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NMR Studies of the Hexaaquoruthenium(III) Ion in Aqueous Solutions

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Aqueous solutions containing the $Ru(H_2O)_6^{3+}$ ion were studied by proton NMR. The magnetic moments of this ion are in the range $\mu_{eff} = 2.02$–2.055 μ_B at temperatures between 278 and 329 K, respectively, corresponding to low-spin d^5 configuration with some orbital contribution according to Kotani's expression. From the chemical shifts of the water protons, a value of the proton hyperfine coupling constant of $A = 3.3 \pm 0.3$ MHz was calculated with the assumption of a spin–orbit coupling constant of 1200 ± 200 cm^{-1}. This value of A which is the largest found yet for a hexaaquo ion corresponds to a covalency parameter of $\lambda = 0.27$. From the water proton relaxation times, values of electron spin relaxation times of 2 and 6 ps were estimated at temperatures of 278 and 327 K, respectively.

Introduction

The concept of covalency finds an extensive use in the field of inorganic chemistry. Yet the amount of available data concerning this concept is limited. Admittedly, its quantitative definition is not unique and is dependent on the choice of the presentation of the wavefunction. Still, its usefulness justifies an effort to obtain spectroscopic results for it. One of the most direct spectroscopic methods for obtaining quantitative measures of covalency is the measurement of the electron–nuclear hyperfine interaction by EPR or by NMR. Ways of estimating covalency parameters of hexaaquo ions based on NMR results[1-3] were discussed in a previous publication.[4] It was particularly interesting to extend these studies to the hexaaquoruthenium(III) ion as a representative of the second-row transition-metal series. Properties of the hexaaquoruthenium(III) ion have not been studied extensively mainly because of its relative instability and its preparation which involves several steps, including column chromatography.[5,6] Recently its optical spectrum was analyzed and compared with other ruthenium(III) complexes[7] and its acid dissociation equilibrium constant was estimated.[7,8] The properties of the hexaaquoruthenium(III) ion as a reagent for electron-transfer reactions were also recently studied.[8] In the present work we report NMR measurements of the magnetic properties of this ion and the transferred hyperfine interaction with the water protons in its first hydration sphere as a measure of covalency.

Experimental Section

The preparation of $Ru(H_2O)_6^{3+}$ was done by a modification of the method of Kallen and Earley[6] as described previously.[7]

NMR measurements were performed with Varian HA-100 spectrometer. T_2 was calculated from the line width and T_1 was measured by the spin-echo attachment to the HA-100 spectrometer[9] with use of the Carr-Purcell inversion recovery method. All solutions contained 2% v/v dioxane as an internal reference.

The measurement of the magnetic susceptibility was done with the NMR method of Evans.[10-14] A capillary containing hexamethyldisiloxane for locking the field and some added dioxane was inserted into a 5-mm sample tube. The sample tube contained the $Ru(H_2O)_6^{3+}$ solution in 1 M CF_3SO_3H with 2% dioxane. The susceptibility measurement was done by recording the frequency separation of the two dioxane signals originating from the sample and from the capillary and comparing it to the separation obtained with the same capillary and a sample tube containing an identical solution with $Al(H_2O)_6^{3+}$ replacing $Ru(H_2O)_6^{3+}$.

Table I. Molar Susceptibilities and Effective Magnetic Moments of $Ru(H_2O)_6^{3+}$

t, °C	$\Delta\nu$,[a] Hz	$10^6\chi_M^{Ru}$,[b] cgsu	μ_{eff},[c] μ_B
5	6.7 ± 0.2	1820	2.02
29	6.3 ± 0.2	1710	2.04
56	5.8 ± 0.2	1590	2.055

[a] The frequency difference between 17.2 mM solutions of $Ru(H_2O)_6^{3+}$ and $Al(H_2O)_6^{3+}$ in 1 M CF_3SO_3H. [b] Corrected molar susceptibility of Ru(III) calculated according to eq 1. Correction of the concentration due to the thermal expansion of the solution was also introduced. [c] Calculated from the relation $\mu_{eff} = 2.84 \cdot (\chi_M T)^{1/2}$.

Results

Magnetic Suspectibility of $Ru(H_2O)_6^{3+}$. The molar susceptibilities of $Ru(H_2O)_6^{3+}$ solutions at three temperatures were estimated with the NMR method of Evans[10-14] by comparing shifts of inert compounds such as dioxane in identical solutions of Ru(III) and Al(III), as was explained in the Experimental Section. The corrected molar susceptibility of the Ru(III) ion was calculated with expression 1, where N is

$$\chi_M^{Ru}(\mathrm{cor}) = (1500/\pi N)(\Delta\nu/\nu_0) + \chi_g^{\circ}(M^{Ru} - M^{Al}) - \chi_g(d_s^{Ru} - d_s^{Al})(1000/N) - \chi_{dia}^{Ru} + \chi_{dia}^{Al} \quad (1)$$

the molar concentrations of the solutions, $\Delta\nu$ is the frequency difference between the Ru(III) and Al(III) solutions, M^{Ru} and M^{Al} are the atomic weights of Ru and Al, respectively, χ_g° is the mass susceptibility of the solvent (-0.72×10^{-6} cgsu for water), d_s^{Ru} and d_s^{Al} are the densities of the Ru(III) and Al(III) solutions, respectively, and χ_{dia}^{Ru} and χ_{dia}^{Al} are the Pascal atomic diamagnetic terms (-23×10^{-6} cgsu for Ru^{3+} and -2×10^{-6} cgsu for Al^{3+}[15]). The molar susceptibilities and the effective magnetic moments of $Ru(H_2O)_6^{3+}$ given in Table I clearly indicate a low-spin d^5 complex. Since the solution of $Ru(H_2O)_6^{3+}$ was relatively dilute, the accuracy of the results is limited. Still, the deviation from the spin-only value of 1.73 μ_B is beyond experimental error, and the results follow Kotani's expression[16] for μ_{eff} of low-spin d^5 complexes (eq 2) with a spin–orbit coupling constant $\zeta = 1400 \pm 300$

$$\mu_{eff}^2 = \frac{3X + 8 - 8\exp(-3X/2)}{X(1 + 2\exp(-3X/2))} \quad (2)$$

cm^{-1} (where $X = \zeta/kT$). This value may be compared with the value of ζ obtained for other ruthenium(III) complexes: $\zeta = 1000$ cm^{-1} for $Ru(NH_3)_6Cl_3$ and $Ru(acac)_3$[17] and $\zeta = 1330$

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(1) Luz, Z; Shulman, R. G. *J. Chem. Phys.* **1965**, *43*, 3750.
(2) Wayland, B. B.; Rice, W. L. *Inorg. Chem.* **1966**, *5*, 54.
(3) Granot, J; Achlama, A. M.; Fiat, D. *J. Chem. Phys.* **1974**, *61*, 3043.
(4) Waysbort, D.; Navon, G. *Chem. Phys.* **1978**, *28*, 83.
(5) Cady, H. H.; Connick, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 2646.
(6) Kallen, T. W.; Earley, J. E. *Inorg. Chem.* **1971**, *10*, 1149.
(7) Harzion, Z.; Navon, G. *Inorg. Chem.* **1980**, *19*, 2236.
(8) Böttcher, W.; Brown, G. M.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1447.
(9) Ginsburg, A.; Lipman, A.; Navon, G. *J. Phys. E* **1970**, *3*, 699.
(10) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
(11) Evans, D. F. *Proc. Chem. Soc.* **1958**, 115.
(12) Evans, D. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2587.
(13) Deutsch, J. L.; Poling, S. M. *J. Chem. Educ.* **1969**, *46*, 167.
(14) Löliger, J.; Scheffold, R. *J. Chem. Educ.* **1972**, *49*, 646.
(15) Mulay, L. N. "Magnetic Susceptibility"; Wiley-Interscience: New York, 1963.
(16) Kotani, M. *J. Phys. Soc. Jpn.* **1949**, *4*, 293.
(17) Figgis, B. N.; Lewis, J.; Mabbs, F. E.; Webb, G. A. *J. Chem. Soc. A* **1966**, 422.

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Table II. Molar Chemical Shifts and Relaxation Rates of Water Protons in Solutions of $Ru(H_2O)_6{}^{3+}$ [a]

t, °C	$1/NT_{1p}$, s^{-1} M^{-1}	$1/NT_{2p}$, s^{-1} M^{-1}	$\Delta\nu_p$, Hz M^{-1}
5	600 ± 30	680 ± 60	690 ± 170
17	520 ± 30		
27.5	460 ± 25		
28		570 ± 60	610 ± 70
37	410 ± 20		
52		430 ± 60	500 ± 40
54	370 ± 20		

[a] The molar concentrations of $Ru(H_2O)_6{}^{3+}$ were in the range of 0.010–0.018 M. T_1 data were taken in solutions containing 1 M CF_3SO_3H. T_2 and $\Delta\nu_p$ data were taken in similar solutions which were partially neutralized to give pH 1–2. The errors indicated include scattering of data obtained for different solutions, at different dates. However, the direction of the temperature dependence was always the same for each one of the solutions.

cm^{-1} for $K_3Ru(oxal)_3$ (oxal = oxalate).[18] With the value of ζ for the octahedral $Ru(NH_3)_6{}^{3+}$ ion taken into account and by allowing for the decrease in covalency in $Ru(H_2O)_6{}^{3+}$, the value of ζ which was adopted by us was 1200 ± 200 cm^{-1}.

Paramagnetic NMR Shifts and Relaxation Times. The results of the net proton chemical shifts and relaxation times in solutions of $Ru(H_2O)_6{}^{3+}$ in 1 M CF_3SO_3H are shown in Table II. The choice of CF_3SO_3H as the acid for our measurements was done since $HClO_4$ oxidizes the $Ru(H_2O)_6{}^{3+}$ ion into a Ru(IV) species[5] while HBF_4 solutions gave broad water lines even in the absence of ruthenium(III) ions.

NMR measurements were performed in solutions where the 1 M CF_3SO_3H was partially neutralized with $NaHCO_3$ to pH 1–2. This was done since at pH <1 the water signal is significantly shifted due to an exchange with H_3O^+. No pH dependence of the shift and the relaxation rates could be observed at this pH range. The direction of the temperature dependences of the chemical shift and the relaxation times indicates fast exchange between the protons of the $Ru(H_2O)_6{}^{3+}$ and bulk water protons. The absence of pH dependence further supports this conclusion since the exchange is expected to be either base catalyzed[19–22] or acid catalyzed.[23–25] Thus the shift and the relaxation times of the protons bound to $Ru(H_2O)_6{}^{3+}$ can be calculated with relation 3 where f, the

$$\Delta\omega_M = \Delta\omega_p/f \qquad T_{1M} = fT_{1p} \qquad T_{2M} = fT_{2p} \tag{3}$$

fraction of protons bound to the complex, is given by eq 4 and

$$f = 6N/55.6 \tag{4}$$

where N is the molar concentration of $Ru(H_2O)_6{}^{3+}$. The chemical shift of bound protons $\Delta\omega_M$ is related to the Fermi contact hyperfine interaction A for low-spin d^5 complexes[26,27] (eq 5).

$$\Delta\omega_M/\omega_0 = -\frac{Ah\beta}{18g_N\beta_N}\,\frac{3/k\mathrm{T} + 16/\zeta - (16/\zeta)\exp(-3\zeta/2kT)}{1 + 2\exp(-3\zeta/2kT)} \tag{5}$$

Table III. Parameters Obtained by Fitting T_1 and T_2 Relaxation Times to the Solomon and Bloembergen Equations

r, Å	2.35 ± 0.15	τ_s(278 K),[a] ps	6.0 ± 1.5
$\tau_c{}^{-1}$(278 K), s^{-1}	(1.9 ± 0.5) × 10^{11}	τ_s(327 K),[a] ps	2.1 ± 0.5
$\tau_c{}^{-1}$(327 K), s^{-1}	(5.5 ± 1.4) × 10^{11}		

[a] Calculated from the correlation times by assuming rotational correlation rates derived from the Stokes–Einstein expression (eq 9) with $a = 3.2 \pm 0.2$ Å are $\tau_R{}^{-1} = (2.2 \pm 0.5) \times 10^{10}$ and (7.7 ± 1.7) × 10^{10} s^{-1} at temperatures of 278 and 327 K, respectively.

On the basis of the chemical shift data given in Table II and by assuming a spin–orbit coupling constant between 1200 and 1400 cm^{-1}, the hyperfine coupling constant, A, was calculated from eq 3–5 to be between 3.3 and 3.6 MHz, respectively.

The relaxation times of the bound protons, T_{1M} and T_{2M}, are determined by dipolar and hyperfine interactions with the unpaired electrons according to Solomon and Bloembergen's equations,[28–31] eq 6–8, where τ_R is the rotational correlation,

$$T_{1M}{}^{-1} = \frac{2}{15}\,\frac{\gamma^2\beta^2\mu_{\mathrm{eff}}{}^2}{r^6}\left[\frac{3\tau_{1c}}{1 + \omega_I{}^2\tau_{1c}{}^2} + \frac{7\tau_{2c}}{1 + \omega_s{}^2\tau_{2c}{}^2}\right] + 2\pi^2A^2\frac{\tau_{2e}}{1 + \omega_s{}^2\tau_{2e}{}^2} \tag{6}$$

$$T_{2M}{}^{-1} = \frac{1}{15}\,\frac{\gamma^2\beta^2\mu_{\mathrm{eff}}{}^2}{r^6}\left[4\tau_{1c} + \frac{3\tau_{1c}}{1 + \omega_I{}^2\tau_{1c}{}^2} + \frac{13\tau_{2c}}{1 + \omega_s{}^2\tau_{2c}{}^2}\right] + \pi^2A^2\left[\tau_{1e} + \frac{\tau_{2e}}{1 + \omega_s{}^2\tau_{2e}{}^2}\right] \tag{7}$$

$$\frac{1}{\tau_{ic}} = \frac{1}{\tau_R} + \frac{1}{\tau_M} + \frac{1}{\tau_{is}} \qquad \frac{1}{\tau_{ie}} = \frac{1}{\tau_M} + \frac{1}{\tau_{is}} \qquad i = 1, 2 \tag{8}$$

τ_M is the exchange lifetime, and τ_{1s} and τ_{2s} are the longitudinal and transverse electronic relaxation times. τ_R was estimated from the Stokes–Einstein formula (eq 9). η was taken as the

$$\tau_R = 4\pi\eta a^3/3kT \tag{9}$$

viscosity of water at the various temperatures;[32] a, the molecular radius, was taken as 3.2 ± 0.2 Å based on the measured τ_R of $Mn(H_2O)_6{}^{2+}$, giving a = 3.3 Å[33] but considering a decrease of 0.07 Å due to the same decrease in the metal oxygen distance (the Ru–O distance is 2.10 and 2.11 Å in $RuCl_5H_2O^{2-}$ and $RuCl_4(H_2O)_2{}^-$, respectively,[34] as compared to 2.17 Å in $Mn(H_2O)_6{}^{2+}$[35]). In eq 8, $\tau_M{}^{-1}$ can be neglected since considerations based on the acid dissociation constant pK_a = 2.4 ± 0.2 of $Ru(H_2O)_6{}^{3+}$[7] and diffusion-controlled limit for k_{-1} in eq 10 give an upper limit of $\tau_M{}^{-1} = k_1 \leq 10^8$, which is

$$Ru(H_2O)_6{}^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(H_2O)_5OH^{2+} + H^+ \tag{10}$$

smaller by several orders of magnitude than $\tau_S{}^{-1}$ (of about 10^{11}). Assuming that $\tau_{1s}{}^{-1} = \tau_{2s}{}^{-1} = \tau_0{}^{-1}e^{-V/RT}$, we have fitted the results of T_{1M} and T_{2M} at the various temperatures to eq

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(18) Olliff, R. W.; Odell, A. L. *J. Chem. Soc.* **1964**, 2467.
(19) Pearson, R. G.; Palmer, J.; Anderson, M. M.; Alfred, A. L. *Z. Elektrochem.* **1960**, *64*, 110.
(20) Palmer, J. W.; Basolo, F. *J. Inorg. Nucl. Chem.* **1960**, *15*, 279.
(21) Waysbort, D.; Navon, G. *J. Phys. Chem.* **1973**, *77*, 960.
(22) Meyer, T. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 2369.
(23) Swift, T. J.; Stephenson, T. A.; Stein, G. R. *J. Am. Chem. Soc.* **1967**, *89*, 1611.
(24) Swift, T. J.; Stephenson, T. A. *Inorg. Chem.* **1966**, *5*, 1100.
(25) Hausser, R.; Laukien, G. *Z. Physik* **1959**, *153*, 394.
(26) Golding, R. M. *Mol. Phys.* **1965**, *8*, 561.
(27) Kurland, R. J.; McGarvey, B. R. *J. Magn. Reson.* **1970**, *2*, 286.
(28) Solomon, I.; Bloembergen, N. *J. Chem. Phys.* **1956**, *25*, 261.
(29) Bloembergen, N. *J. Chem. Phys.* **1957**, *27*, 572, 595.
(30) Rubinstein, M.; Baram, A.; Luz, Z. *Mol. Phys.* **1971**, *20*, 67.
(31) Reuben, J.; Reed, G. H.; Cohn, M. *J. Chem. Phys.* **1970**, *52*, 1617.
(32) "Handbook of Chemistry and Physics"; Chemical Rubber Co.: Cleveland, OH, 1971.
(33) Gradstajn, S.; Navon, G., to be submitted for publication.
(34) Hopkins, T. E.; Zalkin, A.; Templeton, D. H.; Adamson, M. G. *Inorg. Chem.* **1966**, *5*, 1427, 1431.
(35) Waysbort, D.; Navon, G. *J. Chem. Phys.* **1978**, *68*, 3074.

6 and 7. The results are summarized in Table III. The errors given in the table include the experimental random errors in T_1 and T_2 (see Table II) as well as the errors in τ_R calculated from eq 9 with $a = 3.2 \pm 0.2$ Å and in μ_{eff} and A calculated from eq 2 and 5 with the assumption of $\zeta = 1200 \pm 200$ cm^{-1}. A more extensive calculation where dipolar interaction with outer-sphere water molecules with translational diffusion correlation time was included[36,37] has shown that such a contribution can be safely neglected. By substituting the fitted parameters given in Table III in Solomon and Bloembergen equations (eq 6 and 7), it is possible to see that the main contribution to the relaxation rates arises from the dipolar interaction. Within the temperature range used in the present work, the contribution of the contact terms to the relaxation amounts from 5 to 12%.

Discussion

Our magnetic susceptibility measurements of $Ru(H_2O)_6^{3+}$ in aqueous solution clearly indicate that the ruthenium(III) ion is in the low-spin state. This is in agreement with the optical spectrum which was fully accounted for on that basis.[7] However, the magnetic moment has a considerable orbital contribution as is seen from the significant deviation from the spin-only value of $\mu_{\text{eff}} = 1.73\ \mu_B$. In spite of the experimental error which was due mainly from difficulties in obtaining high and reproduceable concentrations of the $Ru(H_2O)_6^{3+}$ ion, it was possible to fit the magnetic moment to Kotani's equations[16] with a reasonable spin–orbit coupling constant.

Since the frequency dependence of the relaxation times was not measured, only a limited significance should be given to the exact values of r and τ_c obtained by fitting the results to the Solomon and Bloembergen equations. It would suffice at this point to mention that the values of T_{1M} and T_{2M} as well as τ_s are all quite similar to the corresponding values obtained for $Ru(NH_3)_6^{3+}$.[21,38] Thus the electronic relaxation mechanism is most probably the same for these two ions.

The value of the hyperfine coupling constant of the water protons in the first coordination sphere of $Ru(H_2O)_6^{3+}$, $A = 3.3 \pm 0.3$ MHz, is the highest value found so far for hexaaquo transition-metal ions (see, e.g., ref 4). This value is related to the covalency parameter λ given by eq 11, where ψ is the

$$\psi = N(\phi_M - \lambda\chi) \tag{11}$$

molecular orbital, N the normalization constant, ϕ_M the metal d orbital, and χ the combination of the ligand orbitals with the appropriate symmetry. Since in the ruthenium(III) complexes which are low-spin d^5 only the t_{2g} orbitals are occupied, there is no need for separating the contributions from the e_g and t_{2g} orbitals. In this case

$$\phi = 3^{-1/2}(i d_{xy} - d_{xz} - i d_{yz}) \tag{12}$$

$$\chi = 12^{-1/2}[i(b_1(1) + b_2(2) + b_1(5) + b_2(4)) - (b_1(3) + b_2(1) + b_1(4) + b_2(6)) - i(b_1(2) + b_2(3) + b_1(6) + b_2(5))] \tag{13}$$

$$N = (1 + \lambda^2 - 2\lambda S)^{-1/2} \tag{14}$$

As was discussed in ref 4, the covalency parameter can be derived directly from the expression of the Fermi contact interaction for spin $^1/_2$ ions:

$$A = (8\pi/3)g_e\beta\gamma_N\hbar\langle\Psi|\sum_i\delta(r_i)|\Psi\rangle \tag{15}$$

For that the explicit wavefunctions should be known. For example, the relevant wavefunctions of water given by Ellison and Shull[39] are

$$b_1 = 2p_x(O) \tag{16}$$

$$b_2 = 0.549(1s(H_1) - 1s(H_2)) + 0.543(2p_y(O)) \tag{17}$$

where 2p(O) and 1s(H) are Slater's atomic orbitals of oxygen and hydrogen with exponents of 1.0 and 2.275 au, respectively.

In a first-order approximation one may proceed in a conventional way of writing the fractional spin density for spin $^1/_2$ ions:

$$f = A/A_0 \tag{18}$$

where A_0 is the hyperfine coupling constant of the free hydrogen atom. Ignoring contribution to A of spin densities on other atoms:

$$f = \frac{0.549^2\lambda^2}{12(1 + \lambda^2 - 2\lambda S)} \tag{19}$$

Since the hydrogen wavefunction 1s(H) in eq 17 is that of a free atomic hydrogen, $A_0 = 1420$ MHz. Ignoring the overlap term $2\lambda s$ in eq 19 and substituting $A = 3.3$ MHz, we obtain $\lambda = 0.32$. A similar result of $\lambda = 0.34$ is obtained also from the more elaborate wavefunction of Aung et al.[40] for the water molecule, requiring that A_0 is calculated from the same wavefunction.[4]

A more detailed calculation takes into account contributions of spin densities on neighboring atoms to the δ function in eq 15.[38] The result of such calculation, with the function of Aung et al. is $\lambda = 0.27$.[4] The same calculation for other hexaaquo transition-metal ions gave values of $\lambda_{t_{2g}}$ of 0.13, 0.13, 0.16, and 0.22 for Mn^{2+}, Fe^{2+}, Co^{2+}, and Cr^{3+}.[4] Thus, the covalency in $Ru(H_2O)_6^{3+}$ is higher than the other ions which are all first-row transition-metal ions, including the trivalent Cr^{3+}. On the other hand, the covalency of $Ru(H_2O)_6^{3+}$ is significantly smaller than that of $Ru(NH_3)_6^{3+}$. The value given for this ion, $\lambda = 0.325$,[41] was obtained after the substitution of contributions fro pseudocontact interactions and was shown to reproduce faithfully the experimental temperature dependence. However, since no correction for pseudocontact interaction was attempted for $Ru(H_2O)_6^{3+}$, the value of $\lambda = 0.27$ obtained for this ion should be compared with a value of $\lambda = 0.39$ obtained for $Ru(NH_3)_6^{3+}$ when the pseudocontact interaction is ignored.

Another indication for the trend in λ may be obtained from the value of the Racah interelectronic repulsion parameters B and C that are calculated from the optical spectrum, i.e., the nephelauxetic effect.[42] Values of $B = 580 \pm 40$ and 640 ± 40 cm^{-1} were estimated for $Ru(NH_3)_6^{3+}$ and $Ru(H_2O)_6^{3+}$, respectively.[7] These values are expected to be proportional to $N_{t_{2g}}^2 N_{e_g}^2$.[42] The functional connetion between the normalization coefficient N and the covalency parameter λ is given by eq 14. However, our measurements give us data only for $\lambda_{t_{2g}}$ and therefore to $N_{t_{2g}}$ but not for N_{e_g}. Therefore, we cannot use the values of the Racah parameter for a quantitative evaluation of the covalency. Yet, the decrease in B going from $Ru(H_2O)_6^{3+}$ to $Ru(NH_3)_6^{3+}$ indicates higher covalency for the latter complex in agreement with the values of λ reported in the present work.

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(36) Pfeiffer, H. *Ann. Phys.* **1961**, *8*, 1.

(37) Pfeiffer, H. *Z. Naturforsch., A* **1962**, *17A*, 279.

(38) Waysbort, D.; Navon, G. *J. Chem. Phys.* **1973**, *59*, 5585.

(39) Ellison, F. O.; Shull, G. *J. Chem. Phys.* **1955**, *23*, 2348.

(40) Aung, S.; Pitzer, R. M.; Chan, S. I. *J. Chem. Phys.* **1968**, *49*, 2071.

(41) Waysbort, D.; Navon, G. *Chem. Phys.* **1980**, *49*, 333.

(42) Jørgensen, C. K. "Oxidation Number and Oxidation States": Springer-Verlag: Berlin, 1969; p 91.