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Effect of Metal–Ligand Bond Distances on Rates of Electron-Transfer Reactions. The Crystal Structures of Hexaammineruthenium(II) Iodide, $[Ru(NH_3)_6]I_2$, and Hexaammineruthenium(III) Tetrafluoroborate, $[Ru(NH_3)_6][BF_4]_3$

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The crystal and molecular structures of hexaammineruthenium(II) iodide and hexaammineruthenium(III) tetrafluoroborate have been determined from three-dimensional X-ray data collected at room temperature by counter methods. The two complexes both crystallize with four formula units in the cubic space group O_h^5-$Fm3m$, with $m3m$ site symmetry imposed on the cations $Ru^{II}(NH_3)_6^{2+}$ and $Ru^{III}(NH_3)_6^{3+}$. The ruthenium(II) complex has a unit cell edge a = 10.841 (4) Å. The structure has been refined by least-squares techniques to a conventional R factor of 2.1% on F, using 139 unique reflections for which $F^2 > 3\sigma(F^2)$. The ruthenium(III) complex has a unit cell edge a = 11.385 (1) Å. The least-squares refinement on F, using 385 independent reflections for which $F^2 > 3\sigma(F^2)$, converged to a conventional R factor of 4.7%. The Ru(II)–NH_3 distance is 2.144 (4) Å and the Ru(III)–NH_3 distance is 2.104 (4) Å, a significant difference of 0.040 (6) Å. This result in conjunction with the known difference of 0.178 (17) Å between the Co(II)–NH_3 and Co(III)–NH_3 bond distances leads to the conclusion that the electrostatic effect on bond distances is significantly smaller than the effect of spin change. From a calculation of ligand field stabilization energy it is found that the anomalous slowness of the electron transfer between $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$ arises from the difference in energy between the spin states of the two exchanging ions and not from the bond length reorganization energy.

Introduction

The chemistry of $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ in aqueous solution has been thoroughly investigated by Endicott and Taube.[1] They have shown that, under ordinary conditions, $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ are sufficiently inert to substitution in aqueous solution so that their electron-transfer reactions are of the outer-sphere type. The rates and mechanisms of outer-sphere reactions have been of great interest in recent years because of the possibility of direct comparisons between experimentally determined and theoretically calculated rate constants. The simplification arising from the absence of bond rupture in the activated complex for outer-sphere electron-transfer reactions facilitates theoretical calculations of rate constants. The calculation of such rate constants requires an accurate value for the energy of activation for the electron transfer. This energy of activation, E_{act}, is made up of three parts:[2] (1) the electrostatic energy, E_{electr}, (2) the energy required to distort the coordination shells of both species, E_r, and (3) the energy required to modify the solvent structure about each species, E_s. Various attempts have been made[3-5] to compute each of these terms and thus to provide a quantitative theory of electron-exchange reactions. Success in this field has been limited somewhat because, to date, little if any data are available in the literature on accurate metal–ligand bond distances for varying oxidation states of the metal atom. Such data are necessary for the calculation of E_r. The transition state for electron exchange will be one in which each species has the same dimensions. This is so because the energy of activation will be a minimum when the electron jump or transfer occurs between species of similar dimensions. The energy of activation, E_{act}, depends therefore to a great extent on the reorganization energy, E_r, of the reacting species prior to electron transfer. This involves the stretching and contraction of the metal–ligand bonds. The greater the reorganization energy, the higher the activation energy will be and hence the slower the rate of the electron transfer. Using the valence force model Orgel[4] indicated that the reorganization energy E_r is $^3/_4(k_n + k_m)(r_n - r_m)^2$ for electron transfer between oxidation states n and m ($m = n + 1$) if one assumes $r^{\ddagger} = {}^1/_2(r_n + r_m)$, where $r^{\ddagger}$ is the equilibrium internuclear bond distance of both the reacting species required to have a minimal E_r. This assumption, however, only holds for the special case $k_n = k_m$, where k is the force constant for the metal–ligand bond. The more general expression for E_r for an octahedral species is

$$E_r = 3k_m(r^{\ddagger} - r_m)^2 + 3k_n(r_n - r^{\ddagger})^2 \qquad (1)$$

where

$$r^{\ddagger} = (k_n^{1/2}r_n + k_m^{1/2}r_m)/(k_n^{1/2} + k_m^{1/2}) \qquad (2)$$

Using these equations Stranks[3] has estimated the "energy barrier" for electron exchange between $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$ to be 32 kcal/mol. These calculations are based on force constants k_{II} and k_{III} taken to be 0.8×10^5 and 2.0×10^5 dyn cm^{-1}, respectively, and bond lengths of 2.39 Å for Co(II)–N and 2.05 Å for Co(III)–N. Since then, however, the Co(II)–N and Co(III)–N bond distances have been accurately determined.[6] The Co(II)–N distance is 2.114 (9) Å, while the Co(III)–N distance is 1.936 (15) Å. Based on these new accurate values and using a more reasonable value of $r^{\ddagger}$ of 1.989 Å calculated from[7]

$$r^{\ddagger} = \frac{k_{II}r_{II} + k_{III}r_{III}}{k_{II} + k_{III}}$$

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(1) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **84**, 4984 (1962); **86**, 1686 (1964); *Inorg. Chem.*, **4**, 437 (1965).

(2) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., p 179.

(3) D. R. Stranks, *Discuss. Faraday Soc.*, **29**, 116 (1960).

(4) L. E. Orgel, Report of the 10th Solvay Conference, Brussels, 1956, p 289.

(5) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964), and references therein.

(6) T. Barnet, B. M. Craven, H. C. Freeman, N. E. Kime, and J. A. Ibers, *Chem. Commun.*, 307 (1966); N. E. Kime and J. A. Ibers, *Acta Crystallogr., Sect. B*, **25**, 168 (1969).

(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 458.

we find E_r = 8 kcal/mol, a discrepancy of 24 kcal/mol which results from the inaccurate bond lengths used by Stranks. For the $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ system an additional energy term, E_{sp}, has to be considered, which arises from a change of spin on the central metal atom. In his discussion Stranks failed to consider E_{sp}, as the value he used for E_r was in itself sufficient to account for the slowness of the reaction. However the more reasonable value of E_r of 8 kcal/mol for the $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ system implies that E_{sp} cannot be ignored and that indeed $E_r < E_{sp}$.

It would seem that further experimental structural data are desirable. The rates of electron-exchange reaction of the $Ru(NH_3)_6^{2+}$–$Ru(NH_3)_6^{3+}$ couple have been extensively studied by Meyer and Taube;[8] however, theoretical calculations on this system have been limited because to date no accurate Ru(II)–NH_3 or Ru(III)–NH_3 bond lengths are known. The objectives of this present work were therefore (1) to obtain accurate values of the Ru(II)–NH_3 and Ru(III)–NH_3 distances, (2) to use these in current theoretical expressions in an attempt to account for the 10^{15} increase in the rate of the electron-exchange reaction in going from Co(II)–Co(III) to Ru(II)–Ru(III), and (3) to make some comparisons of the relative importance of change in oxidation state *vs.* change in spin state on bond distances.

Experimental Section

The iodide and tetrafluoroborate salts of the Ru(II) and Ru(III) complexes, respectively, were chosen for this study since we found that both compounds crystallize in the cubic system with crystallographic symmetry $m3m$ imposed on the cations. This enabled us to determine very accurate Ru–N bond lengths.

Preparations.—The iodide salt was prepared by displacement of the chloride ion from $[Ru(NH_3)_6]Cl_2$ by the addition of an aqueous solution of KI. The $[Ru(NH_3)_6]Cl_2$ was prepared by the method of Lever and Powell.[9] The reaction was carried out in an N_2 atmosphere, and it was found that once the $[Ru(NH_3)_6]I_2$ had crystallized, it was air stable. The $[Ru(NH_3)_6][BF_4]_3$ complex was prepared by the method of Allen and Senoff.[10]

Anal. Calcd for $[Ru(NH_3)_6]I_2$: H, 3.94; N, 18.38. Found: H, 3.81; N, 18.21. Calcd for $[Ru(NH_3)_6][BF_4]_3$: H, 3.89; N, 18.12. Found: H, 4.06; N, 18.11.

Collection and Reduction of Intensity Data.—The $[Ru^{II}(NH_3)_6]I_2$ complex crystallizes as pale yellow, cuboctahedrons of the hexoctahedral class, while crystals of $[Ru^{III}(NH_3)_6][BF_4]_3$ are colorless cuboctahedrons. Preliminary optical and X-ray examination showed both crystals belong to the cubic system. The cell constants and their standard deviations were determined at 22° from a least-squares refinement of the setting angles of a number of high-angle reflections ($52° < 2\theta < 64°$) centered on a Picker four-circle automatic diffractometer[11] using Mo $K\alpha_1$ radiation (λ 0.7093 Å). The ruthenium(II) complex crystallizes in a unit cell of edge a = 10.841 (4) Å (nine reflections) and the ruthenium(III) in a unit cell of edge a = 11.385 (1) Å (four reflections).

A series of Weissenberg and precession photographs of both complexes showed Laue symmetry $m3m$ and systematic absences of hkl for $h + k$ odd and $k + l$ odd. The most likely space groups are therefore $Fm3m$, $F432$, and $F\bar{4}3m$.[12] The calculated density for four molecules of $[Ru(NH_3)_6]I_2$ per cell is 2.38 g/cm³. The material was observed to sink slowly in CH_3I (density 2.28 g/cm³). The calculated density of 2.08 g/cm³ for four units of $[Ru(NH_3)_6][BF_4]_3$ per cell agrees well with the value of 2.07 g/cm³ measured by flotation in a mixture of methyl iodide and carbon tetrachloride.

The experimental and refinement procedures used in the data collection were the same for both compounds and are similar to those described previously.[11,13] Both crystals had faces of the cubic forms {100} and {111}. The dimensions of both crystals were carefully measured on a microscope fitted with a micrometer eyepiece in preparation for the absorption correction.

The ruthenium(II) crystal was mounted on the diffractometer with the [001] direction misset by about 5° from the spindle axis. The ruthenium(III) crystal was mounted with the [111] direction about 5° misset from the spindle axis. Thus the possibility of multiple reflections was minimized. The mosaicities of the data crystals were checked by measuring ω scans through several strong reflections, using a narrow source and an open counter.[14] An average half-width of 0.06° for both crystals was satisfactory.

Mo Kα radiation was used for the collection of each data set, with a θ–2θ scan technique, employing stationary-crystal, stationary-counter background counts of 10 sec at the beginning and end of each scan range. The data were collected at a takeoff angle of 1.3°. An asymmetric scan range of 0.5° on the low side of 2θ and 0.7° on the high side of 2θ at a scan rate of 1°/min was used for the ruthenium(II) crystal; for the ruthenium(III) complex 0.4° on the low side of 2θ and 0.9° on the high side with the same scan rate were used.

The crystal-to-counter distance was 32 cm, with a counter aperture of 4 mm × 4 mm. The pulse height analyzer was set to accept a window of approximately 90% when centered on the Mo $K\alpha_1$ peak.

Coincidence losses for strong reflections were minimized by use of copper foil attenuators with attenuator factors of approximately 2.5. The diffracted beams of Mo Kα radiation in both data collections were filtered through 3.0 mils of niobium foil.

During the course of collection of each data set, the intensities of several standard reflections were measured periodically as a check on crystal and electronic stability. The four standards chosen for both data sets showed a decrease of less than 1% of the original mean during data collection, and no correction for decomposition was necessary.

Intensity data were collected from all hkl planes out to θ(Mo $K\alpha_1$) ⩽ 38.3° for the ruthenium(II) crystal. A unique data set of the hkl planes was collected for the ruthenium(III) complex out to θ(Mo $K\alpha_1$) of 50°.

The data for both compounds were processed in the manner described previously.[11,13] After a correction for background, the standard deviation $\sigma(I)$ of the corrected intensity, I, was estimated using a value of p for both complexes of 0.04. The intensities were then corrected for Lorentz–polarization effects. The calculated linear absorption coefficient, μ, for the ruthenium(II) complex is 60.61 cm^{-1}.[12] A series of tests showed transmission factors varying from 0.27 to 0.22, so an absorption correction[15] was made. The data were next averaged to yield a total of 222 independent reflections of which 139 had $F^2 > 3\sigma(F^2)$. There were no systematic differences between intensities in those two classes of reflections that would exist if Friedel's law failed. Hence the space group $Fm3m$ was assumed. Of the total of 450 unique reflections collected on the ruthenium(III) complex, 385 had $F^2 > 3\sigma(F^2)$. Only reflections satisfying this condition were used in subsequent calculations. The value of the absorption coefficient for the ruthenium(III) complex is 11.9 cm^{-1}, and for the data crystal employed the transmission factors varied from 0.19 to 0.20.

Solution and Refinement of the Structures.—In the least-squares refinements the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. The residuals R_1 and R_2 are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$. The scattering factors used for N, H, B, and F were from the usual tabulation;[12] those for Ru and I were calculated by Cromer and Waber.[16] The effects of anomalous scattering were included in the structure factor

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[8] T. J. Meyer and H. Taube, *J. Amer. Chem. Soc.*, **91**, 2369 (1969).

[9] F. M. Lever and A. R. Powell, *Chem. Soc., Spec. Publ.*, **No. 13**, 135 (1959).

[10] A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **45**, 1337 (1967).

[11] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[12] "International Tables for X-Ray Crystallography," Vol. I and III, Kynoch Press, Birmingham, England, 1962 and 1969.

[13] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

[14] T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

[15] In addition to various local programs for the CDC 6400, local modification of Hamilton's GONO9 absorption program, Zalkin's FORDAP Fourier program, the Büsing–Levy ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program were used in this work.

[16] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

calculations.[17] The values of $\Delta f'$ and $\Delta f''$ for Ru and I were those given by Cromer.[18]

In the solution of the $[Ru(NH_3)_6]_2I_2$ structure the ruthenium(II) atom was placed at (0, 0, 0) and the nitrogen atom approximately 2 Å from it in position $(x, 0, 0)$ and after successive least-squares refinements the iodine atoms were found from a difference Fourier synthesis. In subsequent least-squares refinements the nitrogen atom was allowed to vibrate anisotropically but both the ruthenium and iodine atoms are restricted by symmetry to isotropic vibrations. The refinement in $Fm3m$ of the Ru, N, and I atoms converged to values of R_1 and R_2 of 3.6 and 2.6%. A difference Fourier synthesis computed at this point provided no indication of localized positions for the hydrogen atoms but did exhibit high electron density in the general region expected. Accordingly, the NH_3 ligand was assumed to be rotating freely around thd Ru–N bond and the appropriate contributions of the hydrogen atoms to the structure factors were computed.[19] In this calculation the following quantities were assumed: N–H = 0.96 Å; ∠ Ru–N–H = 109.5°; $B(H)$ = 3.55 Å^2. Inclusion of these contributions reduced R_1 and R_2 to 3.3 and 2.4%. An examination of F_o *vs.* F_c at this stage suggested that secondary extinction was a problem. In a final round of calculations an isotropic extinction parameter was added to the previous variables. After two cycles of least-squares refinement R_1 and R_2 were reduced to 2.1 and 1.8%, respectively.

The structure of the $[Ru(NH_3)_6][BF_4]_3$ complex was solved in a similar manner. A difference Fourier synthesis computed after a least-squares refinement of the Ru, N, and B parameters showed evidence of disorder among the fluorine atoms. R_1 and R_2 had values of 14.8 and 18.6% at this stage. The disorder around B(1) [$m3m$ site symmetry in the 4(b) ($^1/_2$, $^1/_2$, $^1/_2$) position] consisted of eight peaks of equivalent electron density (2.1 e$^-$/Å^3) at the vertices of a cube. This we believe results from a 90° rotation of a tetrahedral BF_4^- ion around any of its fourfold axes. These fluorine atoms, F(1), were refined in the position 32(f), with an occupancy factor of 0.5. A difference Fourier synthesis around B(2) $\bar{4}3m$ site symmetry in the 8(c) ($\pm ^1/_4$, $^1/_4$, $^1/_4$) position] showed ten peaks. Six of these were of equal height (1.4 e$^-$/Å^3) and were at the vertices of a regular octahedron around the B(2) atom. These peaks (F(2)) occurred at atomic coordinates of the type x, $^1/_4$, $^1/_4$ and were assigned to the 48(g) position. The remaining four smaller peaks (0.65 e$^-$/Å^3) were at the vertices of a regular tetrahedron around B(2). These peaks F(2)′ correspond to positions of the type 32(f) (x, x, x). This disorder can be explained by a $\bar{4}$ symmetry operation on a tetrahedral BF_4^- ion comprised of $B(F(2))_3(F(2)')_1^-$ around any of its four threefold axes. Two cycles of least-squares refinement with the coordinates of the Ru, N, B(1), and B(2) atoms as before and the fluorine atoms as just described yielded R_1 = 7.6% and R_2 = 9.5%. The N, F(1), F(2), and F(2)′ atoms were then allowed to vibrate anisotropically; the Ru, B(1), and B(2) are restricted to isotropic vibrations by symmetry. The values of R_1 reduced to 5.5% and R_2 to 6.7% after three cycles of least-squares refinement.

A difference Fourier synthesis computed at this stage indicated that the hydrogen atoms were not localized, but again there was high electron density in the general region expected. The NH_3 ligand was assumed to be rotating freely around the Ru(III)–N bond and the contributions of the hydrogen atoms to the structure factors were computed.[19] In this calculation the following quantities were assumed: N–H, 1.01 Å; ∠ Ru–N–H, 109.5°; $B(H)$ = 3.14 Å^2. Inclusion of these contributions and an extinction parameter reduced R_1 and R_2 to 4.7 and 5.3%, respectively. A final difference Fourier synthesis computed at this stage showed residual electron density of 1.05 e$^-$/Å^3 around the F(2) position and heights less than 0.5 e$^-$/Å^3 at all other positions.

The disorder of the BF_4 groups is more complex than we have described. Thus on the basis of F···F contacts it is clear that a given orientation of a particular BF_4 group places restrictions on the orientations that neighboring BF_4 groups can take. Although local order is imposed, the disorder arises through the many different choices of orientations as one moves away from the given BF_4 group. There is no indication of diffuse scattering from the crystal, so disorder occurs at the molecular level.

That some residual density is found in the region of the F(2) atoms is not surprising and merely suggests that our model for disorder is an oversimplification. The residual density is low, however, and moreover the cationic geometry does not change significantly even when the fluorine scattering is neglected completely.

The positional and thermal parameters derived from the last cycle of least-squares refinement for both crystal structures are given in Tables I and II, along with the associated standard deviations as estimated from the inverse matrix. The final values of $10|F_o|$ and $10|F_c|$ in electrons are given in Table III for $[Ru(NH_3)_6]I_2$ and $[Ru(NH_3)_6][BF_4]_3$; only the reflections which were used in the refinement are listed in this table.[20] A selection of distances and angles is given in Table IV for both structures. The Ru(II)–N and Ru(III)–N bond distances can be corrected for thermal motion using the "riding" and "independent" models of Busing and Levy,[21] but the differences between various bond lengths remain essentially the same when either of these corrections is applied.

TABLE I

FINAL PARAMETERS FOR $[Ru(NH_3)_6I_2$

Atom	Position	Site symmetry	x, y, z	B, Å^2	β_{11}[b]	β_{22}
Ru(II)	4(a)	$m3m$	0, 0, 0	2.56 (1)[a]		
I	8(c)	$\bar{4}3m$	$^1/_4$, $^1/_4$, $^1/_4$	3.46 (1)		
N	24(e)	$4mm$	0.1977 (3), 0, 0		0.0065 (3)	0.0081 (2)
H[c]						

[a] The estimated standard deviation of the least significant digits here and in subsequent tables is given in parentheses. [b] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}(k^2 + l^2))]$. [c] Free rotor.

TABLE II

FINAL PARAMETERS FOR $[Ru(NH_3)_6][BF_4]_3$

Atom	Position	Site symmetry	x	y	z	Occupancy	β_{11}[a] or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru(III)	4(a)	$m3m$	0	0	0	1.0	1.55 (2)					
B(1)	4(b)	$m3m$	$^1/_2$	$^1/_2$	$^1/_2$	1.0	2.55 (16)					
B(2)	8(c)	$\bar{4}3m$	$^1/_4$	$^1/_4$	$^1/_4$	1.0	3.63 (18)					
N	24(e)	$4mm$	0.1848 (3)	0	0	0.5	0.0032 (2)	0.0078 (2)	β_{22}	0	0	0
F(1)	32(f)	$3m$	0.4286 (3)	x	x	1.0	0.0075 (2)	β_{11}	β_{11}	−0.0017 (2)	β_{12}	β_{12}
F(2)	48(g)	mm	$^1/_4$	$^1/_4$	0.1272 (6)	0.5	0.0098 (9)	0.0255 (10)	β_{22}	0	0	−0.0097 (10)
F(2)′	32(f)	$3m$	0.1859 (7)	x	x	0.25	0.0103 (7)	β_{11}	β_{11}	−0.0031 (5)	β_{12}	β_{12}
H[b]												

[a] The form of the general thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Free rotor.

Discussion

Bond Lengths and Their Differences.—The Ru(II)–N bond distance in $[Ru(NH_3)_6]I_2$ is 2.144 (4) Å and

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(17) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

(18) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(19) J. M. Bijvoet and J. A. A. Ketelaar, *J. Amer. Chem. Soc.*, **54**, 625 (1932).

(20) A listing of structure factor amplitudes (Table III) will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(21) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

TABLE IV

SELECTED DISTANCES (Å) AND ANGLES (DEG)

	$[Ru(NH_3)_6]I_2$		
Ru(II)–N	2.144 (4)	N···N	3.032 (5)
N···I	3.875 (1)		
	$[Ru(NH_3)_6][BF_4]_3$		
Ru(III)–N	2.104 (4)	F(1)···F(1)	2.298 (9)
B(2)–F(2)	1.398 (7)	F(2)···F(2)	1.977 (10)
B(2)–F(2)′	1.265 (14)	F(2)′···F(2)′	2.066 (22)
B(1)–F(1)	1.407 (6)	F(2)···F(2)′	2.366 (12)
Ru(III)···F(2)′	3.665 (14)	F(2)′–B(2)–F(2)′	109.4 (7)
N···F(2)′	2.993 (11)	F(1)–B(1)–F(1)	109.4 (1)
N···F(2)	3.279 (4)	F(2)–B(2)–F(2)	90.0
N···N	2.976 (6)	F(2)–B(2)–F(2)′	125.3 (1)

the Ru(III)–N bond length in $[Ru(NH_3)_6][BF_4]_3$ is 2.104 (4) Å.

TABLE V

COMPARATIVE DETAILS OF SOME Ru(II)–NH_3 AND Ru(III)–NH_3 BOND LENGTHS

Compound	Ru(II)–NH_3 or Ru(II)–$NH_2CH_2CH_2NH_2$, Å	Ref
$[Ru(NH_3)_6]I_2$	2.144 (4)	*a*
$[Ru(NH_3)_5N_2Ru(NH_3)_5][BF_4]_4$	2.140 (6) (apical) 2.12 (equatorial)	*b*
$[Ru(N_2)(NH_3)_5][BF_4]$	2.11	*c*
$[Ru(N_3)(N_2)(NH_2CH_2CH_2NH_2)_2][PF_6]$	2.125 (19) (mean)	*d*
	Ru(III)–NH_3 or Ru(III)–$NH_2CH_2CH_2NH_2$, Å	
$[Ru(NH_3)_6][BF_4]_3$	2.104 (4)	*a*
$[Ru(NH_2CH_2CH_2NH_2)_3]Cl_3\cdot 3H_2O$	2.102 (18) 2.117 (18)	*e*

[a] This work. [b] I. M. Treitel, M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Amer. Chem. Soc.*, **91,** 6512 (1969). [c] F. Bottomley and S. C. Nyburg, *Chem. Commun.*, 897 (1966). [d] B. R. Davis and J. A. Ibers, *Inorg. Chem.*, **9,** 2768 (1970). [e] H. J. Peresie and J. A. Stanko, *Chem. Commun.*, 1674 (1970).

TABLE VI

EFFECT OF AN INCREASE IN CHARGE AND SPIN MULTIPLICITY OF THE CENTRAL METAL ATOM ON METAL–LIGAND BOND DISTANCES IN COORDINATION COMPLEXES

Complexes	Net effects	M(II)–L, Å	M(III)–L, Å	Diff	Ref
$Ru(NH_3)_6^{2+}$–$Ru(NH_3)_6^{3+}$	Charge increase ($^1A_{1g}$, $^2T_{2g}$)	2.144 (4)	2.104 (4)	0.040 (6) (Δ_c)	*a*
$Fe(bipy)_2(NCS)_2$–$Im_2FeTPP^+Cl^-$ [f]	Charge increase ($^1A_{1g}$, $^2T_{2g}$)	2.02	1.98 (1)	0.04 (Δ_c)	*b, c*
$RuCl_4(H_2O)(CO)^{2-}$–$RuCl_5(H_2O)^{2-}$	Charge increase ($^1A_{1g}$, $^2T_{2g}$)	2.395 (2)	2.353 (4)	0.04 (Δ_c)	*d*
$Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$	Charge increase, spin change ($^4T_{1g}$, $^1A_{1g}$)	2.114 (9)	1.936 (15)	0.178 (17) ($\Delta_c + \Delta_s$)	*e*
$Fe(bipy)_2(NCS)_2$	Spin change ($^1A_{1g}$, $^2T_{2g}$)	2.02 ($^1A_{1g}$) 2.14 ($^2T_{2g}$)		0.12 (Δ_s)	*b*

[a] This work. [b] E. König and K. J. Watson, *Chem. Phys. Lett.*, **6,** 457 (1970). [c] R. Countryman, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, **91,** 5167 (1969). [d] J. A. Stanko and S. Chaipayungpundher, *ibid.*, **92,** 5580 (1970). [e] Reference 6. [f] These compounds are *cis*-diisothiocyanatobis(2,2′-bipyridyl)iron(II) and bis(imidazole)-α,β,γ,δ-tetraphenylporphinatoiron(III) chloride, respectively.

Table V lists the Ru–NH_3 bond distances found in a series of crystal structures. Our value for the Ru(II)–NH_3 bond distance agrees very well with that found for the Ru–NH_3 apical bond in $[Ru(NH_3)_5N_2Ru(NH_3)_5][BF_4]_4$.[22] The shortening of the Ru–NH_3 bond in the equatorial positions in the last compound arises from the increased formal charge left on the ruthenium atom as a result of back-bonding from its t_{2g} orbitals to the π^* orbitals of the bridging N_2. We note that the value of 2.12 Å found for this equatorial Ru–NH_3 bond length lies between our values for Ru(II)–NH_3 and Ru(III)–NH_3. The only other accurate Ru(III)–N bond length known is that found in $[Ru(NH_2CH_2CH_2NH_2)_3]Cl_3\cdot 3H_2O$, where the average Ru–N bond distance is 2.11 (1) Å.[23]

The difference between our determined values for Ru(II)–NH_3 and Ru(III)–NH_3 bond lengths is 0.040 (6) Å. This is a small but significant difference, as anticipated. The two main determining factors in any pair of metal–ligand bond distances such as those being considered here are (a) the electrostatic charge on the metal atom (the greater the charge on the central metal atom the shorter the metal–ligand bond will be) and (b) the electronic configuration and spin state of the metal atom. The electronic configuration of the d electrons in $Ru(NH_3)_6^{2+}$ is $(t_{2g})^6$ and that for $Ru(NH_3)_6^{3+}$ is $(t_{2g})^5$. An extra electron in a t_{2g} nonbonding molecular orbital will have little, if any, effect on the metal–ligand bond distances. Hence we believe that the difference of 0.040 (6) Å found must be due almost entirely to the electrostatic effect of the greater charge on Ru^{3+} atoms.

In Table VI the effect of an increase in charge and/or spin multiplicity of the central metal atom on metal–ligand (M–L) bond distances is tabulated for complexes whose structures have been determined to date. If Δ_c represents the change in the M–L bond distance as a result of the increase in charge on the central metal atom and Δ_s the change arising from a spin multiplicity difference, one sees that our value of $\Delta_c = 0.040$ (6) Å for the $Ru(NH_3)_6^{2+}$–$Ru(NH_3)_6^{3+}$ couple is in excellent agreement with those found for Ru(II)–Cl—Ru(III)–Cl[24] and Fe(II)–N—Fe(III)–N[25,26] systems. Thus we estimate that Δ_s is 0.138 Å for the Co(II)–Co(III) system. Such a value agrees well with that of $\Delta_s \cong 0.12$ Å found in the Fe(II) system $Fe(bipy)_2(NCS)_2$.[25] From the data available it thus appears that $\Delta_s = 0.13 \pm 0.01$ Å and $\Delta_c = 0.04$ Å.

The Effect of These Bond Lengths on the Rates of Electron Transfer.—The electron transfer reactions between $Co(NH_3)_6^{3+}$ and $Co(NH_3)_n(H_2O)_{6-n}^{2+}$ have been studied, and for $n = 3$–6 $k < 3 \times 10^{-12}$ M^{-1} sec^{-1} at 25°.[3] The slowness of the cobalt reaction has been

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attributed to (1) the large difference in cobalt–nitrogen bond distances, Co(II)–N = 2.114 (6) Å and Co(III)–N = 1.936 (6) Å, a difference of 0.178 (17) Å,[6] and (2) the spin multiplicity change in going from high-spin $\mathrm{Co(NH_3)_6^{2+}}$, whose electronic structure is $(t_{2g})^5(e_g)^2$, to low-spin $\mathrm{Co(NH_3)_6^{3+}}$, with an electronic structure of $(t_{2g})^6$. The rate of self-exchange for the couple $\mathrm{Ru(NH_3)_6^{2+}}$–$\mathrm{Ru(NH_3)_6^{3+}}$ has been measured to be $k = (8.2 \pm 1) \times 10^2\ M^{-1}\ \mathrm{sec}^{-1}$.[8] Thus k differs from the $\mathrm{Co^{2+}}$–$\mathrm{Co^{3+}}$ system by a factor of at least 10^{15}.

The equilibrium internuclear distance $r^{\ddagger}$ which the ruthenium atoms must attain prior to electron transfer is 2.115 Å on the basis of eq 3 and the bond distances found here. In this calculation the two Ru–N stretching force constants were derived from the Ru(III)–N stretching frequency of 474 cm^{-1} [10,27] and a value of 300 cm^{-1} assumed for Ru(II)–N. This value is within the range of M(II)–N stretching vibrations.[28] Thus the change necessary in the Ru–N bond distances in attaining their equilibrium positions is only ≤ 0.029 Å. This contraction or extension can readily be achieved at room temperature if the Ru–N stretching vibrations of the two ions are out of phase. Thus, the bond length reorganization energy, E_r, for the ruthenium system is negligible. Since both the $\mathrm{Ru(NH_3)_6^{2+}}$ and $\mathrm{Ru(NH_3)_6^{3+}}$ ions have low-spin electronic configurations, E_{act} for the electron transfer must be minimal. Accordingly we anticipate and find a fast electron-transfer reaction between the two ions.

For the cobalt hexaammines, however, the value for $r^{\ddagger}$ is 1.989 Å, based on the following data: Co(II)–N = 2.114 Å; Co(III)–N = 1.936 Å; $k_{\mathrm{II}} = 0.7 \times 10^5$ dyn cm^{-1}; $k_{\mathrm{III}} = 1.7 \times 10^4$ dyn cm^{-1}. These force constants, which differ slightly from those used by Stranks, were calculated from known Co–N stretching frequencies.[28] Thus the Co(II)–$\mathrm{NH_3}$ has to contract 0.125 Å while the Co(III)–$\mathrm{NH_3}$ has to expand 0.053 Å so that both species will have the same dimensions prior to electron transfer. One can easily show that 0.80 kcal/mol of energy is required to stretch a Co(II)–N bond by 0.125 Å and 0.34 kcal/mol to cause contraction of a Co(III)–N bond by 0.053 Å. Since the energy required to distort the cobalt species to attain the same dimensions is greater than the energy of their first vibrational levels, the probability that such a configuration would occur in their ground vibrational states is zero for all practical purposes. Thus $E_r = 6(0.80 + 0.34) = 6.8$ kcal/mol.[29] This is too small a value to account for the great difference in exchange rates in the Co(II)–Co(III) and Ru(II)–Ru(III) systems. Clearly the differences must arise from the effects of spin change.

The Effects of Spin Change.—We now consider the crystal field stabilization energy associated with spin change in the Co(II)–Co(III) system.

We propose that the high-spin cobalt(II) species, whose electronic configuration is $(t_{2g})^5(e_g)^2$ ($^4T_{1g}$ ground state), is electronically excited to a cobalt(II) low-spin species presumably with an electronic configuration of $(t_{2g})^6(e_g)^1$, a ^2E_g state.[20] This electronic rearrangement from the ground-state configuration of $(t_{2g})^5(e_g)^2$ is expected to be slow owing to the energy difference between the ^2E_g and $^4T_{1g}$ states. The crystal field parameters Dq and the Racah B parameters for $\mathrm{Co(NH_3)_6^{2+}}$ and $\mathrm{Co(NH_3)_6^{3+}}$ are known:[31] $\Delta = 23{,}000\ \mathrm{cm}^{-1}$, $B = 660\ \mathrm{cm}^{-1}$ for $\mathrm{Co(NH_3)_6^{3+}}$; $\Delta = 10{,}100\ \mathrm{cm}^{-1}$, $B = 900\ \mathrm{cm}^{-1}$ for $\mathrm{Co(NH_3)_6^{2+}}$. Assuming the Racah C parameter is equal to $4B$, we estimate the ^2E_g state to be *ca.* 8600 cm^{-1} or 24.6 kcal/mol above the $^4T_{1g}$ ground state of $\mathrm{Co(NH_3)_6^{2+}}$. Similarly we calculate the $\mathrm{Co(NH_3)_6^{3+}}$ high-spin species $(t_{2g})^4(e_g)^2$ to be *ca.* 21,600 cm^{-1} above its $^1A_{1g}$ ground state, which corresponds to an energy difference of 61.8 kcal/mol.

Therefore the E_{act} will be minimized if the reaction path is

$$\mathrm{Co(NH_3)_6^{2+}\ (high\ spin)} \overset{K}{\rightleftharpoons} \mathrm{Co(NH_3)_6^{2+}\ (low\ spin)} \quad \Delta = 24.6\ \mathrm{kcal/mol}$$

$$\mathrm{Co(NH_3)_6^{2+}\ (low\ spin)} + \mathrm{Co(NH_3)_6^{3+}\ (low\ spin)} \xrightarrow{k} \mathrm{Co(NH_3)_6^{3+}\ (low\ spin)} + \mathrm{Co(NH_3)_6^{2+}\ (low\ spin)}$$

$$\mathrm{Co(NH_3)_6^{2+}\ (low\ spin)} \longrightarrow \mathrm{Co(NH_3)_6^{2+}\ (high\ spin)}$$

where k is the rate-determining step. A reaction where

$$\mathrm{Co(NH_3)_6^{3+}\ (low\ spin)} \rightleftharpoons \mathrm{Co(NH_3)_6^{3+}\ (high\ spin)} \quad \Delta = 61.8\ \mathrm{kcal/mol}$$

is the preequilibrium step would be energetically unfavorable.

From these qualitative calculations we see that the reorganization energy, E_r, for $\mathrm{Co(NH_3)_6^{2+}}$ (6.8 kcal/mol) is insignificant compared with the energy associated with its spin change (24.6 kcal/mol). This spin change energy term in itself is sufficient to account for the difference of approximately 10^{15} in the rate constants. We therefore conclude that the spin multiplicity change associated with the electron transfer from $\mathrm{Co(NH_3)_6^{2+}}$ to $\mathrm{Co(NH_3)_6^{3+}}$ must be the cause of the slowness of this reaction. These findings are in agreement with previously published results on the effect of a spin multiplicity change on the rate of electron transfer for $\mathrm{Co^{2+}}$–$\mathrm{Co^{3+}}$ systems.[5,32,33]

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