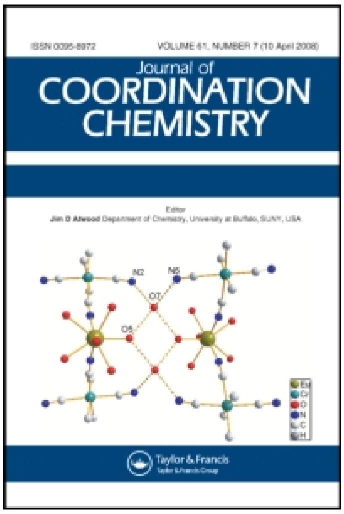

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# Partial molar volumes for inorganic complexes

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# Partial molar volumes for inorganic complexes

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Partial molar volumes are fundamental thermodynamic properties of ions, complexes, and compounds in solution; partial molar volumes of reactants and products are the components of volume profiles for reactions in solution. This review documents partial molar volumes of a varied selection of inorganic coordination complexes, preceded by an outline of partial molar volumes for metal cations, halides, and oxoanions – all in aqueous solution. The final section discusses intrinsic and electrostriction contributions to partial molar volumes and provides examples of their appearance in volume profiles.

*Keywords*: Partial molar volumes; Coordination complexes; Solvation; Volume profiles

## 1. Introduction

Partial molar volumes are thermodynamic properties of intrinsic interest as fundamental properties of species in solution. More specifically, they are key components, alongside reaction volumes and activation volumes, of volume profiles for reactions. These have proved to be of great value in the diagnosis of mechanisms of inorganic reactions during the past half century [1]. Rudi van Eldik has played a central role in the determination of both activation volumes and partial molar volumes of inorganic species, starting with initial investigations with Hartwig Kelm in Frankfurt and continuing with a range of collaborators (documented in references cited below) in Frankfurt, Witten, and Erlangen.

In this review we concentrate on values of partial molar volumes of inorganic complexes; partial molar volumes of simple cations and anions have been well-documented [2–5]. We bring together values for a selection of metal complexes, mainly of transition metal ions of $t_{2g}^3$ or low-spin $t_{2g}^6$ configurations. Such complexes are particularly suitable, as they are substitution inert and therefore amenable to the measuring techniques generally employed for obtaining the required experimental data. We shall outline trends and patterns rather than provide an exhaustive compilation, although we shall provide copious references to data sources and compilations.

The partial molar volumes of ionic species may be obtained from the molar volumes of salts, themselves obtained from density measurements or dilatometry, or they may

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be obtained by ultrasonic vibration potential [6–8] or sedimentation potential [9] techniques. These latter techniques are claimed to give single ion values directly, but there is some disagreement as to their success in so doing – the rather small number of results available from these techniques makes assessment of their validity difficult as yet. In practice almost every molar volume mentioned in this review has been obtained from density determinations. Here there are two main problems. The first problem is the need to obtain sufficiently precise and accurate density data, especially at low concentrations, and thence to extrapolate to obtain estimates for molar volumes at infinite dilution – the often-used Redlich–Mayer extrapolation method has its critics. The second problem is the choice of the most satisfactory method for splitting whole-salt molar volume values into their ionic components. This topic has been much discussed over several decades [2, 3], with numerous estimates for the partial molar volume of the proton in aqueous solution, $V_i(H^+aq)$, ranging from $-11$ to $+6\,cm^3\,mol^{-1}$. Many of the estimates are close to $-5\,cm^3\,mol^{-1}$, especially those in recent critical evaluations based on separating partial molar volumes of $Ph_4AsBPh_4$ or $Ph_4PBPh_4$ into equal ionic components, then applying a small correction to allow for a small difference in intrinsic volume between cation and anion [10, 11]. We shall use $V_i(H^+aq) = -4.5\,cm^3\,mol^{-1}$ as our reference point, reflecting the recent review devoted to aqueous systems [11], Millero's [2, 3] use of this value in his classic reviews, Mukerjee's [12] recommendation in an earlier (1961) overview of approaches to the estimation of partial molar volumes for ions, and, perhaps most relevantly in the present context, the frequent use of this basis for partial molar volumes of inorganic complexes in the references covered in the tables and discussion. Some idea of the effect of single ion assumptions on absolute values will be illustrated in Section 2.3. We shall follow common practice in this area and quote values to one decimal place, unless (a) the original report gives values to the nearest whole number or (b) a value given in the present review is our best estimate based on published values from two or more sources. All values are relative to $V_i(H^+) = -4.5\,cm^3\,mol^{-1}$, recalculated as necessary from published partial molar volumes – as far as possible from data for the salts used for the density measurements.

## 2. Discussion

### 2.1. *Aqua-cations, halides, and oxoanions*

Aqua-cations are the parents of coordination complexes, halide ligands are often leaving groups or bridges in inner-sphere electron transfer, and oxoanions are relevant here both as complexes of oxide ligands and as counterions to the cationic complexes whose partial molar volumes are derived from solution density measurements. Table 1 [4, 5, 13] includes a selection of partial molar volumes for metal ions, for halides, and for oxoanions. The data for metal cations emphasize the role played by electrostriction in determining values for the partial molar volumes of charged species in aqueous solution. Most values for 2+, 3+, and 4+ cations are negative (as is the absolute value for $H^+$), because their particularly high charge density and the consequent extensive electrostriction of water around such cations results in an overall diminution of volume on going from free cation plus water to hydrated cation in solution. In contrast,

Table 1. Partial molar volumes, $V_i$ (cm$^3$ mol$^{-1}$), for cations and anions in aqueous solution at 298.2 K. All values are relative to $V_i(H^+) = -4.5$ cm$^3$ mol$^{-1}$.

| | | | | | |
|---|---|---|---|---|---|
| $Li^+$ | −5.4 | $Be^{2+}$ | −21.0 | $Mn^{2+}$ to $Cu^{2+}$ | −26.7 to −36.8 |
| $Na^+$ | −5.7 | $Mg^{2+}$ | −30.2 | $Al^{3+}$ | −55.7 |
| $K^+$ | 4.5 | $Ca^{2+}$ | −26.9 | $Cr^{3+}$ | −53.0 |
| $Rb^+$ | 9.6 | $Sr^{2+}$ | −27.2 | $Fe^{3+}$ | −57.2 |
| $Cs^+$ | 16.8 | $Ba^{2+}$ | −21.5 | $Th^{4+}$ | −71.5 |
| $F^-$ | 3.3 | $CN^-$ | 29.6 | $CO_3^{2-}$ | 4.6 |
| $Cl^-$ | 22.3 | $NCS^{-a}$ | 45.1 | $SO_4^{2-}$ | 23.0 |
| $Br^-$ | 28.9 | $NO_3^-$ | 33.5 | $S_2O_6^{2-}$ | 66.1 |
| $I^-$ | 40.7 | $ClO_4^-$ | 48.6 | $S_2O_8^{2-}$ | 88.6 |

Values are from references [4, 5], converted to $V_i(H^+) = -4.5$ cm$^3$ mol$^{-1}$, unless otherwise indicated.

[a] This value, based on a consideration [13] of earlier discrepancies in reported values for $V$(KNCS), replaces the earlier often-quoted value of 40.2 cm$^3$ mol$^{-1}$.

the partial molar volumes of particularly large complexes would be expected to be large and positive, with only very small electrostriction contributions (Section 3).

Table 1 shows a steady trend down the alkali metal cations, but uneven progress from $Be^{2+}$ to $Ba^{2+}$. This irregular sequence may well be due to the changes in hydration number – $Be^{2+}$aq is tetrahedral, $Mg^{2+}$aq octahedral, $Ca^{2+}$ perhaps seven-coordinate [14], $Sr^{2+}$ and $Ba^{2+}$ of yet higher hydration number [15–17]. The partial molar volumes of the first-row *d*-block sequence show the usual crystal field pattern, increasing in magnitude from $Mn^{2+}$ to $Cu^{2+}$ (−26.7 to −36.8 cm$^3$ mol$^{-1}$) and then decreasing to $Zn^{2+}$ (−30.6 cm$^3$ mol$^{-1}$). The partial molar volumes of the *f*-block lanthanide sequence (−52 to −59 cm$^3$ mol$^{-1}$ for $La^{3+}$ to $Lu^{3+}$) reflect the change in hydration number from nine to eight around the middle of the series [2–5, 18–21]. All the partial molar volume values for anions are positive; however, the very small values for fluoride and carbonate suggest that solvation of these hydrophilic species is almost balancing the intrinsic size contribution to the overall partial molar volume.

## 2.2. *Binary complexes*

Table 2 [22–37] lists values for the partial molar volumes of a range of binary (homoleptic) complexes $ML_6^{n\pm}$ and $M(LL)_3^{n\pm}$, where L and LL are mono- and bidentate ligands, respectively. The partial molar volume of $Cr(NH_3)_6^{3+}$ is larger than that of $Cr(OH_2)_6^{3+}$ ($V_i = 57.0$ cm$^3$ mol$^{-1}$) [27], in contrast to −53.0 cm$^3$ mol$^{-1}$ for $Cr^{3+}$ (table 1). $V_i\{Cr(urea)_6^{3+}\}$ is 240.3 cm$^3$ mol$^{-1}$ [27]; $V_i\{Cr(NCS)_6^{3-}\} = 249.2$ cm$^3$ mol$^{-1}$ [23]. The hexa-ammine complexes follow the expected sequence Cr > Co < Rh < Ir; $Cr(en)_3^{3+}$ similarly has a larger value (127 cm$^3$ mol$^{-1}$ [27, 29] than $Co(en)_3^{3+}$, whose recommended value ($V_i = 121$ cm$^3$ mol$^{-1}$) is based on data in references [25, 27, 29, 38]. Partial molar volumes for the $Ni(en)_3^{2+}$ and $Pt(en)_3^{4+}$ analogs are 162.1 cm$^3$ mol$^{-1}$ [29] and 95.3 cm$^3$ mol$^{-1}$ [25], respectively; for $Co(pn)_3^{3+}$ [39] and $Co(tn)_3^{3+}$ [29, 39] $V_i = 174$ and 164 cm$^3$ mol$^{-1}$.

The 1,10-phenanthroline analogs of the $M(bipy)_3^{2+}$ cations have partial molar volumes approximately 40 cm$^3$ mol$^{-1}$ larger [38, 40, 41], although the value reported for $Zn(phen)_3^{2+}$ is, unexpectedly, not smaller than that for $Cu(phen)_3^{2+}$ [40]. The partial molar volumes for a series of tris-diimine-iron(II) cations cover the range

Table 2. Partial molar volumes, $V_i$ (cm$^3$ mol$^{-1}$), for binary complexes at 298.2 K. All values are relative to $V_i(H^+) = -4.5$ cm$^3$ mol$^{-1}$.

| | | | | | |
|---|---|---|---|---|---|
| $Cr(NH_3)_6^{3+}$ | 70[a] | $PdBr_4^{2-}$ | 111 | $PdBr_6^{2-}$ | 154 |
| $Co(NH_3)_6^{3+}$ | 58[b] | $PdCl_4^{2-}$ | 84 | $PdCl_6^{2-}$ | 112 |
| $Rh(NH_3)_6^{3+}$ | 65[c] | $PtCl_4^{2-}$ | 82 | $PtCl_6^{2-}$ | 110[e] |
| $Ir(NH_3)_6^{3+}$ | 72[d] | $Pt(SCN)_4^{2-}$ | 175 | $Pt(SCN)_6^{2-}$ | 240 |
| $Zn(CN)_4^{2-}$ | 122 [22] | $Fe(bipy)_3^{2+}$ | 364 | $Al(ox)_3^{3-}$ | 100 |
| $Cd(CN)_4^{2-}$ | 130 [22] | $Ni(bipy)_3^{2+}$ | 379 | $Cr(ox)_3^{3-}$ | 131 |
| $Cr(CN)_6^{3-}$ | 147.8 [23] | $Cu(bipy)_3^{2+}$ | 375 | $Fe(ox)_3^{3-}$ | 111 |
| $Fe(CN)_6^{3-}$[f] | 133[g] | $Zn(bipy)_3^{2+}$ | 360 | $Co(ox)_3^{3-}$ | 127 |
| $Co(CN)_6^{3-}$ | 132 [24] | | | $Zr(ox)_4^{4-}$ | 148 |
| $Mo(CN)_8^{4-}$ | 145.7 [25] | | | | |

Except for the cyanide complexes, all sources are referenced in the text or footnotes.

[a] Mean value from references [26, 27].

[b] Recommended value based on data in references [26–30, and references cited therein]; consistent values of 58, 60, and 56 cm$^3$ mol$^{-1}$ have been determined from the chloride, triflate, and nitrate salts, respectively – albeit at 293 K rather than at 298 K [88–90].

[c] Mean value from references [31–33].

[d] Mean value from references [31, 32].

[e] The much higher value of 159 cm$^3$ mol$^{-1}$ (relative to $V_i(H^+) = -4.5$ cm$^3$ mol$^{-1}$) for $PtCl_6^{2-}$, which appears in several earlier publications, appears to be based on density data dating from 1895 [34].

[f] $V_i = 90$ cm$^3$ mol$^{-1}$ for $Fe(CN)_6^{4-}$ [2, 3, 35–37].

[g] Recommended value based on data in references [2, 3, 36, 37].

163–605 cm$^3$ mol$^{-1}$ going from $Fe(gmi)_3^{2+}$ to $Fe(Me_2bsb)_3^{2+}$ – gmi is the small ligand MeN=CHCH=NMe, while Me$_2$bsb is the large and hydrophobic Schiff base formed from phenyl 2-pyridyl ketone and 3,4-dimethyl aniline [42]. Partial molar volumes of a number of halide and thiocyanate complexes of palladium and platinum, in 2+ and 4+ oxidation states, are available [34]. The sequence of oxalate complexes in table 2 [43] puts the aluminum complex in context with its *d*-block analogs (the $Cr(ox)_3^{3-}$ value is a mean [43, 44]), and includes the value for the tetra-oxalate complex of zirconium(IV) [44], where the bulk of the extra oxalate has a larger effect than the increase in charge.

### 2.3. *Ternary complexes*

In relation to volume profiles, binary complexes $ML_x^{n\pm}$ are preferable for studying outer-sphere electron transfers, but the ternary complexes of the form $ML_yX^{m\pm}$ – e.g. $Co(NH_3)_5Cl^{2+}$ – are usually more appropriate for study of inner-sphere electron transfer and substitution processes. Table 3 [30, 45, 46] forms a link between this and the previous section, showing how partial molar volumes vary with successive ligand replacements as one binary complex undergoes stepwise change to another. Secondly, it shows how the choice of single-ion reference assumption affects partial molar volumes. For the iron-diimine-cyanide sequence, the change in overall charge from 2+ to 4− results in a change in the range of values, with the difference between $Fe(phen)_3^{2+}$ and $Fe(CN)_6^{4-}$ being 314 cm$^3$ mol$^{-1}$ for $V_i(H^+) = -4.5$ cm$^3$ mol$^{-1}$, 341 cm$^3$ mol$^{-1}$ for $V_i(H^+) = 0$. Thirdly, the entries for the $Fe(CN)_4(diimine)^{2-}$ anions [45] illustrate the effect of varying ligand size.

Table 3. Partial molar volumes, $V_i$ (cm$^3$ mol$^{-1}$), for cobalt(III)-nitro-ammine and iron(II)-diimine-cyanide complexes, in aqueous solution at 298.2 K.

| Complex[a] | $V_i(H^+) = -4.5$ cm$^3$ mol$^{-1}$ | Complex | $V_i(H^+) = -4.5$ cm$^3$ mol$^{-1}$ | $V_i(H^+) = 0$ |
|---|---|---|---|---|
| $Co(NH_3)_6^{3+}$ | 58.0 | $Fe(phen)_3^{2+}$ | 404 | 413 |
| $Co(NH_3)_5(NO_2)^{2+}$ | 80.6 | $Fe(phen)_2(CN)_2$ | (300)[b] | (300)[b] |
| *trans*-$Co(NH_3)_4(NO_2)_2^+$ | 99.8 | $Fe(phen)(CN)_4^{2-}$ | 189 | 180 |
| $Co(NH_3)_3(NO_2)_3$ | 116.2 | $Fe(CN)_6^{4-}$ | 90 | 72 |
| $Co(NH_3)_2(NO_2)_4^-$ | 134.3 | $Fe(CN)_4(gmi)^{2-}$ | 96 | 87 |
| $Co(NH_3)(NO_2)_5^{2-}$[c] | – | $Fe(CN)_4(bipy)^{2-}$ | 190 | 181 |
| $Co(NO_2)_6^{3-}$[c] | – | $Fe(CN)_4(Me_2bsb)^{2-}$ | 248 | 239 |

Values for the cobalt complexes are from reference [30], for the iron-diimine-cyanide complexes from reference [45].

[a] Values from sedimentation potential measurements [46] agree well with the tabulated values, which are derived from density measurements.

[b] Interpolated value; $Fe(phen)_2(CN)_2$ is too sparingly soluble in water for solution density measurements to be practicable.

[c] These complexes are not sufficiently stable in aqueous solution for density measurements to be practicable.

**2.3.1. Ternary metal(III) ammine or amine complexes.** Table 4 [26, 28, 30–32, 47, 48] illustrates the dependence of partial molar volumes on the nature of the metal ion, $Cr^{3+}$, $Co^{3+}$, $Rh^{3+}$, or $Ir^{3+}$ (there is minimal information on $Ru^{3+}$ [49, 50]), and on the nature of water, halide, thiocyanate, or oxoanion for several series of ternary ammine complexes. The values in table 4 for some of the most-studied complexes are our recommendations based on data in several publications. This is the case for $Cr(NH_3)_5(H_2O)^{3+}$ [26, 28, 51, 52], $Co(NH_3)_5(H_2O)^{3+}$ [26, 28, 37, 48, 52–54], $Rh(NH_3)_5(H_2O)^{3+}$ [48, 51, 52], and $Co(NH_3)_5Cl^{2+}$ [26, 28, 47, 54]. There are expected trends of Ir complexes appearing slightly larger than their Rh analogs, and both Rh and Cr complexes having significantly larger partial molar volumes than their Co analogs. The 2+ oxoanion complexes have $V_i$ values markedly less than their 1+ analogs, presumably attributable to electrostrictive effects. The –ONO complex has essentially the same volume as the $–NO_3$ complex, markedly higher than the $–NO_2$ analog. Partial molar volumes of penta-ammine complexes, $M(NH_3)_5L^{3+}$, containing uncharged potential leaving groups L = dimethyl sulfoxide, urea, or amide ligands have been determined for M = Co [53, 54] and Cr [55] in connection with the establishment of volume profiles for aquation (Section 3). Ligand volumes, with their provenance cited, are given in these publications. This series documents the effects of varying the potential leaving ligand; the effects of varying a non-leaving ligand have been established for $Co(NH_3)_4(RNH_2)X^{2+}$ (X = $N_3$, R = H; X = Cl, R = H, Me, $^i$Bu) [56], for $M(RNH_2)_5Cl^{2+}$ (M = Cr, Co; R = H, Me) [57], and, at 293 K, for $Co(NH_3)_5L^{2+}$ with L = various amine and nitrile ligands [88–90].

Table 5 [58, 59] documents partial molar volumes for two series of d$^8$ complexes, determined in connection with the establishment of volume profiles for substitution at square-planar complexes [60], predominantly associative at the Pt-dien complexes, dissociative at the Pd complexes of the sterically demanding Et$_4$dien ligand.

Partial molar volumes have been determined for a few polynuclear complexes, including the binuclear and tetranuclear cobalt(III) complexes $[(H_3N)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4]^{4+}$ ($V_i = 101$ cm$^3$ mol$^{-1}$ [61]), the tetranuclear hexol complex $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ ($V_i = 304$ cm$^3$ mol$^{-1}$ [25]), and heterobinuclear $[(H_3N)_5Rh\text{-}I\text{-}Hg]^{4+}$ ($V_i = 160$ cm$^3$ mol$^{-1}$ [33]) – cf $V_i = 94$ cm$^3$ mol$^{-1}$ for $Rh(NH_3)_5I^{3+}$ (table 4).

Table 4. Partial molar volumes, $V_i$ ($cm^3 mol^{-1}$), for ternary penta-ammine metal(III) complexes with water, halide, pseudohalide, or oxoanion sixth ligands, in aqueous solution at 298.2 K. All values are relative to $V_i(H^+) = -4.5\ cm^3 mol^{-1}$.

| | Cr | Co | Rh | | Co | Rh | Ir |
|---|---|---|---|---|---|---|---|
| $M(NH_3)_5(H_2O)^{3+}$ | 69 | 59 | 65 | $M(NH_3)_5(CO_3)^+$ | 93.6 | 98.0 | 99.3 |
| $M(NH_3)_5Cl^{2+}$ | 87.5 | 83 | 82.3 | $M(NH_3)_5(SO_4)^+$ | 92 | | |
| $M(NH_3)_5Br^{2+}$ | 92.9 | 88.5 | 91.5 | $M(NH_3)_5(ONO)^{2+}$ | 86.5 [31] | | |
| $M(NH_3)_5I^{2+}$ | 101.3 | 94.8 | 94.1 | $M(NH_3)_5(NO_2)^{2+}$ | 80.6 [30] | 88.9 [31] | 89.8 [31] |
| $M(NH_3)_5(NCS)^{2+}$ | 106.8 | 97 | | $M(NH_3)_5(NO_3)^{2+}$ | 85.4 [47] | 93.2 [32] | |

Values for $Cr(NH_3)_5X^{2+}$ complexes are from reference [26], for $Co(NH_3)_5X^{2+}$ from references [28, 47] (however, see text for X = Cl), for $Rh(NH_3)_5X^{2+}$ from reference [32], and for $M(NH_3)_5(CO_3)^+$ from reference [48] (where values for $[M(NH_3)_5(CO_3H)]^{2+}$ are also available), otherwise as indicated in the table or text.

Table 5. Partial molar volumes, $V_i$ ($cm^3 mol^{-1}$), for ternary platinum(II) and palladium(II) complexes, in aqueous solution at 298.2 K.

| Complex | $V_i$ ($cm^3 mol^{-1}$) | Complex | $V_i$ ($cm^3 mol^{-1}$) |
|---|---|---|---|
| $Pt(dien)Cl^+$ | 114.0 | $Pd(Et_4dien)Cl^+$ | 245.3 |
| $Pt(dien)Br^+$ | 120.1 | $Pd(Et_4dien)Br^+$ | 249.8 |
| $Pt(dien)I^+$ | 130.2 | $Pd(Et_4dien)I^+$ | 256.8 |
| $Pt(dien)(N_3)^+$ | 123.6 | $Pd(Et_4dien)(N_3)^+$ | 254.1 |
| $Pt(dien)(SCN)^+$ | 141.5 | $Pd(Et_4dien)(NCS)^+$ | 253.0 |

Values for $Pt(dien)X^+$ complexes are from reference [58]; for $Pd(Et_4dien)X^+$ complexes from reference [59].

Table 6. Partial molar volumes, $V_i$ ($cm^3 mol^{-1}$), for edta complexes, and for protonated forms of this ligand, at 298.2 K. All values are relative to $V_i(H^+) = -4.5\ cm^3 mol^{-1}$.

| $M(edta)^{3-}$ | | $M(edta)^{2-}$ | | | | | | $M(edta)^{-}$ | |
|---|---|---|---|---|---|---|---|---|---|
| Na | 162 | Mg | 171.9 | Mn | 173 | Zn | 177.7 | Al | 170.7 |
| K | 165 | Ca | 167.5 | Co | 177 | Cd | 174.2 | Fe | 175.2 |
| | | Sr | 170.2 | Ni | 174 | Hg | 178.4 | | |
| | | Ba | 173.9 | Cu | 177 | Pb | 187.7 | | |
| H | 164.7[a] | | | $H_2$ | 166 | | | $H_3$ | (164) |

[a] $V_i(edta^{4-}) = 149\ cm^3 mol^{-1}$ [66].

**2.3.2. Polyaminocarboxylate complexes.** A series of determinations of partial molar volumes for complexes of ethylenediamine tetraacetate (edta) provides an opportunity for linking complexes of first-row transition metal ions, $TM1^{2+}$ [62, 63], of $Cd^{2+}$, $Hg^{2+}$, and $Pb^{2+}$ [64], and of the alkaline earth cations [63, 65], as well as providing comparisons between these complexes and those of a few 1+ [66] and 3+ [63] ions (table 6). The bottom row in table 6 gives data for variously protonated forms of edta [63, 66]. Further comparisons are possible, including those with *N*-hydroxyethyl-edta, hedta, complexes of $TM1^{2+}$ [62], and of $Ni(edta)^{2-}$ with its bis-bidentate methyliminodiacetate analog Ni(mida)$_2^{2-}$, for which $V_i = 174.8\,\mathrm{cm^3\,mol^{-1}}$ [67]. The data in table 6 provide an opportunity to examine trends according to the charge and nature of the metal ion across and down the *p*- and *d*-blocks of the Periodic Table, and to compare values for the complexes with those for variously protonated forms of the ligand.

## 3. Overview

### 3.1. *Intrinsic and electrostriction contributions*

The main components of partial molar volumes are the intrinsic and electrostriction contributions. There may also be contributions from so-called void space effects [68], and from differences between solute–solvent interactions for complexes with hydrophilic or hydrophobic peripheries. The orientation of waters at the surfaces of positively and negatively charged species will also differ. The dominant role of solvation effects for small and highly charged ions is documented in Section 2.1 in relation to metal cations. The partial molar volumes of anions and of small complexes generally reflect a balance between electrostriction [69] and intrinsic contributions. It is only with particularly large complexes that electrostrictive effects become negligible. Such is believed to be the case for the large and predominantly hydrophobic organic ions $BPh_4^-$, $Ph_4P^+$, $Ph_4As^+$, and $Bu_3N(CH_2)_8NBu_3^{2+}$, which are 263.5, 287.7, 296.2, and $520\,\mathrm{cm^3\,mol^{-1}}$[70], respectively. The large and hydrophobic iron(II)-diimine complex Fe(Me$_2$bsb)$_3^{2+}$ ($V_i = 605\,\mathrm{cm^3\,mol^{-1}}$ [42]), probably aquacobalamin and methylcobalamin ($V_i = 918$ and $940\,\mathrm{cm^3\,mol^{-1}}$ [71]) and M(phen)$_3^{2+}$ complexes (M = Fe, Co, Ni, Cu, Zn; $V_i = 400$–$415\,\mathrm{cm^3\,mol^{-1}}$ [40, 41]), and perhaps the tetranuclear cobalt(III) complex $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$, $V_i = 304\,\mathrm{cm^3\,mol^{-1}}$ [25], also fall into this category. The pyrazolylborate complex Fe{HB(pz)$_3$}$_2^{2+}$ has $V_i = 341\,\mathrm{cm^3\,mol^{-1}}$, whereas in the solid state $V_0 = 337\,\mathrm{cm^3\,mol^{-1}}$ [72]; this complex, together with $Al_{13}O_{40}H_{48}^{7+}$ {$V_i = {\sim}460\,\mathrm{cm^3\,mol^{-1}}$ [73]} provide examples of inorganic species whose partial molar and intrinsic volumes are essentially equal.

For complexes of moderate size it is possible to correlate partial molar volumes with computed intrinsic volumes, particularly if account is taken of charge. Such correlation plots for ranges of 2+, 1+, and 1− cations and anions, simple and complex, give almost parallel lines, with differences in intercepts on the $V_i$ axis reflecting electrostriction [74]. The few points available for 3− and 4− complexes lie just below the line for the 2+ species, which may again be attributed to electrostriction effects. For the specific case of complexes $Co(NH_3)_5L^{3+}$ with L = one of eleven uncharged ligands there is a very good correlation of $V_i\{Co(NH_3)_5L^{3+}\}$ values with intrinsic volumes of the ligands L (from water to dimethylurea, $18$–$80\,\mathrm{cm^3\,mol^{-1}}$). For $Co(NH_3)_5X^{2+}$ with X = one of a number of singly charged ligands there is a less good, but still tolerable correlation, of almost the same slope but separated from the $Co(NH_3)_5L^{3+}$ line by $\sim 15\,\mathrm{cm^3\,mol^{-1}}$ ($V_i$ scale). Attempted correlations of $V_i$ with relative molecular masses are, as one might expect, less satisfactory. However, for restricted groups, for example, cobalt(III)-ammine and -amine complexes, satisfactory correlations may be obtained, while an overall qualitative pattern can be discerned for a wide range of inorganic complexes [45].

### 3.2. *Volume profiles*

Full analysis of volume profiles, comprising the partial molar volumes of reactants and products, the volumes of reaction, and the volumes of activation, can provide valuable information on mechanisms of reaction. Most applications of volume profiles in the diagnosis of mechanisms deal with substitution at inert metal centers, including the cases of $Pt(dien)X^+$ [58, 60] and $Pd(Et_4dien)X^+$ [59, 60] already mentioned in Section 2.3.1. However the majority of examples refer to cobalt(III), where this approach has been employed for such reactions as aquation of $Co(NH_3)_5X^{2+}$ with $X = Cl$, Br, I [75] and $X =$ (halogenated) carboxylate [76]. The use of uncharged leaving groups (alcohols, dmso, etc.) simplifies the discussion, thanks to the much smaller role played by electrostriction [53–55, 75]. Volume profile analysis indicated the operation of an $I_a$ mechanism for aquation of chromium(III) complexes, in contrast to the $I_d$ mechanism for cobalt(III) analogs [26, 28, 55], and has been used in the characterization of the $S_N1CB$ base hydrolysis mechanism [47, 77], specifically for $Co(NH_3)_4(RNH_2)Cl^{2+}$ [78]. Efforts have been made over many years to estimate partial molar volumes of transition states for dissociative substitutions, extensively for $[Co(NH_3)_5^{3+}]^\ddagger$ [26, 28, 53, 75, 79] and occasionally for transition states for limiting dissociative (*D*) substitution, for example, of $Co(CN)_5X^{3-}$ [80]. Estimates for $V_i\{[Co(NH_3)_5^{3+}]^\ddagger\}$ have ranged from about 40 to about $60\,cm^3\,mol^{-1}$ $\{V_i$ for $[Co(NH_3)_6]^{3+}$ is $58\,cm^3\,mol^{-1}$ (table 2)$\}$, while the estimated $V_i$ for $[Co(CN)_5^{2-}]^\ddagger$ is $114\,cm^3\,mol^{-1}$, which seems compatible with the value of $132\,cm^3\,mol^{-1}$ for $V_i\{Co(CN)_6^{3-}\}$ (table 2). Volume profiles have also been established for *trans*/*cis* isomerization of $Co(en)_2(H_2O)Cl^{2+}$ [81, 82], and for reaction of the hydroxo ligands of $M(NH_3)_5(OH)^{2+}$ ($M = Co$, Rh, Ir) with carbon dioxide to give carbonate complexes [48]. This last reference provides good examples of illustrations of complete volume profiles, including the partial molar volumes of reactants, transition states, and products, as well as the volumes of reaction and of activation.

Detailed volume profiles have been established for complex formation reactions between $Ni^{2+}$ and several bidentate carboxylates, for example, succinate and lactate [83]. Volume changes were determined for the successive formation of the initial association equilibrium, of the monodentate intermediate, and of the final chelate ring closure step. As volume changes for overall reaction are determined, and partial molar volumes of $Ni^{2+}$ (table 1) and of the carboxylate ligands are known [84], the complete volume profile is available on an absolute scale. Volume profiles have been particularly important in establishing the modes of activation for water exchange at the 2+ aqua ions of the first-row of the *d*-block, at the 3+ lanthanide ions [21], and at the complexes $M(NH_3)_5(H_2O)^{3+}$ ($M = Cr$, Co, Rh, Ir) [51, 52]. Here volume profiles are extremely simple, with known partial molar volumes of the (identical) reactants and products well established [table 1; 2–5, 51, 52]. The volume profile for equilibrium between $Ni(edta)^{2-}$ and $Ni(edta)(H_2O)^{2-}$, where the edta is hexa- and pentadentate, respectively, can be placed on an absolute volume scale thanks to the availability of $V_i\{Ni(edta)^{2-}\}$ (table 6) as well as activation and reaction volumes [85].

Both reactants and products are ions of known partial molar volumes for electron transfers such as the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, $Fe^{3+}/Fe^{2+}$, and $Tl^{3+}/Tl^+$ reactions [79, 86]. Apart from these rather simple reactions, full volume profiles are very difficult to achieve for electron transfer reactions, as their kinetics are often complicated by pre-equilibria. In some systems, for example, reduction of $Co(NH_3)_5L^{3+}$ or $Co(NH_3)_5X^{2+}$ by $Fe(CN)_6^{4-}$, observed activation volumes have been dissected into volume changes consequent on preliminary association of the reactants and activation volumes for the subsequent electron transfer step, but partial molar volumes are generally not available for all the reactants, intermediates, and products. Indeed, particularly for oxidations by species such as peroxodisulfate, or reduction by ascorbate, products may not be fully characterized. Similar situations often arise in bioinorganic systems, although full volume profiles have been obtained for such reactions as electron transfer in the cytochrome $c - \mathrm{Co(phen)}_3^{2+/3+}$ system. Here useful information, such as the difference in partial molar volume between oxidized and reduced forms, may be derived from volume profiles [87].

## Ligand abbreviations

| | |
|---|---|
| bipy | 2,2′-bipyridyl |
| dien | diethylenetriamine ($H_2NCH_2CH_2NHCH_2CH_2NH_2$) |
| dmso | dimethyl sulfoxide |
| edta | ethylenediamine tetra-acetate (ethane-1,2-diamine *N*,*N*,*N*′,*N*′-tetra-acetate) |
| en | ethane-1,2-diamine |
| $Et_4$dien | *N*,*N*,*N*″,*N*″-tetraethyl-diethylenetriamine ($Et_2NCH_2CH_2NHCH_2CH_2NEt_2$) |
| gmi | glyoxalbismethyleneimine (MeN=CHCH=NMe) |
| hedta | *N*-hydroxyethyl ethylenediamine tetra-acetate |
| $HB(pz)_3$ | tris(1-pyrazolyl)borate |
| $Me_2$bsb | Schiff base from phenyl 2-pyridyl ketone and 3,4-dimethyl aniline |
| mida | *N*-methyliminodiacetate |
| ox | oxalate |
| phen | 1,10-phenanthroline |
| pn | propane-1,2-diamine |
| tn | propane-1,3-diamine |

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