Table I. Calculated Magnetic Dipole Moments (MDM) and $R_K/D_K^{1/2}$ Values for Different Transitions in the Nd^{3+} and Eu^{3+} Double Nitrate Single Crystals

band positions, nm	state ($^{2S+1}L_J$)	10^{21} × MDM_{calcd},[a] esu cm	10^{23} × $R_K/D_K^{1/2}$, esu cm
	Nd Transitions		
674[b]	$^4I_{9/2} \rightarrow {}^4F_{9/2}$	3.43	1.66
623[b]	$^4I_{9/2} \rightarrow {}^2H_{11/2}$	−0.58	0.94
574[c]	$^4I_{9/2} \rightarrow {}^4G_{5/2}$		
565[d]	$^4I_{9/2} \rightarrow {}^2G_{7/2}$	−0.13	
510	$^4I_{9/2} \rightarrow {}^2G_{9/2}$	−1.01	1.22
459	$^4I_{9/2} \rightarrow {}^4G_{11/2}$	0.64	0.14
353	$^4I_{9/2} \rightarrow {}^2I_{11/2}$	−0.75	−0.86
	Eu Transitions		
595	$^7F_1 \rightarrow {}^5D_0$	−3.15	0.71
535[b]	$^7F_1 \rightarrow {}^5D_1$	−0.284	0.33
524	$^7F_0 \rightarrow {}^5D_1$	−1.54	0.146
471	$^7F_1 \rightarrow {}^5D_2$	−1.05	0.99

[a] Calculated from free ion wave functions: (i) Wybourne, B. G., *J. Chem. Phys.*, **1961**, *34*, 279. (ii) Ofelt, G. S. *Ibid.* **1963**, *38*, 2171. [b] Absorption spectrum is not resolved and R_K's are determined from the sigmoid CD band. This unavoidable procedure is admittedly approximate and very probably leads to loss of CD band area through overlap of oppositely signed band. [c] CD is very small (see Figure 1B). [d] Absorption could not be resolved.

$\Delta J \geq 2$ transitions. This is only roughly borne out by Table I for Nd^{3+} transitions. The transition $^4I_{9/2} \rightarrow {}^2G_{7/2}$ (565 nm) is principally magnetic dipole allowed and hence stands out prominently over the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transitions in the CD spectrum, in contrast to the normal absorption spectrum. Particularly noteworthy is the high $R_K/D_K^{1/2}$ values for $^4I_{9/2} \rightarrow {}^4F_{9/2}$ (674-nm) transitions. For such transitions with high magnetic dipole moment, CD may be used as a diagonistic tool.

It is interesting to compare the CD spectra of principally magnetic-dipole-allowed Eu^{3+} $^7F_0 \rightarrow {}^5D_1$, $^7F_1 \rightarrow {}^5D_0$ and $^5D_1$ transitions with those of principally electric-dipole-allowed Nd^{3+} transitions. Some of the Nd^{3+} transitions such as $^4I_{9/2} \rightarrow {}^4F_{9/2}$, $^2G_{7/2}$ have $R_K D_K^{1/2}$ values as high as those of Eu^{3+} transitions. The high magnetic dipole contribution to some of the Nd^{3+} transitions should be carefully looked into in other nonoptically active Nd^{3+} crystals through a comparison of axial and polarized spectra.

A detailed calculation on the optical activity of $K_3Pr_2(NO_3)_9$ has been done and will be discussed elsewhere.

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Effects of Pressure on the Reduction of $Co(NH_3)_5N_3^{2+}$ by Iron(II) in Dimethyl Sulfoxide

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In a recent paper[1] Watts et al. investigated the effects of solvent on the reduction of $Co(NH_3)_5N_3^{2+}$ by Fe(II). Similar to their earlier findings[2-4] for the reduction of $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ by Fe(II), $\Delta H^{\ddagger}$ for the second-order rate constant increases from 63 to 80.5 kJ mol^{-1} and $\Delta S^{\ddagger}$ increases from −74 to −10 J K^{-1} mol^{-1} on changing the reaction medium from water to Me_2SO. The reduction of $Co(NH_3)_5N_3^{2+}$ by Fe(II) is believed to proceed according to an inner-sphere mechanism in Me_2SO and in water[1,5] as is the case for the reduction of $Co(NH_3)_5X^{2+}$ (X = Cl, Br, F).[2-4] The observed changes in the activation parameters are interpreted in terms of a change in the stereochemistry of the iron(II) atom from an octahedral to a tetrahedral geometry in the bridged intermediate.[1]

According to Stranks,[6] a positive volume of activation is expected for inner-sphere redox reactions primarily due to the expulsion of a solvent molecule upon forming the bridged intermediate. Indeed, Halpern et al.[7] reported a value of +14 cm^3 mol^{-1} at 25 °C for the title reaction in water. Along these lines it is expected[8] that $\Delta \bar{V}^{\ddagger}$ should be remarkably more positive for this reaction in Me_2SO since three solvent molecules are released when a bridged intermediate with a tetrahedral Fe(II) center is formed.

Experimental Section

$[Co(NH_3)_5N_3]Cl_2$ was prepared according to standard procedures[9] and converted into the perchlorate salt. UV-visible absorption spectra are in excellent agreement with those published elsewhere.[10,11] $[Fe(OH_2)_6](ClO_4)_2$ was used as source of Fe(II).[12] Chemicals of analytical reagent grade, freshly distilled Me_2SO, and doubly distilled water were used in all solutions. Kinetic runs were performed on a modified Zeiss PMQ II spectrophotometer equipped with a thermostated (±0.1 °C) high-pressure cell,[13] under conditions very similar to those chosen by Watts et al.[1] The observed pseudo-first-order rate constants were calculated in the usual way, and such plots were linear for at least three to four half-lives of the reaction.

Results and Discussion

The results in Table I clearly illustrate that k_{obsd} and, therefore, the second-order rate constant k decrease with increasing pressure. Plots of ln k vs. pressure are linear, from which the volume of activation, $\Delta \bar{V}^{\ddagger}_{exptl}$, was calculated in the usual way. The reported rate constants at normal pressure are in close agreement with the values 2.7 × 10^{-2} and 7.1 × 10^{-2} M^{-1} s^{-1} (for water and Me_2SO, respectively) extrapolated from the activation parameters reported by Watts et al.[1] A similar agreement exists between $\Delta \bar{V}^{\ddagger}$ found for the redox reaction in water and that reported by Halpern et al.[7]

The volume of activation for an inner-sphere redox reaction is a composite of the volume change associated with the precursor formation ($\Delta \bar{V}_{PC}$) and the volume of activation for the electron-transfer step ($\Delta \bar{E}^{\ddagger}_{ET}$) such that

$$\Delta \bar{V}^{\ddagger}_{exptl} = \Delta \bar{V}_{PC} + \Delta \bar{V}^{\ddagger}_{ET}$$

A detailed discussion[8] has illustrated that two major contributions are expected to determine the magnitude of $\Delta \bar{V}_{PC}$ and, therefore, $\Delta \bar{V}^{\ddagger}_{exptl}$: first, a large volume increase due to the

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Table I. k_{obsd} as a Function of Pressure for the Reduction of $Co(NH_3)_5N_3^{2+}$ by Fe(II)[a]

	solvent = H_2O[b]			solvent = Me_2SO[c]		
p, bar	10^2[Fe(II)],[d] M	$10^4 k_{obsd}$, s^{-1}	$10^2 k$,[e] M^{-1} s^{-1}	10^2[Fe(II)],[d] M	$10^4 k_{obsd}$, s^{-1}	$10^2 k$,[e] M^{-1} s^{-1}
10	2.10	3.08	1.47	2.05	1.61	7.87
	2.12	3.35	1.58	2.07	1.62	7.84
500	2.01	2.31	1.15	1.93	1.31	6.80
	2.07	2.51	1.21	1.98	1.35	6.82
1000	2.04	1.96	0.96	2.15	1.31	6.08
	2.04	2.00	0.98	2.04	1.25	6.14
1500	2.18	1.61	0.74	1.95	1.05	5.40
	2.19	1.65	0.75	1.97	1.04	5.27
$\Delta\bar{V}^{\ddagger}_{exptl}$, cm^3 mol^{-1}		12.1 ± 0.5			6.5 ± 0.2	

[a] [Co(III)] = 1.2×10^{-3} M, $[H^+]$ = 0.1 M, ionic strength = 0.34 M, temp = 40 °C, wavelength = 515 nm. [b] $[H^+]$ controlled with $HClO_4$; ionic strength controlled with $NaClO_4$. [c] $[H^+]$ controlled with *p*-toluenesulfonic acid; ionic strength controlled with $KClO_4$. [d] Weighed as $[Fe(OH_2)_6](ClO_4)_2$; not corrected for the compressibility of the solvent, which amounts to 2, 3, and 4% at 500, 1000, and 1500 bar, respectively. [e] $k_{obsd} = k$[Fe(II)].[1]

Table II. Activation Parameters for the Reduction of $Co(NH_3)_5X^{2+}$ by Fe(II)[a]

	solvent = H_2O			solvent = Me_2SO		
X	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta\bar{V}^{\dagger}_{exptl}$,[b] cm^3 mol^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta\bar{V}^{\ddagger}_{exptl}$,[b] cm^3 mol^{-1}
F	56.0	−96[14]	10.7 ± 0.1 (25)[16]	36.8	−108[2]	10.3 ± 0.4 (35)[8]
	57.2	−96[15]				
Cl	60.6	−96[14]	8.7 ± 0.3 (35)[16]	88.6	+12[2]	3.8 ± 0.7 (35)[8]
	52.2	−125[15]				
Br	65.2	−84[14]	6.4 ± 1.1 (35)[16]	90.7	+8[2]	0.0 ± 0.4 (35)[8]
	55.6	−117[15]				
N_3	63.0	−74[1]	12.1 ± 0.5 (40)	80.5	−10[1]	6.5 ± 0.2 (40)

[a] References for literature data are given as superscripts. [b] Temperature (in °C) is quoted in parentheses.

release of a solvent molecule on forming the precursor complex[6] and, second, a volume decrease stemming from bond formation between Fe(II) and the bridging ligand (i.e., Cl, Br, N_3). The latter contribution should depend on the size of the species involved and is, therefore, expected to vary with the van der Waals radii of the bridging atoms. The results in Table I illustrate positive $\Delta\bar{V}^{\ddagger}_{exptl}$ values for the reduction of $Co(NH_3)_5N_3^{2+}$ in both solvents. The even smaller value of Me_2SO than for water is not in agreement with the suggested mechanism of Watts et al.[2] since when a tetrahedral Fe(II) center is present in the precursor complex in Me_2SO, three solvent molecules must be released during this formation process, which would result in a large positive $\Delta\bar{V}^{\ddagger}_{exptl}$. We cannot, therefore, support the suggested change in geometry around the Fe(II) center in the precursor complex on changing the solvent from water to Me_2SO. Our earlier results[8] on the Fe(II) reduction of $Co(NH_3)_5X^{2+}$ (X = F, Cl, Br) showed similar tendencies (see Table II), and an alternative explanation was presented to account for the observed effects.

Watts,[17] however, suggested that a possible explanation for the latter tendencies may lie in the difference in volume of the separate octahedral iron(II) complex and the contribution made to the precursor complex by a tetrahedral iron(II) center. Although this may partially be true, the release of an additional two Me_2SO molecules during the formation of the precursor complex must at least result in some volume increase since it is generally true[6] that the partial molar volume of a solvent molecule in the first coordination sphere surrounding a metal ion is significantly smaller than that in the bulk solvent. In addition, recent measurements[18] illustrated that $\Delta\bar{V}_{PC}$ is indeed a large positive quantity for such precursor formation processes. However, the experimental results of this and our earlier study[8] do not provide any evidence to support the suggestions of Watts and co-workers,[1-4] such that the suggested change in geometry around the Fe(II) center seems to be highly unlikely.

Combining the present results with those reported before,[8] as illustrated in Table II, allows for some general comments to be made. $\Delta\bar{V}^{\ddagger}_{exptl}$ for the reduction of $Co(NH_3)_5N_3^{2+}$ lies between the values for $Co(NH_3)_5F^{2+}$ and $Co(NH_3)_5Cl^{2+}$ in Me_2SO and is the largest of the data reported for the reaction in water. The decrease in $\Delta\bar{V}^{\ddagger}_{exptl}$ according to the series F > N_3 > Cl > Br parallels the increase in the van der Waals or covalent radii of the bridging atoms, if N_3 is assumed to behave like a nitrogen atom. Thus the negative contribution toward $\Delta\bar{V}_{PC}$ and $\Delta\bar{V}^{\ddagger}_{exptl}$ due to bond formation (see earlier discussion) increases along the series and fits the observed tendency in $\Delta\bar{V}^{\ddagger}_{exptl}$.

The activation parameters in Table II show a strong solvent dependence. The decrease in $\Delta H^{\ddagger}$ for $Co(NH_3)_5F^{2+}$ on going from water to Me_2SO was ascribed[8] to a decrease in hydrogen bonding and electrostriction. For the remaining systems, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ increase significantly, whereas $\Delta\bar{V}^{\ddagger}$ decreases approximately 5 cm^3 mol^{-1} on going from water to Me_2SO as solvent. This is ascribed to the increased steric crowding on the $Fe(Me_2SO)_6^{2+}$ ion, which results in a later transition state,[19,20] accompanied by a more negative $\Delta\bar{V}^{\ddagger}_{exptl}$ value. In addition, the process is expected to be less associative in character, in line with the increase in $\Delta S^{\ddagger}$. It follows that changes in solvation and steric crowding can possibly account for the observed changes in the activation parameters on changing the solvent.

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