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Molar Volumes of Coordination Complexes in Nonaqueous Solution: Correlation with Computed van der Waals Volumes, Crystal Unit Cell Volumes, and Charge

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Little information is available to aid the prediction of molar volumes of large ions in nonaqueous solvents. This has hampered the interpretation of volume of activation results for electron-transfer and atom/electron-transfer reactions. In order to help alleviate this problem, the molar volumes of coordination complexes and a variety of other neutral and charged compounds have been studied in acetonitrile and methylene chloride solution at 1–10 mM concentrations. These data along with data from the literature have been correlated with intrinsic volumes estimated by computer graphics techniques. It is found that the molar volumes and intrinsic volumes are linearly related. In acetonitrile, as well as in methanol and in water, neutral compounds give a uniformly larger molar volume than salts of equal calculated intrinsic volume whereas, in methylene chloride, salts and neutral compounds are not distinguished.

Introduction

Through our studies of the volumes of activation for electron-transfer and atom/electron-transfer reactions of metal ion complexes in nonaqueous solution,[1-6] we have become interested in gaining a better understanding of the factors which influence the molar volumes of such complexes. A great deal of work has been done on molar volumes of solutes in aqueous solution, especially focusing on detailed thermodynamic analysis of solute–solvent interactions in dilute solutions of relatively small, simple electrolytes such as acids and alkali metal and alkaline earth metal cation salts of halides, hydroxides, and oxyanions, as well as aqua transition metal ions.[7,8] These studies evolved to a high degree of precision in both the theory and the experiment. In many cases, the apparent radii of the ions are established from the molar volume measurements. In contrast, our interests have been in the apparent molar volumes of large, often irregularly shaped complexes at concentrations of millimolar and higher in solvents such as acetonitrile and methylene chloride. We want to better understand how structural and charge distribution changes that occur on transition-state formation can lead to changes in the molar volume of the transition state compared to that of the reactants.

A common approach in analyzing molar volume data for ions is to consider two components of the molar volume, an intrinsic volume and a contribution from electrostriction of the solvent:

$$\bar{V}_{\mathrm{app}} = \bar{V}(\mathrm{int}) + \bar{V}(\mathrm{elec})$$

In the current study, we have sought to establish intrinsic volumes through computer graphics techniques. A surface is defined using crystallographic data for the complexes and the van der Waals radius about each atom; then volume within this surface is calculated. The volumes so calculated will be referred to as "van der Waals volumes". As a check, the volumes calculated in this manner can be compared to the volume of a unit cell in the crystallographic studies. Once the intrinsic volumes are established as the van der Waals volumes, the correlation between the measured apparent molar volumes and the intrinsic volumes can be analyzed, and the electrostatic term evaluated. To the extent that a correlation can be established among van der Waals volume, charge, and molar volume, this method can be extended to estimating the molar volume of proposed transition-state structures that can be constructed with molecular mechanics techniques.

Experimental Section

All commercial compounds were reagent grade and were recrystallized prior to use. The cobalt clathrochelates[9,10] and chromium isocyanide complexes[11] were prepared by literature methods. Solvents were dried over P_2O_5 and distilled under nitrogen prior to use. Solution densities were determined with a Mettler/Paar digital density meter, Model DMA 60, using a Model DMA 602 cell. The temperature of the samples was controlled to ±0.005 K using a Neslab EX-100 UHP circulating water bath. The cooling coils of the Neslab bath were controlled at 20.0 ± 0.5 K using a Precision Scientific circulating bath which in turn was cooled using tap water. The density meter was calibrated with air and the solvent of interest. The density (g/cm^3) of acetonitrile was taken as 0.7766 at 25.0 °C,[12] that of air as 0.001 185, and that of methylene chloride as 3.316 78.[12] Each batch of solvent was checked for a consistent density.

Typically, ~15-mL solutions were prepared with concentrations of 1–10 mM. The solutions were prepared by mass (±0.2 mg), and the molarity of each solution was calculated from the solution density and the molality. The density meter measures the period of oscillation of a fixed-volume glass loop containing the solution; thus the density of the solution is proportional to the square of the period. The best results were obtained by measuring the period for 5000 oscillations to 7 figures. Reproducibility between samples of the same solution was ±5 in the least significant figure. At least five samples from each solution were measured after 2–3 minutes for each reading to stabilize. The procedure was repeated for a second solution. The resulting apparent molar volumes were calculated from the density (ρ_s) and the molarity (c) of the solution, the density of the pure solvent (ρ), and the molecular weight of the solute (M):

$$\bar{V} = \frac{1000(\rho_s - \rho)}{c\rho_s} + \frac{M}{\rho_s}$$

The precision of these final values, after consideration of errors from the weighing of the samples and the period measurement, as well as the reproducibility, is estimated as 5% or 5 mL/mol, whichever is greater.

The van der Waals volumes were calculated using the volume function of MacroModel, version 3.0.[13] For comparison with molar volumes, the volume obtained, in Å^3/molecule, is converted to mL/mol by multiplying by 0.602. The algorithm, used is that of Stouch and Jurs.[14] The atomic radii (Å) used in the calculation are as follows: H, 1.2; C, 1.7; N, 1.6; O and F, 1.4; P, S, and Cl, 1.8; Br, 2.0; I and Si, 2.1; all other atoms, 1.2. This use of a small radius for metal atoms and boron appeared to have little effect, since these atoms were typically buried in the structures and contributed little to the overall volume. However, for individual ions

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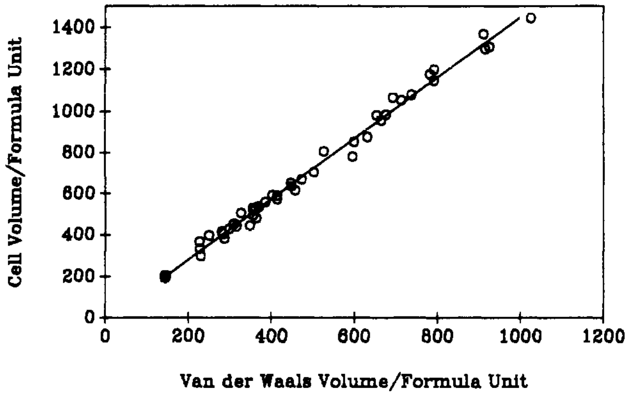

Figure 1. Correlation between the crystallographic unit cell volume per formula unit (Å^3) and the calculated van der Waals volume (Å^3) of the molecules in a formula unit.

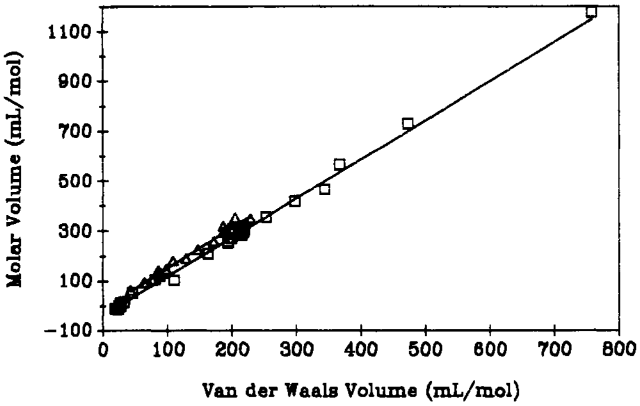

Figure 2. Correlation between the measured apparent molar volumes and calculated van der Waals volumes of solutes ((□) ionic, (△) uncharged) in acetonitrile.

not in coordination compounds, the 6-coordinate radii (Å) of Shannon[15] were used: Li^+, 0.90; Na^+, 1.16; K^+, 1.52; Cs^+, 1.81; Ag^+, 1.29. In a few cases, the crystallographic information was not available, and the coordinates were obtained by starting with a compound for which the structure was known and substituting the volume for the energy-minimized molecular fragments. An example of this was the calculation of the volume of $Co(nox)_3(BF)_2$ (ligand abbreviations are given in Table I) from the structure for $Co(dmg)_3(BF)_2$ and the difference between the volumes of dmg and nox. For salts, the volumes of the anion and cation were commonly taken from data for different structures and added. Crystallographic data were obtained from the Cambridge Structural Database System.[16] In several cases, multiple structures were used, as well as different orientations of a structure. The variation in the calculated van der Waals volumes was less than 5 Å^3. Linear least squares analysis[17] was done using ordinate values weighted by $1/\sigma^2$, where σ was estimated as 5% of the molar volume or 5 mL, whichever was greater, for the literature data as well as our own.

Results

Table I presents the molar volume data measured in this study and values from the literature, along with the van der Waals volumes that were calculated for the compounds. Table II and Figure 1 give the data for the calculated van der Waals volumes of the formula unit and the total volume of the unit cell, per formula unit, for a number of structures used in the calculations. The line in Figure 1 is the unweighted linear least squares fit to the data. It has a slope of 1.46 ± 0.02 and an intercept of −13 ± 10 Å^3. The errors in this case are calculated from the scatter about the line. Figure 2 depicts the neutral molecule and 1:1 electrolyte data for solutes in acetonitrile as a plot of molar volume vs van der Waals volume. The lines are the linear least squares fits to the two classes, weighted by the error in the molar volume as described above. Similarly, data for methylene chloride as the solvent are shown in Figure 3. The slopes and intercepts of the lines in Figures 2 and 3 are given in Table III, which also gives the analysis of literature data from Table I obtained for methanol and water as solvents.

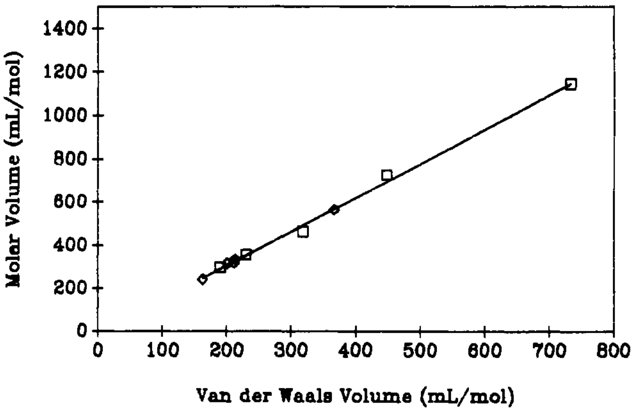

Figure 3. Correlation between the measured apparent molar volumes and calculated van der Waals volumes of solutes ((□) ionic, (◇) uncharged) in methylene chloride.

Discussion

The first concern in using the calculated van der Waals volumes to represent the intrinsic volumes of the molecules and ions is to establish that these calculated volumes do correlate with a more commonly used measure of the space occupied by the molecules. This has been approached by comparing the van der Waals volumes with the volume occupied by a formula unit in a crystal. There is expected to be some scatter, both because of the approximations made in calculating the volumes from the van der Waals radii and because of the variation in the efficiency of packing between compounds, especially due to the inclusion of ionic and neutral compounds. Figure 1 shows that there is a simple linear correlation between the two measures of volume, with the van der Waals volumes being about 70% of the volumes that are obtained from unit cell dimensions. There is no significant change in the correlation when the charged and neutral compounds are analyzed separately. The van der Waals volumes have the distinct advantage, compared to unit cell volumes, that they can be directly calculated for individual ions. In most cases, the salts for which molar volumes are available are not the same as those used in the crystallographic studies.

The majority of the data we have acquired are for the polar, aprotic solvent acetonitrile. The data presented in Table I and Figure 2 show that there is a simple linear relationship between the measured molar volume and the calculated van der Waals volume. The difference between the ionic solutes, expected to be free ions at the concentrations studied in a solvent as polar as acetonitrile, and the neutral solutes is expressed only in the intercept. The neutral solutes give an intercept near zero, while the 1:1 electrolytes give an intercept of −38 cm^3/mol, presumably reflecting electrostriction of the solvent by the ionic solutes. The linearity of the correlation is unexpected for the ionic solutes. On the basis of the Drude–Nernst equation[18]

$$\bar{V}^0(\text{elec}) = -BZ^2/r$$

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Table I. Measured Apparent Molar Volumes and Calculated van der Waals Volumes (cm^3/mol)

compound[a]	vdW vol	exptl mol vol	solvent	ref
$Co(dmg)_3(BF)_2$	140.5	295.3	CH_2Cl_2	*b*
$Co(nox)_3(BF)_2$	230.0	355.9	CH_2Cl_2	*b*
$Co(nox)_3(BPh)_2$	318.5	462.1	CH_2Cl_2	*b*
$Co(dpg)_3(BPh)_2$	447.6	727.3	CH_2Cl_2	*b*
$Cr(CNDiip)_6$	733.2	1149.5	CH_2Cl_2	*b*
I_2	42.9	62.3	CH_3CN	*b*
dimethylglyoxime	63.9	92.7	CH_3CN	*b*
nioxime	77.0	105.1	CH_3CN	*b*
$Os(cp)_2$	88.0	118.2	CH_3CN	*b*
$Ru(cp)_2$	88.0	134.8	CH_3CN	*b*
bipyridine	88.0	136.7	CH_3CN	*b*
$Fe(cp)_2$	86.2	141.9	CH_3CN	*b*
phenanthroline	97.8	145.8	CH_3CN	*b*
$Fe(CH_3cp)_2$	108.8	180.6	CH_3CN	*b*
terpyridine	128.6	190.3	CH_3CN	*b*
$HC(C_6H_5)_3$	146.5	225.0	CH_3CN	*c*
$Co(acac)_3$	171.4	256.6	CH_3CN	*b*
$Cr(acac)_3$	171.4	257.4	CH_3CN	*b*
$Os(Me_5cp)_2$	186.7	296.2	CH_3CN	*b*
$Fe((CH_3)_5cp)_2$	186.6	318.7	CH_3CN	*b*
$Zr(acac)_4$	228.6	347.8	CH_3CN	*b*
$Fe(bpy)_2(CN)_2$	205.1	351.9	CH_3CN	*b*
$CuNO_3$	23.3	−15.0	CH_3CN	*d*
NaCl	18.7	−12.0	CH_3CN	*d*
$AgNO_3$	26.8	−3.0	CH_3CN	*d*
$NaNO_3$	24.7	0.0	CH_3CN	*d*
NaI	27.4	4.9	CH_3CN	*c*
NaI	27.4	7.3	CH_3CN	*c*
NaI	27.4	11.0	CH_3CN	*d*
KI	32.3	15.7	CH_3CN	*c*
KPF_6	45.8	53.2	CH_3CN	*b*
$Fe(cp)_2BF_4$	110.4	102.2	CH_3CN	*b*
$N(CH_3)_4BF_4$	80.7	105.0	CH_3CN	*b*
$N((CH_2)_2CH_3)_4BF_4$	162.8	209.2	CH_3CN	*b*
$NaB(C_6H_5)_4$	194.0	255.0	CH_3CN	*c*
$NaB(C_6H_5)_4$	194.0	258.0	CH_3CN	*c*
$KB(C_6H_5)_4$	198.9	271.0	CH_3CN	*c*
$Co(dmg)_3(BF)_2BF_4$	215.5	282.5	CH_3CN	*b*
$As(C_6H_5)_4Cl$	211.1	284.0	CH_3CN	*c*
$As(C_6H_5)_4Cl$	211.1	285.0	CH_3CN	*c*
$N((CH_2)_3CH_3)_4I$	200.6	290.4	CH_3CN	*b*
$As(C_6H_5)_4Br$	216.5	292.0	CH_3CN	*c*
$As(C_6H_5)_4NO_3$	217.7	296.0	CH_3CN	*d*
$N((CH_2)CH_3)_4ClO_4$	204.0	304.3	CH_3CN	*b*
$As(C_6H_5)_4I$	219.9	305.0	CH_3CN	*c*
$N((CH_2)_3CH_3)_4BF_4$	201.7	307.0	CH_3CN	*b*
$As(C_6H_5)_4I$	219.9	307.0	CH_3CN	*d*
$Fe((CH_3)_5cp)_2BF_4$	211.5	308.0	CH_3CN	*b*
$Co(nox)_3(BF)_2BF_4$	253.1	355.5	CH_3CN	*b*
$Co(dmg)_3(BPh)_2BF_4$	297.7	417.8	CH_3CN	*b*
$Co(nox)_3(BPh)_2BF_4$	343.4	465.8	CH_3CN	*b*
$N((CH_2)_3CH_3)_4BPh_4$	366.8	566.8	CH_3CN	*b*
$Co(dpg)_3(BPh)_2BF_4$	472.7	730.3	CH_3CN	*b*
$Cr(CNDiip)_6BF_4$	758.2	1178.5	CH_3CN	*b*
$Cr(CNDiip)_6(BF_4)_2$	783.2	1166.9	CH_3CN	*b*
$HC(C_6H_5)_3$	146.6	221.0	CH_3OH	*e*
LiCl	16.6	−9.7	CH_3OH	*g*
NaCl	18.7	−6.0	CH_3OH	*g*
LiCl	16.6	−3.8	CH_3OH	*f*
NaCl	18.7	−3.3	CH_3OH	*f*
LiBr	22.0	−2.6	CH_3OH	*g*
NaBr	24.1	1.0	CH_3OH	*g*
NaBr	24.1	1.0	CH_3OH	*f*
KCl	23.5	6.0	CH_3OH	*g*
KCl	23.6	7.3	CH_3OH	*f*
NaI	27.4	11.8	CH_3OH	*f*
KBr	29.0	13.0	CH_3OH	*g*
NH_4Cl	23.4	13.8	CH_3OH	*g*
NH_4Br	28.8	20.7	CH_3OH	*g*
KI	32.3	21.1	CH_3OH	*g*
NH_4Br	28.8	21.9	CH_3OH	*h*
KI	32.3	21.9	CH_3OH	*f*
NH_4NO_3	30.0	29.8	CH_3OH	*g*
$N(CH_3)_4Cl$	70.5	83.0	CH_3OH	*g*
$N(CH_3)_4Br$	75.9	88.1	CH_3OH	*h*
$N(C_2H_5)_4Cl$	111.2	140.7	CH_3OH	*g*
$N(C_2H_5)Br$	116.6	146.6	CH_3OH	*h*
$N(C_2H_5)_4Br$	116.6	148.0	CH_3OH	*g*
$N(C_3H_7)_4Br$	157.7	216.6	CH_3OH	*h*
$N(C_3H_7)_4Br$	157.7	220.0	CH_3OH	*g*
$NaB(C_6H_5)_4$	194.0	241.0	CH_3OH	*e*
$NaB(C_6H_5)_4$	194.0	245.0	CH_3OH	*i*
$LiB(C_4H_9)_4$	191.9	267.8	CH_3OH	*i*
$As(C_6H_5)_4Cl$	211.1	283.0	CH_3OH	*e*
$N(C_4H_9)_4Br$	196.9	286.2	CH_3OH	*g*
$N(C_4H_9)_4Br$	196.9	286.7	CH_3OH	*g*
phenanthroline	97.5	142.2	H_2O	*j*
CH_3OH	22.2	38.05	H_2O	*k*
CH_3CH_2OH	31.5	54.97	H_2O	*k*
i-$CH_3(CH_2)_2OH$	41.4	71.73	H_2O	*k*
n-$CH_3(CH_2)_2OH$	42.7	70.2	H_2O	*k*
2-$CH_3(CH_2)_3OH$	50.2	86.64	H_2O	*k*
n-$CH_3(CH_2)_3OH$	51.4	85.72	H_2O	*k*
$C_6H_5CH_2OH$	64.8	100.82	H_2O	*k*
bipyridine	88.0	133.7	H_2O	*l*
NaCl	18.7	16.0	H_2O	*d*
NaCl	18.7	16.6	H_2O	*f*
LiCl	16.6	17.1	H_2O	*f*
NaBr	23.8	23.5	H_2O	*f*
KCl	23.6	26.8	H_2O	*f*
$NaNO_3$	24.7	28.0	H_2O	*d*
$AgNO_3$	26.8	28.0	H_2O	*d*
NaI	27.4	35.0	H_2O	*f*
LiI	25.3	35.3	H_2O	*f*
CsCl	29.7	39.2	H_2O	*f*
KI	32.3	45.2	H_2O	*f*
CsI	38.4	57.6	H_2O	*f*
$NaB(C_6H_5)_4$	194.0	276.0	H_2O	*d*
$NaB(C_6H_5)_4$	194.0	277.0	H_2O	*e*
$Pd(Et_4dien)NCSNCS$	206.4	285.9	H_2O	*m*
$Pd(Et_4dien)N_3N_3$	195.5	285.9	H_2O	*m*
$As(C_6H_5)_4Cl$	211.1	315.0	H_2O	*d*
$As(C_6H_5)_4Cl$	211.1	319.0	H_2O	*e*
$As(C_6H_5)_4Br$	216.5	329.0	H_2O	*n*
$Na_2Ni(EDTA)$	143.6	163.3	H_2O	*j*
$Na_2Ni(EDTA)$	143.6	162.7	H_2O	*o*
$Na_2Co(EDTA)$	151.4	166.0	H_2O	*j*
$Na_2Co(EDTA)$	151.4	165.4	H_2O	*o*
$Na_2Cu(EDTA)$	142.9	168.0	H_2O	*j*
$Na_2Cu(EDTA)$	142.9	163.2	H_2O	*o*
$K_2Fe(CN)_4(C_6H_6N_2)$	139.2	116.0	H_2O	*p*
$Ni(en)_3Cl_2$	154.8	206.7	H_2O	*q*
$Co(terpy)_2Cl_2$	290.8	418.9	H_2O	*r*
$Fe(phen)_3Cl_2$	321.7	445.1	H_2O	*j*
$Fe(phen)_3Cl_2$	321.7	456	H_2O	*l*
$Fe(bpy)_3Cl_2$	290.6	409	H_2O	*l*
$Ni(phen)_3Cl_2$	322.2	454.2	H_2O	*j*
$Co(phen)_3Cl_2$	321.2	456.3	H_2O	*j*
$Cu(phen)_3Cl_2$	326.7	456.5	H_2O	*j*
$Co(NH_3)_6Cl_3$	123.6	130.8	H_2O	*s*
$Co(NH_3)_6(NO_3)_3$	143.5	159.5	H_2O	*t*
$Co(en)_3Cl_3$	160.1	189.5	H_2O	*q*
$Co(en)_3Cl_3$	160.1	190.0	H_2O	*t*
$Cr(en)_3Cl_3$	170.0	192.7	H_2O	*q*
$Cr(en)_3Cl_3$	170.0	200.6	H_2O	*t*
$Co(NH_3)_6(ClO_4)_3$	161.5	207.6	H_2O	*u*

[a] Ligand abbreviations: dmg, dimethylglyoxime; nox, cyclohexanedione dioxime; dpg, diphenylglyoxime; Ph, phenyl; CNDiip, 2,6 diisopropylphenyl isocyanide; cp, cyclopentadienide; acac, acetylacetonate; bpy, bipyridine; Et_4dien, tetraethyldiethylenetriamine; en, ethylenediamine; EDTA, ethylenediaminetraacetate; terpy, terpyridine; phen, phenanthroline. [b] This work. [c] Reference 19. [d] Reference 20. [e] Reference 21. [f] Reference 7. [g] Reference 22. [h] Reference 23. [i] Reference 24. [j] Reference 25. [k] Reference 26. [l] Reference 27. [m] Reference 28. [n] Reference 29. [o] Reference 30. [p] Reference 31. [q] Reference 32. [r] Reference 33. [s] Reference 34. [t] Reference 35. [u] Reference 36.

Table II. Crystallographic Unit Cell Volumes, per Formula Unit, and van der Waals Volumes (Å^3)

compound[a]	Cambridge Refcode	vdw vol	cryst vol
$Fe(cp)_2$	FEROCE24	144.1	192
$Ru(cp)_2$	CYCPRU07	145.9	197
$Fe(cp)_2$	FEROCE01	143.3	205
$Ru(cp)_2$	CYCPRU	146.5	205
EDTA	EDTAXX02	230.3	296
EDTA	EDTAXX01	231.0	297
$Cu(en)_2(ClO_4)_2$	BETDCU10	227.7	332
$Al(Me_3)(CH_3CO_2)Me_4N$	AACMAL	226.2	365
$Ru(cp_2I)I_3$	RUTCIT10	286.5	381
$Re(MeCN)_3(CO)_3BF_4$	ACNCRE	250.4	395
$W(CO)_3(cp)(C_3H_8N_2)$	AHZCCW	283.8	403
$Tl(phen)(C_7H_5O_3)$	SAPLTL	280.0	415
$Cu(H_2N(CH_2)_4NH_2)(ClO_4)_2$	ABUCUP	298.0	426
$Co(dmg)_3(BF)_2$	COXAME	316.4	439
$Co(en)_3HgCl_3ICl$	SAYKUY	349.0	443
$Fe(Me_5cp)_2$	DMFERR01	309.1	451
$Fe(Me_5cp)_2$	DMFERR	310.5	453
$ReBr_4(NO)(C_2H_6O)(Et_4N)$	ABENRE	364.1	479
$ReBr_4(NO)(MeCN)(Et_4N)$	ABACRE	356.1	493
$Ge(acac)_3ClO_4$	ACACGE	327.1	504
$PhSiF_4(Pr_4N)$	BEPCAA	361.5	523
$Co(dmg)_3(BF)_2BF_4$	OAMECO	355.1	527
$C_{12}H_{24}O_6(MeNH_2)CF_3SO_3$	BUHBOV	369.0	534
$Cu(bpy)_2(CH_3CO_2)BF_4$	ACPCUB	385.2	556
PPh_4Br_3	BEPZEB	414.0	571
$Cu(C_7H_5N_3S_2)(ClO_4)_2$	ACMCUA	414.0	589
$W(CO)_5(C_8H_9O)Et_4N$	AMBZCW	402.1	591
$W_2C_{20}H_{20}Cl_3O(C_8H_{20}N)$	ALLCOW	457.7	613
$Na(phen)_2(C_6H_4NO_3)$	NPENRS	448.0	635
$Rb(phen)_2(C_6H_4NO_3)$	NPENRB	447.0	649
$Ph_4PTc(C_4H_8O_3S_2)$	ASMETE	474.1	668
$Cu(phen)(Me_2CS)_2I(phen)$	PBTUCU	503.0	703
$Et_4NW(CO)_2Cl_2(Ph_3P)C_3H_5$	AMACLW	596.6	780
$Ph_4PC_4H_5F_6N_2O_5S_3$	BESDOS	528.0	805
$NaC_{15}H_8N_5OMo(phen)_2$	COKZUX	601.0	852
$Ph_4PMo_2C_4H_{12}Cl_7S_2$	BIHDAX	633.0	875
$(Pr_4N)_2Cl_8Sb_8$	BOKBOS	655.1	953
$C_{41}H_{39}N_2P_2Pt(ClO_4)$	ACBEPT	654.0	980
$(CH_3CO_2)(PMe_2Ph)_4RuPF_6$	ACMPRU	677.0	982
$Ni(phen)_3(Mn(CO)_5))_2$	PNIMNC10	714.0	1050
$Me_4NFe_4(C_{24}H_{20}S_4Se_4)$	AFESES	694.0	1064
$(Bu_4N)_2Pd_2(CO)_2Cl_4$	BAHMOM	739.0	1076
$Rh(Ph_3P)_2(MeCN)_3NO\ PF_6$	ACNPRH	793.0	1142
$Ir(Ph_3P)_2(MeCN)_3NO\ PF_6$	ANPHIR	781.8	1173
$(Bu_4N)_2Ni(C_8N_4S_2Se_2)$	ASENIA	792.7	1196
$(Ph_4As)_2NbOCl_5\ CH_2Cl_2$	ASCLNB	915.0	1296
$(Ph_4As)_2MoCl_5NO\ CH_2Cl_2$	ASNOMO	925.0	1307
$(Bu_4N)_2Fe_2C_8H_{16}S_2$	BAEDTF	910.9	1367
$(Ph_4P)_2C_{18}H_{15}N_3O_6S_4$	BADCAK	1025.0	1445

[a] Abbreviations: en, ethylenediamine; Me, CH_3; Et, CH_3CH_2; Pr, $CH_3CH_2CH_2$; Ph, C_6H_5; Bu, $CH_3(CH_2)_3$.

Table III. Fit Parameters for Plots of Apparent Molar Volumes vs van der Waals Volumes

solvent	solute charge	slope	intercept, cm^3	points
CH_3CN	0	1.61 ± 0.08	−10 ± 8	17
	+1/−1	1.56 ± 0.03	−38 ± 2	32
CH_2Cl_2	0,+1/−1	1.58 ± 0.14	−12 ± 34	10
CH_3OH	+1/−1	1.53 ± 0.04	−29 ± 2	31
H_2O	0	1.44 ± 0.14	+9 ± 6	9
	+1/−1	1.54 ± 0.05	−9 ± 2	23
	±2/±1	1.68 ± 0.09	−84 ± 15	17

where Z is the charge on an ion and r is its radius, the electrostriction term should be much larger for the smaller ions. The origin of this lack of any apparent dependence of the electrostriction term on the size of the ions can be sought in several sources. First, we have avoided the consideration of particularly small ions. Second, the ions we have studied are not spheres, and thus the distance of closest approach of the solvent to the charge centers is not related to the total van der Waals volume. This is especially apparent for the substituted oxime clathrochelates $Co(dmg)_3(BX)_2^+$. Third, we are not working at the low concentrations for which limiting expressions are derived.

The data for methylene chloride as a solvent are expected to show a somewhat different pattern, since the low dielectric constant of this solvent will lead to more extensive ion pairing than for acetonitrile as the solvent. The result shows no distinction between the +1/−1 electrolytes and the neutral compounds, and a correlation line similar to that for the neutral compounds in acetonitrile is observed.

Data from the literature for methanol and water are also included. For methanol, only 1:1 electrolytes are available, and the pattern is quite similar to that observed for acetonitrile, with a slope of the molar volume vs molecular volume plot near 1.5 cm^3/(mol Å) and a negative intercept. For water as the solvent, data are available for neutral compounds and two charge types. Again, as in acetonitrile, the neutral compounds give an intercept near 0, while the more highly charged ions give correlations with negative intercepts of progressively higher magnitudes. The aqueous data are included as a general comparison with those for acetonitrile and methylene chloride. These data include some rather small ions and in many cases have higher precision than many of the remaining results, including extrapolations to infinite dilution in some cases. They could, and have been, analyzed by much more elaborate approaches.

Conclusion

We have demonstrated that, for the range of compounds we have considered, at millimolar concentrations and the precision of our measurements, there is a particularly simple relationship between the van der Waals volume of a molecule and its apparent molar volume in acetonitrile, methylene chloride, methanol, and aqueous solution. The apparent molar volume for each charge type varies linearly with the van der Waals volume, and there is an added, negative term which represents electrostriction by ionic solutes in the polar solvents but not methylene chloride. The application of this method to the calculation of reasonable estimates for the molar volume of transition-state models is anticipated. For such applications, the most important result for the polar solvents is that the electrostriction term for 1:1 electrolytes is independent of the intrinsic volume of the ions and is a large effect, amounting to −38 cm^3/mol for acetonitrile. Thus, the predicted molar volume change for the formation of an activated complex between a neutral molecule and a monocation will just be the change in intrinsic volume caused by the association. We note that the scatter about the linear correlations for a given charge type is still significant compared to volumes of activation often measured, ±10 cm^3/mol.

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Registry No. CH_3CN, 75-05-8; CH_2Cl_2, 75-09-2; $Co(dmg)_3(BF)_2$, 34248-47-0; $Co(nox)_3(BF)_2$, 141017-86-9; $Co(nox)_3(BPh)_2$, 121354-70-9; $Co(dpg)_3(BPh)_2$, 121354-69-6; $Cr(CNDiip)_6$, 61770-86-3; I_2, 7553-56-2; $Os(cp)_2$, 1273-81-0; $Ru(cp)_2$, 1287-13-4; $Fe(cp)_2$, 102-54-5; $Fe(CH_3cp)_2$, 1291-47-0; $Co(acac)_3$, 21679-46-9; $Cr(acac)_3$, 21679-31-2; $Os(Me_5cp)_2$, 100603-32-5; $Fe((CH_3)_5cp)_2$, 12126-50-0; $Zr(acac)_4$, 17501-44-9; $Fe(bpy)_2(CN)_2$, 14841-10-2; KPF_6, 17084-13-8; $Fe(cp)_2BF_4$, 1282-37-7; $N(CH_3)_4BF_4$, 661-36-9; $N((CH_2)_2CH_3)_4BF_4$, 338-38-5; $N((CH_2)_3CH_3)_4I$, 311-28-4; $Fe((CH_3)_5cp)_2BF_4$, 100021-51-0; $Co(nox)_3(BF)_2BF_4$, 130319-76-5; $Co(dmg)_3(BPh)_2BF_4$, 100113-33-5; $Co(nox)_3(BPh)_2BF_4$, 100113-35-7; $N((CH_2)_3CH_3)_4BPh_4$, 15522-59-5; $Co(dpg)_3(BPh)_2BF_4$, 100113-37-9; $Cr(CNDiip)_6BF_4$, 129239-15-2; $Cr(CNDiip)_6(BF_4)_2$, 129239-16-3; dimethylglyoxime, 95-45-4; nioxime, 492-99-9; bipyridine, 37275-48-2; phenanthroline, 66-71-7; terpyridine, 1148-79-4.

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Molecular Structure of 1-Thia-*closo*-dodecaborane(11) Studied by Electron Diffraction Complemented by ab Initio Calculations

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The molecular structure of 1-thia-*closo*-dodecaborane(11), 1-$SB_{11}H_{11}$, has been determined by gas-phase electron diffraction. A model assuming C_{5v} symmetry lead to a determination of the distortions from a regular icosahedron consisting mainly in the substantial expansion of the pentagonal belt adjacent to sulfur, with r_g(B–B) = 1.905 ± 0.004 Å. Well-determined parameters are the S–B and $(B–H)_{mean}$ distances, r_g = 2.010 ± 0.005 and 1.190 ± 0.003 Å, respectively. The geometric parameters calculated at the ab initio 3-21G(*) level, as well as the IGLO calculations (individual gauge for localized orbitals) ^{11}B chemical shifts, are in overall agreement with the experimental findings.

Introduction

Very little is known about the structures of thiaboranes. For example, the structure of the dimeric form of 1-thia-*closo*-decaborane(9), 2,2′-(1-SB_9H_8)$_2$, has been determined by X-ray diffraction.[1] A short B–B bond links the two bicapped square antiprismatic frameworks of the SB_9H_8 moieties. 1-SB_9H_9 is isoelectronic with $B_{10}H_{10}^{2-}$. In accord with Wade's rules,[2] S formally replaces a $[BH]^{2-}$ unit,[3] but causes a substantial lengthening of the nearest B–B bonds. In another investigation,[4] the photoelectron spectra of the 1-SB_9H_9 monomer and some other thiaboranes, including 1-$SB_{11}H_{11}$, have been reported and analyzed in terms of a simple approach known as the equatorial-apex model. The PES data of 1-SB_9H_9 have been assigned by means of MNDO calculations, which also revealed the cluster-bonding molecular orbitals (constructed from a B_9H_9 unit and a sulfur atom).[5] The MNDO-optimized structure also was reported, but the electronic structure of 1-$SB_{11}H_{11}$ was analyzed using an assumed molecular geometry. In order to obtain the structure of 1-$SB_{11}H_{11}$, we now report the results of an electron diffraction study (GED) complemented by ab initio calculations on the geometry and ^{11}B NMR chemical shifts.

Experimental Section

The sample of 1-thia-*closo*-dodecaborane(11) (purity >98% as assessed by TLC) was prepared by Dr. J. Plešek according to literature procedures.[6]

The electron diffraction patterns were recorded in Budapest with a modified EG-100A unit,[7] using a membrane nozzle system.[8] The nozzle temperature was about 110 °C. The accelerating voltage of the electron beam was 60 kV. Eight photographic plates were used for both camera distances (50, 19 cm), respectively. The ranges of intensity data used in the analysis were $2.0 \le s \le 13.875$ Å^{-1} and $9.50 \le s \le 33.0$ Å^{-1} with data intervals 0.125 and 0.25 Å^{-1} [$s = (4\pi/\lambda)\sin(\theta/2)$, where λ, the electron wave length, is 0.049132 Å for both camera distances and θ is the scattering angle]. The method of data treatment is described elsewhere.[9] The structure analysis was based on least-squares refinement of molecular intensities.[10] Literature coherent[11] and incoherent[12] scattering factors were employed. The final experimental and calculated molecular intensities and radial distributions are shown in Figures 1 and 2, respectively.

Structure Analysis

The 1-thia-*closo*-dodecaborane(11) molecule was assumed to have C_{5v} symmetry. The following independent parameters were used for the description of the geometry (see Figure 2): the B_3–B_7, B_7–B_8, B_7–B_{12} and $(B–H)_{mean}$ distances and the differences between S–B and B_3–B_7 (Dif_1) and B_2–B_3 and B_3–B_7 (Dif_2), as well as the S–B–H and B_{12}–B_7–H bond angles. In some refinements only the bond lengths within the cage as independent parameters (without Dif_1 and Dif_2) were used. Since no vibrational spectroscopic data were available, the vibrational parameters for 1,12-$C_2B_{10}H_{12}$[13] provided the initial values for the refinements. The vibrational amplitudes of similar distances were coupled by fixing the differences between them. Shrinkage effects were neglected.

Refinements using different starting values of S–B and B–B bonds, or using various Dif_1 and Dif_2 values converged to the same minimum without affecting the geometric parameters. Nevertheless, various refinement conditions for vibrational amplitudes may produce a strong influence on the results. Since theoretical calculations for getting better starting values of vibrational amplitudes could not be performed due to the lack of force field, a lot of refinements with various starting *l* values

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