{3+} + Cl^- \rightleftharpoons Ru(NH_3)_5Cl^{2+} + H_2O$$

is completely established *via* the reactions[26]

$$Ru(NH_3)_5H_2O^{3+} + V(aq)^{3+} \rightleftharpoons Ru(NH_3)_5H_2O^{2+} + VO^{2+} + 2H^+$$

$$Ru(NH_3)_5H_2O^{2+} + Cl^- \rightleftharpoons Ru(NH_3)_5Cl^+ + H_2O$$

$$Ru(NH_3)_5Cl^+ + Ru(NH_3)_5H_2O^{3+} \rightleftharpoons Ru(NH_3)_5Cl^{2+} + Ru(NH_3)_5H_2O^{2+}$$

$Ru(NH_3)_5H_2O^{2+}$, once formed, catalyzes the conversion, and since $Ru(NH_3)_5Cl^{2+}$ is itself reduced by V(III), the equilibration of aquo and chloride ligands takes an autocatalytic course. In order to simplify the kinetic analysis as much as possible, $Ru(NH_3)_5Cl^{2+}$ was used as the source of Ru(III), since then the autocatalytic equilibration process (in the presence of chloride) during the beginning of the reaction is avoided.

Definite proof for the intervention of $Ru(NH_3)_5H_2O^{2+}$ as an intermediate comes from the observation that $Ru(NH_3)_5N_2{}^{2+}$ is formed when the reaction between Ru(III) and V(III) is carried out in solutions saturated with nitrogen and in the absence of vanadyl. The rate constants for the reactions of $Ru(NH_3)_5H_2O^{2+}$ with vanadyl ($k = 8.9 \times 10^{-2}$ M^{-1} sec^{-1} at 25° and $I = 0.11$ *M*) and nitrogen ($k = 7 \times 10^{-2}$ M^{-1} sec^{-1} at 25° and $I = 0.1$ *M*) are very similar. If there is formation of $Ru(NH_3)_5H_2O^{2+}$ we should indeed see principally the appearance of $Ru(NH_3)_5N_2{}^{2+}$ because VO^{2+}, especially in the early stages of the reaction, is present only in very low concentration and hence not able to compete with N_2 for $Ru(NH_3)_5H_2O^{2+}$. The most important spectral change for the reaction between Ru(II) and V(III) in a solution saturated with nitrogen and in absence of vanadyl should hence be an increase in absorbance at 221 nm ($Ru(NH_3)_5N_2{}^{2+}$) together with a rather slight increase at 378 nm due to small amounts of $RuOV^{4+}$. This is exactly what is observed.

With these confirmations of our hypothesis, the reaction rate obtained from the kinetic measurements of the rate of complex formation between Ru(III) and V(III) in excess vanadyl may be identified with the rate of the redox reaction [2] → [1]. When the different hydrolytic forms of V(III) in the pH range considered are taken into account, the general rate expression for this reaction may be written

$$\frac{d[RuOV^{4+}]}{dt} = -\frac{d[Ru(NH_3)_5Cl^{2+}]}{dt} = [Ru(NH_3)_5Cl^{2+}]\{k_V[V^{3+}] + k_{VOH}[VOH^{2+}] + k_{VO}[V(OH)_2^+] + k_{VOV}[VOV^{4+}]\}$$

Introducing the appropriate equilibrium expressions

$$K_1 = \frac{[H^+][V(H_2O)_5OH^{2+}]}{[V(H_2O)_6{}^{3+}]} = 1.4 \times 10^{-3}\ M^{27}$$

---

(24) P. C. Ford, J. R. Kuempel, and H. Taube, *Inorg. Chem.*, 7, 1976 (1968).

(25) R. Patel and H. Diebler, *Ber. Bunsenges. Physik. Chem.*, 76, 1035 (1972); A. M. Chmelnick and D. Fiat, *J. Magn. Resonance*, 8, 325 (1972); W. Kruse and D. Thusius, *Inorg. Chem.*, 7, 464 (1968); B. R. Baker, N. Sutin, and T. Y. Welch, *ibid.*, 6, 1948 (1967).

(26) Equilibrium conditions are fulfilled as may be derived from the redox potentials measured by H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, 11, 1460 (1972).

(27) L. Pajdowski, *Rocz. Chem.*, 37, 1351 (1963).

$$K_2 = \frac{[\mathrm{H^+}][\mathrm{V(H_2O)_4(OH)_2^+}]}{[\mathrm{V(H_2O)_5OH^{2+}}]} = 1.4 \times 10^{-4}\,M^{27}$$

$$K_\mathrm{d} = \frac{[\mathrm{H^+}]^2[\mathrm{(H_2O)_5VOV(H_2O)_5^{4+}}]}{[\mathrm{V(H_2O)_6^{3+}}]} = 10^{-4}\,M^{28}$$

the rate equation may be transformed to

$$\frac{d[\mathrm{RuOV^{4+}}]}{dt} = \left(k_\mathrm{V} + \frac{k_\mathrm{VOH}K_1}{[\mathrm{H^+}]} + \frac{K_\mathrm{VO}K_1K_2}{[\mathrm{H^+}]^2} + \frac{K_\mathrm{VOV}K_\mathrm{d}[\mathrm{V^{3+}}]}{[\mathrm{H^+}]^2}\right)[\mathrm{Ru(NH_3)_5Cl^{2+}}][\mathrm{V^{3+}}]$$

At very low pH (<1) where V(III) is present only as $\mathrm{V(H_2O)_6^{3+}}$ the reaction is exceedingly slow, indicating that we can neglect k_V compared to the other terms. In the pH range where the reaction was studied ($1.6 < \mathrm{pH} < 2.6$) V(III) is present as $\mathrm{V(H_2O)_6^{3+}}$ and $\mathrm{V(H_2O)_5OH^{2+}}$ with a negligible amount of $\mathrm{(H_2O)_5VOV(H_2O)_5^{4+}}$ and $\mathrm{V(OH)_2^+}$. The total analytic concentration of V(III) is hence equal to the sum of $[\mathrm{V^{3+}}]$ and $[\mathrm{VOH^{2+}}]$. Taking this into account, we can write in good approximation, with [V(III)] as the total concentration of all V(III) species

$$\frac{d[\mathrm{RuOV^{4+}}]}{dt} = \left(\frac{k_\mathrm{VOH}K_1}{[\mathrm{H^+}] + K_1} + \frac{k_\mathrm{VO}K_1K_2}{[\mathrm{H^+}]([\mathrm{H^+}] + K_1)} + \frac{k_\mathrm{VOV}K_\mathrm{d}[\mathrm{V(III)}]}{([\mathrm{H^+}] + K_1)^2}\right)[\mathrm{Ru(NH_3)_5Cl^{2+}}][\mathrm{V(III)}]$$

or, introducing k_exptl

$$d[\mathrm{RuOV^{4+}}]/dt = k_\mathrm{exptl}[\mathrm{Ru(NH_3)_5Cl^{2+}}][\mathrm{V(III)}]$$

As may be seen from Figure 6, k_exptl is independent of the V(III) concentration which means that, within experimental precision, the term containing k_VOV must be negligible. Hence we can put k_exptl in the form

$$k_\mathrm{exptl} = \frac{k_\mathrm{VOH}K_1}{[\mathrm{H^+}] + K_1} + \frac{k_\mathrm{VO}K_1K_2}{[\mathrm{H^+}]([\mathrm{H^+}] + K_1)}$$

From this equation it is apparent that $k_\mathrm{exptl}([\mathrm{H^+}] + K_1)$ should depend linearly on the inverse of $[\mathrm{H^+}]$; this fact is borne out in Figure 7. Since the intercept on the ordinate is zero, k_VOH may also be neglected. We finally obtain for the rate equation

$$\frac{d[\mathrm{RuOV^{4+}}]}{dt} = \frac{k_\mathrm{VO}K_1K_2}{[\mathrm{H^+}]([\mathrm{H^+}] + K_1)}[\mathrm{Ru(NH_3)_3Cl^{2+}}][\mathrm{V(III)}] = k_\mathrm{exptl}[\mathrm{Ru(NH_3)_5Cl^{2+}}][\mathrm{V(III)}]$$

A numerical value of 1×10^{-3} for K_1, the first acidity constant of $\mathrm{V(H_2O)_6^{3+}}$, was obtained from a linearization procedure for k_exptl as a function of $1/[\mathrm{H^+}]$. This value compares favorably with that given by Pajdowski,[27] who obtained the value $1.4 \times 10^{-3}\,M$ at 20°. From the product $k_\mathrm{VO}K_1K_2$ we calculate for k_VO a value of $1.75\,M^{-1}\,\mathrm{sec}^{-1}$ using Pajdowski's value of $2 \times 10^{-7}\,M^2$ for the product K_1K_2 at 30°.

From the preceding analysis it has been shown that $\mathrm{VO^+}$ (or $\mathrm{V(OH)_2^+}$, as written in its hydrated form) is the only reactive species that reduces Ru(III). This may be explained by the fact that the oxidation of $\mathrm{VO^+}$ proceeds directly to $\mathrm{VO^{2+}}$ while the oxidation of $\mathrm{V^{3+}}$ (or $\mathrm{V(OH)^{2+}}$) gives rise to energetically unfavorable forms, such as $\mathrm{V^{4+}}$ or $\mathrm{VOH^{3+}}$. Stated otherwise, we can say that the free energy of activation for the oxidation of $\mathrm{VO^+}$ to $\mathrm{VO^{2+}}$ is considerably lower than the free energy of activation for the formation of the ions $\mathrm{V^{4+}}$ and $\mathrm{VOH^{3+}}$, which are never observed, even in strong-acid media.[29]

This finding is also in agreement with current views on outer-sphere electron-transfer reactions, which are rate limited by the processes that lead to the formation of suitably stabilized solvation and coordination structures corresponding to a transition-state intermediary to the stable forms of the ionic reaction partners.

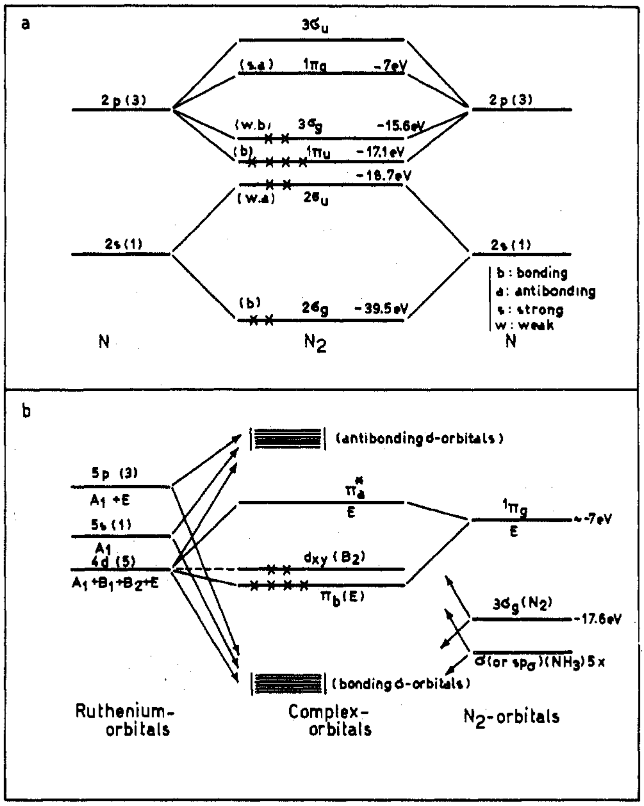


Figure 8. (a) MO scheme of the nitrogen molecule as given by Chatt.[30] (b) π back-donation in $\mathrm{Ru(NH_3)_5N_2^{2+}}$. The bonding ($\pi_\mathrm{b}$) and antibonding ($\pi_\mathrm{a}^*$) π orbitals of E symmetry are formed by overlap of the ruthenium d_{xz} and d_{yz} orbitals with the nitrogen $1\pi_\mathrm{g}$ orbitals at −7 eV. The metal d_{xy} orbital remains nonbonding.

Bonding. The formation, stability, and spectral data provide some information concerning the bonding in $\mathrm{RuOV^{4+}}$. The kinetic analysis of the formation reaction from $\mathrm{Ru(NH_3)_5H_2O^{2+}}$ and $\mathrm{VO^{2+}}$ shows $\mathrm{VO^{2+}}$ as a ligand analogous to $\mathrm{N_2}$, $\mathrm{CH_3CN}$, CO, etc., with which $\mathrm{VO^{2+}}$ has comparably weak σ-donor properties (weak Bronsted basicity) in common. All these ligands are, however, good π acceptors with orbitals favorably positioned for overlap with the d_{xz} and d_{yz} orbitals of ruthenium (π back-donation). On this basis MO schemes for $\mathrm{Ru(NH_3)_5N_2^{2+}}$ and $\mathrm{RuOV^{4+}}$ may be proposed which show some striking similarities (Figures 8 and 9). In $\mathrm{Ru(NH_3)_5N_2^{2+}}$ we have a π bonding due to the overlap of the d_{xz} and d_{yz} ruthenium orbitals (E symmetry) with the 1 π_g antibonding orbital of the nitrogen molecule (see Figure 8a as given by Chatt[30]). In Figure 8b a qualitative picture is given for the π back-donation in $\mathrm{Ru(NH_3)_5N_2^{2+}}$ where bonding (π_b) and antibonding (π_a) π orbitals are formed. The ruthenium d_{xy} orbital remains nonbonding.

---

(28) L. Pajdowski, *J. Inorg. Nucl. Chem.*, **28**, 23 (1966).

(29) J. Sellin, *Chem. Rev.*, **65**, 153 (1965), and references therein.

(30) J. Chatt, *Platinum Metals Rev.*, **13**, 9 (1969).

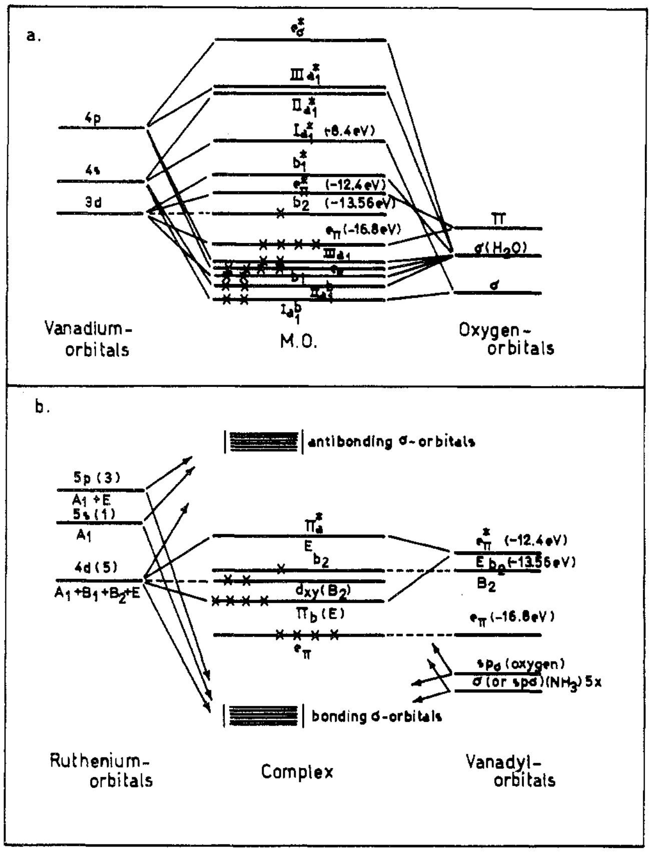


Figure 9. (a) MO scheme of the vanadyl ion as given by Ballhausen and Gray.[31] (b) π back-donation in RuOV^{4+}. The bonding (π_b) and antibonding ($\pi_a{}^*$) π orbitals of E symmetry are formed by overlap of the ruthenium d_{xz} and d_{yz} orbitals with the vanadyl $e_\pi{}^*$ orbital at −12.4 eV. Both the ruthenium d_{xy} and the vanadyl b_2 orbital remain nonbonding.

The six electrons of ruthenium occupy the π_b and d_{xy} orbitals as shown in Figure 8b. A very similar scheme can be made for the bonding in RuOV^{4+}. As shown in Figure 9a (after Ballhausen[31]) the vanadyl ion, analogous to the nitrogen molecule, has vacant antibonding orbitals with E symmetry, *e.g.*, the $e_\pi{}^*$ orbital at −12.4 eV. Since the energy of the d orbitals of ruthenium is not known, no conclusion can be reached about the relative position of the nonbonding d_{xy} orbital of ruthenium and the b_2 orbital of the vanadyl ion. In the complex RuOV^{4+} the six ruthenium electrons occupy the π_b orbital and one of the nonbonding b orbitals. The free electron of the vanadyl ion occupies the nonbonding b_2 orbital belonging to vanadium. This picture is partly supported by the esr results although a definite conclusion cannot be made from our esr measurements on powders. Therefore the relative positions of the d_{xy} orbital of ruthenium with respect to the b_2 orbital of vanadyl cannot be ascertained unequivocally. Although a state with three unpaired electrons cannot be ruled out from our esr measurements, such a state is highly improbable as may be deduced from the MO schemes (Figures 8b and 9b). A state with three unpaired electrons should indeed have an electron in the antibonding $\pi_a{}^*$ orbital which should considerably weaken the bond, contradicting the high stabilities found.

The ultraviolet and visible spectra of RuOV^{4+} resemble the spectra of all Ru(NH$_3$)$_5$L^{2+}, where L is a π-bonding ligand, in having an intense charge-transfer absorption band. In contrast, the spectra of Ru(NH$_3$)$_6{}^{2+}$ and Ru(NH$_3$)$_5$H$_2$O^{2+} are typical ligand field spectra with weak absorptions in the ultraviolet regions, presumably due to the fact that the transitions in this low-spin d^6 system are Laporte forbidden. The transitions $d_{xy}(B_2) \rightarrow \pi^*(E)$ and $\pi_b(E) \rightarrow \pi^*(E)$ (see Figures 8b and 9b) are, however, not forbidden for Ru(NH$_3$)$_5$L^{2+} complexes when L is a π-bonding ligand. The spectral data obtained for RuOV^{4+} therefore also support the proposed binding scheme.

Conclusion

The high stability of RuOV^{4+} is explained by the strong back-bonding capacity of Ru(II). The d_{xz} and d_{yz} orbitals of ruthenium have the proper energy and symmetry to overlap with low-lying vacant orbitals of E symmetry of π-acceptor molecules, *e.g.*, N$_2$ and VO^{2+}, leading to strong attractive interactions with these otherwise relatively inert species.

The stable complex ion Ru(NH$_3$)$_5$OV(H$_2$O)$_5{}^{4+}$, in which two different transition metal ions are in close interaction, seems very promising with respect to theoretical problems from the viewpoint of ligand field theory; a careful study of its optical and magnetic properties will be required. A detailed physicochemical and kinetic study of its behavior with respect to oxidation and reduction will certainly reveal further interesting properties.

Acknowledgment. Financial support from the N.F.W.O. and F. K.F.O. Belgium is gratefully acknowledged. We are much indebted to Professor G. Smets (Department of Chemistry, Katholieke Universiteit Leuven) and Professor J. Witters (Department of Physics, Katholieke Universiteit Leuven) for the use of their laboratory facilities. H. De S. is grateful to the I.W.O.N.L. Belgium for the award of a fellowship.

Registry No. VO^{2+}, 20644-97-7; Ru(NH$_3$)$_5$H$_2$O^{2+}, 21393-88-4; Ru(NH$_3$)$_5$Cl^{2+}, 21560-19-0; V(H$_2$O)$_6{}^{3+}$, 21374-21-0; Ru(NH$_3$)$_6{}^{2+}$, 19052-44-9; [Ru(NH$_3$)$_5$OV(H$_2$O)$_4$SO$_4$]SO$_4$, 42402-06-2.

---

(31) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1, 111 (1962).