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Pressure Effects and the Associative Mechanism of Substitution in Aqueous Ruthenium(III) Chemistry

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The volume of activation for aquation of $Ru(NH_3)_5Cl^{2+}$ in acidic aqueous solution at 60 °C is -30 cm^3 mol^{-1} at zero pressure but is markedly pressure dependent. The corresponding parameter for the reverse process is -20 cm^3 mol^{-1}, as measured directly and confirmed by densimetry. These and other data support accumulating evidence that an associative (A, or S_N2 limiting) mechanism is quite general in simple substitution reactions of ruthenium(III) complexes in solution.

Introduction

The recent lively activity in ruthenium chemistry has produced several lines of evidence which suggest that simple ligand substitution processes at ruthenium(III) centers in aqueous solution may be associatively activated. These include the effect of charge on the aquation rates of ruthenium(III) haloammines,[1] the extraordinarily high rate[2] and low activation enthalpy (ΔH^*) and entropy (ΔS^*)[3] of substitution of NH_3 by NO in $Ru(NH_3)_6^{3+}$, $Ru(NH_3)_5Br^{2+}$, etc., the effect of water activity on the aquation rate of $RuCl_6^{3-}$,[4] and the strong dependence of the rate of substitution of water in $Ru(edta)OH_2^-$ upon the nature of the incoming ligand.[5] Even for the anation of $Ru(NH_3)_5OH_2^{3+}$ in its solid halide salts, a seven-coordinate intermediate seems to be involved.[6] Certainly, the strict stereoretentivity of substitution in ruthenium(III) ammine and ethylenediamine complexes in solution[1,7-9] stands in contrast to the stereochemical change found for many of the analogous cobalt(III) complex reactions for which dissociative activation has been established and would be consistent with associative attack on the ruthenium(III) center cis to the ligand being replaced, as in platinum(II) complexes.[10-12]

Arguments for dissociative activation of ruthenium(III) complexes, however, have been made on various grounds, e.g., the effects of the composition of solvent mixtures on the rates of solvolysis of $Ru(NH_3)_5Cl^{2+}$ and *cis*-$Ru(NH_3)_4Cl_2^+$ [13] and the existence of a linear free energy relationship of unit slope for aquation of some halo(carboxylato)pentaammineruthenium(III) complexes.[14] We have, therefore, examined the effect of pressure on reaction 1 to help clarify the mechanistic

$$Ru(NH_3)_5Cl^{2+} + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ru(NH_3)_5OH_2^{3+} + Cl^- \qquad (1)$$

question. This appears to be the first high-pressure study of ruthenium solution chemistry to be reported.

Mechanistic information is most readily gleaned from pressure effects on rate coefficients k when the reaction is symmetrical and involves no major charge redistribution (solvational change) in the activation process,[12,15-17] e.g., the exchange of solvent ligands in species such as $M(NH_3)_5(solvent)^{3+}$, for which ln k is a linear function of pressure P, yielding a pressure-independent volume of activation ΔV^*.[16-18] Attempts in our laboratories by S. B. Tong and others to extend this series to include the $Ru(NH_3)_5OH_2^{3+}$ water exchange, however, failed for technical reasons, such as our inability to recover from the reaction media pure, dry, stable,[6] solid salts of $Ru(NH_3)_5OH_2^{3+}$, free of lattice water, from which the coordinated water could be extracted with reproducible isotopic composition. Reactions such as (1) involve net chemical change, which necessitates correlation of ΔV_1^* for the forward reaction with ΔV_2^* for the reverse process (or, equivalently, with the equilibrium volume of reaction ΔV[19,20] or with the molar volumes of the reactants and products in a "volume profile"[21]). Furthermore, solvational changes can be important for reactions such as (1), obscuring bond-making/bond-breaking contributions to ΔV^* and introducing pressure dependence in ΔV^* (i.e., nonlinear dependence of ln k on P).[12,15,17,19,20] We show here that, in spite of these complications, high-pressure studies yield significant mechanistic information about reaction 1, especially in relation to analogous reactions of other complexes $M(NH_3)_5X^{(3-n)+}$.

Experimental Section

Chloropentaammineruthenium(III) chloride was made from commercial (Alfa Inorganics) or recycled[22] $RuCl_3 \cdot 3H_2O$ by the method of Allen and Senoff[23] and converted to $[Ru(NH_3)_5Cl](CF_3SO_3)_2$ by precipitation from water with CF_3SO_3H. The purity of the product was confirmed spectroscopically (absorption maximum at 328 nm, ϵ 1930 M^{-1} cm^{-1}; M defined as mol dm^{-3} at 21 °C and 0.1 MPa)[24] and by elemental microanalysis.

Trifluoromethanesulfonic acid (3M Co.) was purified by fractional distillation.[25] All other reagents were Certified Reagent grade. Distilled water was passed through Barnstead deionizer and organic removal cartridges before use.

Kinetic Measurements. In all cases, the $Ru(NH_3)_5Cl^{2+}$ concentration was monitored at 328 nm with a Cary Model 17H spectrophotometer. Runs at atmospheric pressure were carried out by withdrawing samples at suitable intervals from solutions in ordinary glassware, darkened with aluminum foil, in a conventional thermostated bath (±0.02 °C; thermometer calibrations traceable to NBS). Runs under elevated pressure were made by three different methods: (a) withdrawal of samples from a thermostated, pressurized syringe through a tantalum capillary;[19] (b) in situ measurement of the optical density of the solution sample contained in a le Noble–Schlott cell[26] inside an Aminco 41-11551 optical pressure vessel; and (c) in situ spectrophotometric measurements on the solution sealed in a flexible PTFE tube closed with sapphire windows in an optical pressure vessel similar to the 400-MPa cell described by Scholz, Lüdemann, and Franck[27] but serviceable only to about 200 MPa. These methods avoided contact between the Ru-containing solutions and ferrous alloys, as the latter catalyzed decomposition of the former with precipitation of a black solid. In methods b and c, pressure was transmitted to the sample cell by water, and the temperature of the pressure vessel was controlled (±0.05 °C) by circulating water from a thermostat through a jacket.

For the aquation of $Ru(NH_3)_5Cl^{2+}$, solutions of the trifluoromethanesulfonate salt ($\sim 1 \times 10^{-4}$ M for method a, 5×10^{-4} to 2×10^{-3} M for methods b and c) in 0.01 M trifluoromethanesulfonic acid were made up immediately before use. For the chloride anation of $Ru(NH_3)_5OH_2^{3+}$, the latter ion was freshly generated in solution[24] by base hydrolysis of $[Ru(NH_3)_5Cl]Cl_2$ followed by reacidification with HCl and CF_3SO_3H to give a final $[H^+]$ of 0.010 M and the desired $[Cl^-]$, the ionic strength being adjusted to 0.11 M with CF_3SO_3Na; the reaction was followed by method c.

Density Measurements. Densities of solutions relative to dry N_2 and to pure water were measured to ±3 ppm, by using a Sodev Model O2D vibrating tube densimeter, thermostated to ±0.001 °C, in conjunction with a Systron-Donner 6150 frequency meter. The volume change ΔV accompanying reaction 1 was obtained from density measurements on a series of solutions made up in two ways. (i) Solid $[Ru(NH_3)_5Cl]Cl_2$ was dissolved in water at 21 °C and treated with 0.3 M NaOH; when base hydrolysis was complete,[24] an excess of 1.5 M HCl was added, the solution was made up to 50.0 cm^3, and the

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Table I. Pressure Dependence of the Rate of Aquation of $[Ru(NH_3)_5Cl](CF_3SO_3)_2$ in Aqueous CF_3SO_3H at 60.0 °C

P/MPa	[Ru]/mM	method[a]	$10^5k_1/s^{-1}$
0.1	0.101	glassware	4.23
4.5	0.60	c	4.07
5.0	0.102	a	4.36
10.0	0.102	a	4.38
25.0	0.107	a	5.14
30.0	1.65	c	5.54
40.0	0.104	a	5.71
40.0	0.103	a	5.70
50.0	1.04	c	6.42
70.0	1.61	c	6.50
80.0	0.107	a	7.98
90.0	0.130	a	7.99
125.0	0.099	a	8.11
150.0	0.103	a	8.92
183.0	1.02	c	9.14
205.0	1.01	c	10.0
210.0	0.104	a	10.4
258.0	0.94	b	11.1
290.0	0.102	a	12.5

[a] See Experimental Section.

Table II. Least-Squares Analysis of Data of Table I

$\ln k_1$	$10^5k_1^0$/ s^{-1} calcd	ΔV_1^{0*}/ $cm^3\ mol^{-1}$	10^3(MSE) (19 data)	remarks
$a + bP^a$	4.09	−24.4 ± 1.6		$r^2 = 0.971$
$a + bP^b$	4.18	−20.9 ± 1.3		$r^2 = 0.964$
$a + bP^c$	4.82	−9.8 ± 0.8	14.0	$r^2 = 0.894$
$a + bP + cP^{2\ c}$	4.33	−19.1 ± 1.8	4.9	$(\partial\Delta V_1^*/\partial P)_T = (6.8 \pm 1.3) \times 10^{-2}\ cm^3\ mol^{-1}\ MPa^{-1}$
$a + bP + cP^2 + dP^{3\ c}$	4.05	−30.2 ± 2.4	1.9	
eq 4[c]	4.28	−20.7 ± 1.9	4.3	$x = +16 \pm 2$

[a] 0.1–50 MPa (9 data); *r* = correlation coefficient. [b] 0.1–100 MPa (12 data). [c] 0.1–290 MPa (19 data).

Table III. Pressure Dependence of the Rate of Anation of $Ru(NH_3)_5OH_2^{3+}$ by Chloride Ion at Ionic Strength 0.11 M[a] and 60.0 °C

P/MPa	$10^2k_2^b/M^{-1}\ s^{-1}$	*P*/MPa	$10^2k_2^b/M^{-1}\ s^{-1}$
0.1	1.06[c]	80.7	1.69
5.0	1.08	115.0	2.35
40.5	1.39	125.0	2.75

[a] $[Cl^-] = 0.008–0.08$ M, $[Ru] = 5 \times 10^{-4}$ M, $[H^+] = 0.01$ M; balance, $CF_3SO_3^-$ and Na^+. [b] $k_2 = k_{obsd}/[Cl^-]$. [c] In ordinary glassware; others by method c (see text).

Table IV. Volume of Reaction ΔV for the Aquation of $[Ru(NH_3)_5Cl]Cl_2$ at 25.00 °C

method[a]	[Ru]/ M	$[Cl^-]$/ M[b]	$[H^+]$/ M	$[Na^+]$/ M	*I*/M[b]	$\Delta V/cm^3\ mol^{-1}$
ii	0.0158	0.1515	0.0841	0.0199	0.199	−9.4 ± 1.0
i	0.0164	0.1095	0.0315	0.0288	0.159	−8.6 ± 1.0
ii	0.0160	0.0794	0.0074	0.0240	0.127	−8.1 ± 0.4

[a] See text. [b] After aquation.

density was measured at 25.00 °C[28] immediately. The solution was then kept at 60.0 °C, and the densities of samples were measured at intervals until the reaction was calculated to be complete[24] and no further change was observable. A small correction for incompleteness of the reanation[24] was made to the derived ΔV value. (ii) Three solutions were made up for comparison: one in which an aliquot of $[Ru(NH_3)_5Cl]Cl_2$ in solution was base hydrolyzed with NaOH and then reacidified with HCl to give $Ru(NH_3)_5OH_2^{3+}$, one in which the same amounts of NaOH and HCl as in the first solution were mixed *before* the $[Ru(NH_3)_5Cl]Cl_2$ was added (i.e., $Ru(NH_3)_5Cl^{2+}$ remained unhydrolyzed), and one reference solution with NaOH and HCl mixed as before but with water in place of the $[Ru(NH_3)_5Cl]Cl_2$ solution.

Results

Aquation of $Ru(NH_3)_5Cl^{2+}$. It was confirmed[24] that the equilibrium constant *K* for reaction 1 under our conditions (60.0 °C, 0.01 M CF_3SO_3H, $[Ru] < 2 \times 10^{-3}$ M) was ~5 × 10^{-3} M, and consequently, for the higher [Ru], it was necessary to calculate the aquation rate coefficient k_1 from eq 2, where the concentrations c_t of $Ru(NH_3)_5Cl^{2+}$ at times

$$k_1t = \frac{c_0 - c_\infty}{c_0 + c_\infty} \ln \frac{c_0^2 - c_tc_\infty}{(c_t - c_\infty)c_0} \tag{2}$$

t were calculated from the absorbance A_t, c_0 was the initial $Ru(NH_3)_5Cl^{2+}$ concentration, and c_∞, the small but sometimes significant equilibrium concentration of $Ru(NH_3)_5Cl^{2+}$, was computed along with k_1, the reaction having been followed for at least 3 half-periods. The values of c_∞ so obtained were consistent with the experimental *K* and ΔV data, although not precise enough to supplement these, and the values of k_1 for low c_0 were in good agreement with those calculated from expression 3 which assumes $k_2[Cl^-]$ to remain negligible. As

$$k_1t = \ln \{(A_t - A_\infty)/(A_0 - A_\infty)\} \tag{3}$$

expected,[29,30] experiments involving continuous exposure of the solutions to the spectrophotometer light beam gave the same k_1 values as ones in which the exposure was intermittent (i.e., photolysis was negligible) and no side reactions such as are associated with the hydrolysis of some of other ruthenium(III) haloammines[31] could be detected.

Values of k_1 obtained by the various methods were reproducible within their standard deviation of the fit to eq 2, which was typically 1–3% (method c giving the best results); these data are collected in Table I, k_1 values with standard deviations greater than 3% having been rejected despite consistency with those listed.

A plot of $\ln k_1$ vs. *P* is unmistakably nonlinear; i.e., ΔV_1^* is pressure dependent. The choice of an appropriate analytical function relating ln *k* to *P* is controversial[32–34] and will be considered in detail elsewhere. The results of nonlinear least-squares reductions of values of $\ln k_1$ to various polynomials in *P*, as well as to the adapted Tait equation[19]

$$\ln k_1 = \ln k_1^0 - P\Delta V_1^{0*}/RT - (Vx\rho/2.303RT)[(\Pi + P) \ln (1 + P/\Pi) - P] \tag{4}$$

in which *x* is the number of solvating water molecules gained in the activation process, $V = 18.3\ cm^3\ mol^{-1}$, $\rho = 0.315$, and $\Pi = 306.8$ MPa for water at 60 °C, are listed in Table II. It is evident, on the basis of the mean square errors (MSE), that the purely empirical cubic equation gives the best representation of the data, and the value it gives for the volume of activation at zero pressure, ΔV_1^{0*} ($= -bRT$ for all the polynomials), may be confirmed graphically (−30 ± 3 $cm^3\ mol^{-1}$; Table II shows that linear least-squares reduction of groups of low-pressure data also gives values approaching this).

Anation of $Ru(NH_3)_5OH_2^{3+}$ by Chloride. Because the reverse of reaction 1 was studied by initial base hydrolysis of $[Ru(NH_3)_5Cl]Cl_2$ followed by reacidification, the reproducibility of k_2 values (~4%) was poorer than for k_1, even though reanation could be driven to virtual completion with excess chloride to give pseudo-first-order kinetics (rate coefficient k_{obsd}). Accordingly, the reaction was studied only over a limited pressure range, in which $\ln k_{obsd}$ at a given chloride concentration appeared to be a linear function of pressure within the experimental uncertainty. The data of Table III give $\Delta V_2^* = -20 \pm 1.4\ cm^3\ mol^{-1}$ at 60.0 °C and ionic strength 0.11 M.

Densimetry. Table IV summarizes multiple measurements of the volume change ΔV associated with reaction 1. A slight effect of ionic strength *I* (or possibly of ion pairing between Cl^- and $Ru(NH_3)_5OH_2^{3+}$) is discernible, but a value of ΔV

$= -8$ cm^3 mol^{-1} is appropriate for the ionic strength used in the measurement of ΔV_2^* ($I \sim 0.11$ M). Since k_1 and hence ΔV_1^{0*} should be almost independent of I, we can estimate ΔV at 60 °C to be $\Delta V_1^{0*} - \Delta V_2^* = (-30) - (-20) = -10 \pm 3$ cm^3 mol^{-1}, which is in good agreement with the value for 25 °C, in view of the temperature difference. Conversely, the densimetric value of ΔV serves to confirm the validity of the volumes of activation.

The apparent molar volume of $[Ru(NH_3)_5Cl]Cl_2$ at $I = 0.119$ M (third entry in Table IV, prior to aquation) was 125.8 ± 0.9 cm^3 mol^{-1}. Assuming that the Masson parameter S_V^* for chloride ion is the same as for NaCl,[35] a small correction to the partial molal volume gives a conventional molar volume of 18.57 cm^3 mol^{-1} for aqueous chloride at $I = 0.119$ M and 25 °C, whence the conventional molar volume of aqueous $Ru(NH_3)_5Cl^{2+}$ under these conditions is 88.7 cm^3 mol^{-1} relative to $\bar{V}_{H^+}{}^0 = 0$. If $\bar{V}_{H^+}{}^0$ is taken to be -4.5 cm^3 mol^{-1},[21,35] the absolute molar volume of aqueous $Ru(NH_3)_5Cl^{2+}$ becomes 79.7 ± 1.0 cm^3 mol^{-1} which is similar to the values reported[21] for $Cr(NH_3)_5Cl^{2+}$ (83.2 cm^3 mol^{-1}) and $Co(NH_3)_5Cl^{2+}$ (85.8 cm^3 mol^{-1}). These data suggest a slight *inverse* dependence of the molar volumes of $M(NH_3)_5Cl^{2+}$ on the crystal radii of M^{3+} (70, 62, and 50 pm, respectively). The absolute molar volume of $Ru(NH_3)_5OH_2^{3+}$ may be estimated to be 66.5 ± 1.4 cm^3 mol^{-1}, again close to that reported for the Cr analogue (70.6) but markedly larger than for the Co (54.0).[21]

Discussion

The accuracy of the k_1 values is insufficient to warrant a detailed discussion of the relative merits of the equations listed in Table II, but the correlation coefficients r, the mean square errors, and the ΔV_1^* values of the first three entries emphasize that the dependence of $\ln k_1$ upon P is nonlinear and that the true value of ΔV_1^{0*} is somewhat more negative than -25 cm^3 mol^{-1}, so confirming the -30 cm^3 mol^{-1} indicated by the empirical cubic equation and by drawing a tangent at $P = 0$ to the plot of $\ln k_1$ vs. P. Thus the adapted Tait equation (4) underestimates ΔV_1^{0*} quite significantly and also produces an unreasonable value of x (the number of water molecules added during the activation process) of ~ 16 for $Ru(NH_3)_5Cl^{2+}$. This is not compatible with $x \sim 8$ for the rather extreme case of aquation of $Co(NH_3)_5SO_4^+$ (a dissociative interchange process for which additional solvation is believed to be essentially complete in the transition state[10-12]) and $x \sim 2$–4 for the more closely analogous complexes $Co(NH_3)_5X^{2+}$ and $Cr(NH_3)_5X^{2+}$.[19,20] Furthermore, deviations of the $\ln k_1$ values from the best fit to eq 4 appear to be systematic.

Equation 4 was derived[19] on the assumption of an *interchange* mechanism, i.e., one in which the intermediate of expanded or reduced coordination number is short-lived on the time scale of the relaxation of the outer coordination sphere[12] and of the nonreacting ligands,[36] and it represents the data for such reactions well. It is likely, therefore, that the inadequacy of eq 4 in representing the data for the aquation of $Ru(NH_3)_5Cl^{2+}$ reflects the operation of a mechanism in which the intermediate is *not* short-lived, and since ΔV_1^{0*} is so strongly negative, this mechanism must be of the associative (A or limiting S_N2) type. The curvature of the plot of $\ln k_1$ vs. P could presumably include a contribution from a preequilibrium generating a seven-coordinate intermediate, as well as from solvational change, and hence eq 4, which ascribes all curvature to the latter, would be inappropriate (cf. curvature for D mechanisms[36]).

More direct evidence for an A mechanism, however, comes from the experimental value of ΔV_2^* of -20 cm^3 mol^{-1} for the *anation* reaction. This reaction involves a neutralization of overall charge in forming the transition state, and hence any change in ionic solvation during the activation process can be expected to be a decrease, which would make a *positive* contribution to ΔV_2^*. The strongly negative value of ΔV_2^* can therefore be ascribed to a highly collapsed transition state, i.e., to the operation of a rather extreme associative mechanism. By contrast, values of ΔV_2^* for *interchange* mechanisms of related complexes $M^{III}(NH_3)_5X$ (calculated from $\Delta V_1^{0*} - \Delta V$) are much smaller: $\sim +1$ cm^3 mol^{-1} for M = Co, indicating I_d, and -2 to -6 cm^3 mol^{-1} for M = Cr, indicating I_a.[17,19,20] Significantly, volumes of activation on the order of -20 ± 10 cm^3 mol^{-1} have been reported for all those ligand-substitution reactions of square-planar complexes of platinum(II)[36-41] and palladium(II)[42] in solution that have been studied under pressure to date, and there is little doubt that an associative mechanism (A, or possibly I_a in some cases) operates in these systems.

We conclude that simple ligand substitution in octahedral ruthenium(III) complexes in solution occurs rather generally by an A mechanism; base hydrolyses may, however, proceed differently.[24,44,45]

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Synthesis of High-Pressure Phases of VCoSb and VFeSb with a Ni_2In ($B8_2$) Type Structure

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The high-pressure transformation of VCoSb and VFeSb from the MgCuSb-type structure ($C1_b$) to the Ni_2In-type structure ($B8_2$) was found to occur under high temperature–pressure conditions. The decrement of unit cell volume associated with the phase transformation was calculated to be about 15% in both cases, and average coordination numbers of the transition metal increased from 6 to 8.5 in the pressure-induced phase transformation.

Introduction

Pnictides with a chemical formula of MM′X (M and M′ are 3d transition metals) are best understood as intermetallic compounds and concepts of classical valency are not easily applied to them. In fact, most of these compounds show metallic behavior in electrical conductivity. On the other hand, they exhibit a variety of magnetic properties such as ferromagnetism, ferrimagnetism, antiferromagnetism, and Pauli paramagnetism. Unlike the phosphides and arsenides, systematic syntheses and investigations of antimonides have rarely been carried out.[1] We have tried to prepare antimonides in order to increase our understanding of the structures and magnetic properties which they exhibit. In the present study, hexagonal new phases of VCoSb and VFeSb with the Ni_2In-type structure ($B8_2$) were synthesized under high pressures. Cubic phases of these compositions with the MgCuSb-type structure ($C1_b$) have been previously prepared.[2] These results indicate that for these compounds polymorphic transformation from the MgCuSb- to the Ni_2In-type takes place under high pressures. This transformation is discussed from the viewpoint of crystal chemistry.

Experimental Section

For the preparation of the low-pressure phases of VCoSb and VFeSb, vanadium (99.9%), cobalt (99.99%), iron (99.99%), and antimony (99.999%) powders were mixed in the desired ratio, sealed in an evacuated silica tube, and heated in an electric furnace at 1200 °C for 24 h. After the reaction was complete, the reacted matter was cooled slowly to room temperature.

For the high-pressure experiments, the starting material obtained in this way was placed into a cylindrical BN capsule, which was thereafter inserted into a carbon tube. This assemblage was placed in a pyrophyllite cube, and the cube was subjected to high temperature–pressure conditions with a cubic anvil device. The cell assemblage is shown in Figure 1. The magnitude of pressure generated inside the cell was calibrated on the basis of the electrical transitions for Bi (2.55 and 7.7 GPa) and Ba (5.5 GPa). The temperature of the sample was determined by using a Pt/Pt/13% Rh thermocouple placed in the center of the cube.

The reaction was carried out at 5.0 GPa and 900 °C for 1 h. The sample was quenched to room temperature prior to the release of applied pressure. The products were identified by X-ray powder diffraction. Silicon was used as an internal standard.

Results and Discussion

The X-ray diffraction patterns of the low-pressure phase of VCoSb, denoted as VCoSb-I, were completely indexed on the basis of the cubic unit cell (Table I), and the value of the lattice parameter is in good agreement with that previously reported.[2] The crystal structure of this cubic phase is found to be that for MgCuSb (C1b), and atomic distribution of the low-pressure phase of VCoSb is expected to be as follows: Co, A site; V, B site; Sb, D site (Figure 2). This distribution is based on the results of the neutron diffraction analysis of MnCoSb and MnCuSb with the MgCuSb-type structure.[3,4] In the case of VFeSb, however, the product prepared by the same method as that used for VCoSb did not result in a single phase with a MgCuSb-type structure but contained a small

Table I. X-ray *d* Spacings for VCoSb-I[a] with the MgCuSb-Type Structure ($C1_b$)

hkl	d_{obsd}/nm	d_{calcd}/nm	I/I_0
111	0.3357	0.3350	61
200	0.2903	0.2901	39
220	0.2053	0.2051	100
311	0.1752	0.1749	18
222	0.1675	0.1675	7
400	0.1451	0.1450	8
331	0.1332	0.1331	3
420	0.1298	0.1297	4
422	0.1185	0.1184	11
440	0.1026	0.1026	3
531	0.09810	0.09807	3
600, 442	0.09672	0.09670	3
620	0.09176	0.09174	4

[a] $a = 0.5802$ nm.

Table II. X-ray *d* Spacings for the High-Pressure Phase of VCoSb-II with the Ni_2In-Type Structure ($C1_b$)[a]

hkl	d_{obsd}/nm	d_{calcd}/nm	I/I_0
101	0.3018	0.3016	97
002	0.2698	0.2697	29
102	0.2166	0.2166	98
110	0.2099	0.2100	100
201	0.1725	0.1723	11
112	0.1658	0.1657	17
103	0.1613	0.1612	10
202	0.1510	0.1508	15
004	0.1347	0.1349	4
211	0.1332	0.1332	4
203	0.1278	0.1279	3
212	0.1225	0.1225	10
300	0.1213	0.1212	5
114	0.1135	0.1135	9

[a] $a = 0.4200$ nm, $c = 0.5398$ nm.

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