Size and Shape Characteristics of Inorganic Molecules and Ions and their Relevance to Molecular Packing Problems

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The manner in which molecular inorganic molecules and ions pack in the solid state is important not only for the formation of crystals suitable for diffraction studies, but also contributes significantly to the conduction, magnetic and non-linear optical properties of these molecular inorganic compounds in the solid state. In order to provide a basis for discussing the role of molecular size and shape on the packing of molecular salts, the volumes, surface areas and shapes of a wide range of ions observed in co-ordination and organometallic chemistry have been calculated from the van der Waals radii of the constituent atoms. The calculated cation volumes range from 24–795 Å^3 and for the anions from 34–467 Å^3 and their shapes have been classified as spherical, discoidal and cylindrical on the basis of the calculated moments of inertia. The calculated packing coefficients for molecular salts containing spherical cations and anions lie between 65 and 71.5%. This relatively narrow range provides a methodology for estimating the volumes of spherical ions not given in this compilation. The surface areas of the ions were found to be linearly correlated with the volumes. The calculated volumes and surface areas may be used to calculate the effective radii of the ions. These radii are relevant to the development of radius ratio rules for inorganic molecular salts.

The packing of molecules in the solid state has a crucial effect on their properties.[1,2] The crystallization of salts is a prerequisite for structural characterization by diffraction techniques and depends on the relative sizes and solubility properties of the constituent ions of a molecular salt.[3] There have, however, been few attempts to model the packing modes of inorganic and organometallic molecular compounds[4] and salts.[5] The conductivity[6] and magnetic properties[7] of these salts and the non-linear optical properties of co-ordination[8] and organometallic[9] compounds also depend on the packing properties of the molecules and ions in the crystal. Although the molecular design of solid-state materials which optimize these desirable physical properties will prove to be an increasingly important concern for inorganic chemists,[10] our understanding of packing effects remains at a very primitive stage of its development. The inorganic chemist has at his disposal a wide range of cations and anions which may be used to optimize the crystallization and crystal morphology of inorganic salts, but does not have access to data on the relative sizes and shapes of the ions. In this paper the computed volumes of a large range of commonly used cations and anions are presented together with parameters for defining their shapes. It is recognised that the packing properties of inorganic compounds are not only shape and size dependent, because the intermolecular forces even for simple molecules take on a complex form,[11] but nevertheless the molecular dimensions of an ion provide an initial starting point for discussing their solid-state properties.

Calculation of Size and Shape Factors Associated with Molecular Ions

Size of Molecules.—Two parameters describing molecular shape are the molecular volume and the molecular free surface area. Several methods, both analytic[12–15] and numerical,[16–20] have been developed to calculate these quantities. All of these methods assume that a molecule consists of overlapping spheres centred on the atomic positions. The radii of these spheres are set equal to the van der Waals radii of the constituent atoms. The van der Waals radii for the non-metallic elements have been well characterized by Bondi[21] and have been extended by Gavezzotti.[16] For metallic elements, however, no complete tabulation of the van der Waals radii exists because non-bonding interactions between metal atoms are rare.[22] The radii for the small number of metals that have been determined by Bondi have been criticized by Allinger[23] who claims that they are too small by a linear deviation. Hence we have modified the radii for those metals determined by Bondi according to equation (1) where rv_B is the radius determined by Bondi.

$$rv_A = 1.34rv_B - 0.38 \qquad (1)$$

To be able to calculate the volumes and surface areas of inorganic molecules, a complete set of van der Waals radii is needed. Our solution was to set the van der Waals radius of iron arbitrarily to 2.0 Å and use this value to generate the van der Waals radii for other undetermined metal atoms according to equation (2) where rc_{metal} and rc_{Fe} are the covalent radii of the metal and iron respectively.

$$rv_{\text{metal}} = 2.0rc_{\text{metal}}/rc_{\text{Fe}} \qquad (2)$$

The values of the covalent radii were taken from the program PLUTO, part of the Cambridge Structural Database suite.[24] Although this is an approximation, the errors in the value of the volume and surface area it introduces are small for most inorganic salts. This is because most inorganic cations and anions consists of a central metal atom (or cluster) surrounded by many organic atoms, *i.e.* the metal atom(s) have a high connectivity. As a result the free surface area and volume attributed to the central metal atom(s) are small.

Nyburg and Faerman[25] have shown that the van der Waals shapes of many elements are spheroidal rather than spherical. Their study was restricted to non-metallic elements singly bonded to a carbon atom. They found that for O and N the shapes are virtually spherical but the remainder (F, S, Cl, Se, Br and I) are spheroidal, always having the shorter radius along the atom-to-carbon vector (polar flattening). We have not taken this effect into account in this work since most of the ions examined do not contain the atom–carbon bonds which display the greatest distortion. Furthermore in the molecular ions considered here the majority of the surface atoms are hydrogen.

The simplest and computationally quickest method of calculating ionic or molecular volume is the analytical approximation put forward by Kitaigorodsky.[12] This method, commonly known as the caps and spheres method, considers each atom in a molecule as a sphere with a cap cut off it for each atom to which it is bonded. Hence the volume attributed to the ith atom in the molecule is given by equation (3) where R_i is

$$V_i = \tfrac{4}{3}\pi R_i^3 - \sum_j \tfrac{1}{3}\pi h_j^2(3R_i - h_j) \qquad (3)$$

the van der Waals radius of the ith atom, the subscript j is over all atoms to which the ith atom is bonded and the h_j is the height of the cap. Hence the volume of the ion is given simply by equation (4) where N is the number of atoms in the ion. This

$$V_m = \sum_{i=1}^{N} V_i \qquad (4)$$

method has severe limitations in two situations. Firstly in sterically hindered molecules, where overlapping of the van der Waals surface occurs between atoms in the ion which are not bonded to each other, *e.g.* overlap between carbon atoms on two neighbouring CN groups in the anion $[Mo(CN)_8]^{4-}$. This shortcoming gives a volume which is too large but correcting for it is fairly straightforward. Instead of subtracting only those caps due to bonded atoms, the caps due to all atoms whose van der Waals surface intersects the van der Waals surface of the atom under consideration are subtracted. The second deficiency in the caps and spheres method occurs when two caps of an atom intersect. In this case the intersected volume is subtracted twice, giving a volume which is too small. This situation occurs in systems which have large co-ordination numbers or strained cyclic rings—a fact noted by Gavezzotti.[16] In inorganic and organometallic chemistry these conditions occur frequently therefore the caps and spheres method is an inappropriate method for volume calculations in these systems.

The methods and programs used to calculate the volume and surface area in this paper are those of Gavezzotti.[16,17] The molecular volume, V_m, was calculated by sampling a parallelepiped which contains the molecule with a large number of probe points (N), and counting the number (N_{occ}) of points inside at least one of the atomic spheres. If the volume of the parallelepiped is V_{ppd}, then the molecular volume is given by equation (5).

$$V_m = V_{ppd}(N_{occ}/N) \qquad (5)$$

By assuming that molecular ions are spherical, an effective radius based either on the calculated volume or free surface area can be derived. The effective radius based on the molecular volume can be calculated using equation (6) whilst the

$$R_{eff}(V_m) = (3V_m/4\pi)^{1/3} \qquad (6)$$

effective radius as calculated from the surface area is given by equation (7).

$$R_{eff}(S_m) = (S_m/4\pi)^{1/2} \qquad (7)$$

Another radius that can be calculated is the maximum radius, R_{max}. It is defined as the largest distance between the centroid of the ion and its outer surface. The radius R_{max} is determined by calculating the distances from the centroid of the molecule ion to the centres of the constituent atoms. The van der Waals radius of the atom is then added to each distance and the largest value obtained is defined as R_{max}.

Shapes of Molecules.—The above factors are all used to describe the size of a molecule. The parameters used in this paper to describe molecular shape are based on the moments of inertia calculated without mass weighting.[26] These values differ from those obtained by Gavezzotti[27] since his procedure generates a large moment for a short axis in a molecule which is rather counter-intuitive. Denoting the largest of the moments M_1, the middle one M_2 and the smallest one M_3, it is possible to define the following three normalised indices [equations (8)–(10)].

$$F_s = M_3/M_1 \qquad \text{spherical index} \quad (8)$$

$$F_c = 1 - [(M_2 + M_3)/2M_1] \qquad \text{cylindrical index} \quad (9)$$

$$F_d = 1 - [2M_3/(M_1 + M_2)] \qquad \text{discoidal index} \quad (10)$$

Discussion of Parameters. In Tables 1 and 2 the size and shape parameters associated with some common anions and cations taken from co-ordination and organometallic chemistry are summarised. In this section some general features associated with the parameters are discussed and specific applications to crystallization and packing problems are dealt with in subsequent papers in this series.

Molecular Volumes.—The cations and anions in Tables 1 and 2 have been chosen because they are widely used and give a reasonable spread of volumes. The largest cation listed is $[Au(PMePh_2)_4]^+$ with a volume of 795 Å^3, but the largest commonly used cation is $[N(PPh_3)_2]^+$ which has a volume of 490 Å^3 and has been used extensively for crystallizing organometallic anions. The largest anion chosen was $[Os_6(CO)_{18}]^{2-}$, which has a volume of 467 Å^3. The smallest cation and anion have volumes of 24 and 34 Å^3 respectively. Commonly used inorganic anions such as $[NO_3]^-$, $[BF_4]^-$ and $[ClO_4]^-$ have volumes in the range 100–250 Å^3. In order to estimate the variation in volume as a function of counter-ion, we have calculated the volumes of 11 randomly selected $[BPh_4]^-$ salts. The calculated volumes of the anions vary between 320.4 and 324.6 Å^3, with a mean of 323.1 Å^3 and standard deviation of 1.4 Å^3. The variation is surprisingly small considering that these ions show a large range of conformations involving rotations of the phenyl rings. Similar analyses[28] of cluster cations and anions with large volumes (>207 Å^3) have shown that the calculated volume of ions is not structure dependent. The volumes of cations occur over a wider range and cannot be partitioned into such clearly defined categories. The volumes given in Tables 1 and 2 can be used to define a packing coefficient for ionic salts in a particular crystal according to equation (11) where Z = number of formula units in the unit

$$C_k = Z[(n_a V_a + n_c V_c)/V_{cell})] \times 100\% \qquad (11)$$

cell, n_a is the number of anions and n_c the number of cations per formula unit, V_a is the volume of the anion, V_c the volume of the cation and V_{cell} the volume of the unit cell. Packing coefficients for some representative crystal structures derived from the cations and anions in Tables 1 and 2 are given in Table 3. The packing coefficients lie between 64.4 and 76.1% with an average value of 69.0% and a standard deviation of 2.3%. These values are only slightly smaller than the packing coefficients commonly observed for organic molecules.[12,28] An interesting aspect of Table 3 is that salts with discoidal cations and anions, *e.g.* [tcnq]$^-$ or $[PtCl_4]^{2-}$, generally have higher packing coefficients (70–76%) than those involving spherical cations and anions (64–71%). This is a direct consequence of the higher packing coefficients for cylinders relative to spheres. The relative constancy of the packing coefficients for inorganic salts with spherical cations and anions has several important implications. Firstly, a comparison of the calculated volume of the cell *versus* that derived crystallographically should provide confirmation of the contents of the unit cell and indicate the presence of molecules of solvent of crystallization. Indeed in the course of this work, the cell volume of one of the salts given in the literature was found to be incorrect by this process.

Table 1 Size and shape parameters of some common inorganic and organometallic cations

Cation	V_m/Å^3	S_m/Å^2	I	$R_{eff}(V_m)$/Å	$R_{eff}(S_m)$/Å	R_{max}/Å	R_{eff}/R_{max}	F_s	F_c	F_d
$[NH_4]^+$	24	43	5.22	1.78	1.85	2.15	0.83	1.00	0.00	0.00
$[NH_3Me]^+$	41	64	5.45	2.13	2.26	2.62	0.81	0.39	0.61	0.44
$[NMe_4]^+$	91	123	6.10	2.79	3.13	3.27	0.85	1.00	0.00	0.00
$[Pt(NH_3)_4]^{2+}$	99	142	6.62	2.87	3.36	3.74	0.77	0.12	0.44	0.88
$[H_3dien]^{+}$[a]	108	148	6.52	2.95	3.43	5.61	0.53	0.04	0.94	0.93
$[Cr(NH_3)_6]^{3+}$	126	176	7.03	3.11	3.75	3.70	0.84	0.93	0.07	0.04
$[Co(NH_3)_4(NO_2)_2]^+$	134	191	7.32	3.17	3.90	4.18	0.76	0.84	0.10	0.14
$[Me_2HNCH_2CH_2NHMe_2]^+$	140	182	6.77	3.22	3.81	5.14	0.63	0.09	0.81	0.85
$[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$	140	166	6.17	3.22	3.64	4.69	0.69	0.83	0.15	0.11
$[Fe(\eta\text{-}C_5H_5)_2]^+$	145	168	6.07	3.26	3.65	4.03	0.81	0.56	0.44	0.29
$[Hg(en)_2]^{2+}$[b]	150	195	6.91	3.30	3.94	5.27	0.63	0.12	0.81	0.81
$[NEt_4]^+$	156	183	6.34	3.34	3.82	4.60	0.72	0.35	0.33	0.65
$[NBu_2H_2]^+$	157	206	7.08	3.35	4.05	5.82	0.57	0.09	0.87	0.85
$[Cr(\eta\text{-}C_6H_6)_2]^+$	175	196	6.25	3.47	3.94	4.25	0.82	0.79	0.21	0.13
$[Cr(en)_3]^{3+}$	192	236	7.09	3.58	4.33	4.96	0.72	0.38	0.32	0.61
$[Co(pn)_3]^{3+}$[c]	253	317	7.94	3.92	5.03	6.13	0.64	0.39	0.30	0.61
$[Cr(tn)_3]^{3+}$[d]	256	303	7.53	3.94	4.91	5.69	0.69	0.39	0.38	0.58
$[PMePh_3]^+$	271	310	7.39	4.01	4.96	6.65	0.60	0.39	0.32	0.60
$[AsMePh_3]^+$	278	311	7.29	4.05	4.97	6.69	0.61	0.49	0.25	0.51
$[NBu_4]^+$	287	346	7.95	4.09	5.25	7.07	0.58	0.14	0.43	0.86
$[Fe(\eta\text{-}C_5Me_5)_2]^+$	309	362	7.92	4.20	5.37	5.31	0.79	0.89	0.06	0.11
$[PPh_4]^+$	317	349	7.52	4.23	5.27	6.69	0.63	0.90	0.08	0.07
$[AsPh_4]^+$	334	364	7.57	4.30	5.38	6.94	0.62	0.82	0.09	0.17
$[Co(PMe_3)_4]^{3+}$	338	425	8.75	4.32	5.82	5.74	0.62	0.83	0.16	0.10
$[Co(\eta\text{-}C_6Me_6)_2]^+$	361	397	7.82	4.42	5.62	5.50	0.80	0.81	0.10	0.19
$[Fe_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]^+$	384	390	7.39	4.51	5.57	5.71	0.79	0.57	0.36	0.33
$[Ni(bipy)_3]^{2+}$[e]	448	483	8.26	4.75	6.20	7.17	0.66	0.88	0.08	0.09
$[Ni_6(\eta\text{-}C_5H_5)_6]^+$	470	504	8.33	4.82	6.33	5.45	0.68	1.00	0.00	0.00
$[Ni(phen)_3]^{2+}$[f]	485	514	8.32	4.87	6.39	7.49	0.65	0.60	0.26	0.36
$[N(PPh_3)_2]^+$	490	543	8.73	4.89	6.57	7.76	0.63	0.70	0.27	0.20
$[Au(PPh_3)_3]^+$	761	836	10.03	5.66	8.15	8.33	0.44	0.60	0.23	0.38
$[Au(PMePh_2)_4]^+$	795	879	10.25	5.75	8.36	8.21	0.52	0.78	0.22	0.12

[a] dien = Diethylenetriamine. [b] en = Ethylenediamine. [c] pn = Propylenediamine (1,2-propanediamine). [d] tn = Trimethylenediamine (1,3-propanediamine). [e] bipy = 2,2′-Bipyridine. [f] phen = 1,10-Phenanthroline.

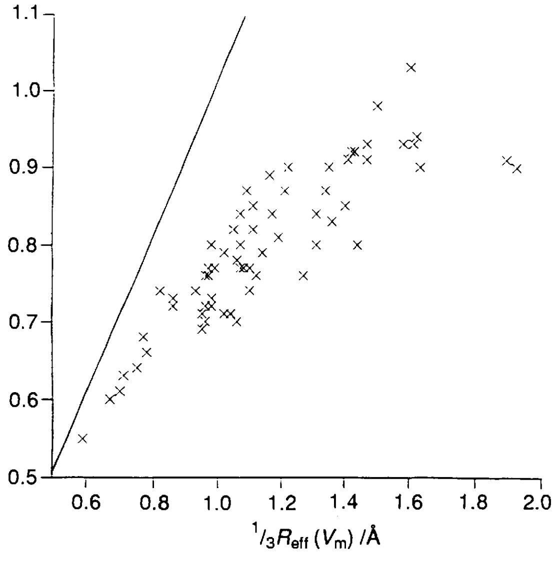

Fig. 1 Plot of the exposure ratio *versus* $\frac{1}{3}R_{eff}(V_m)$

Secondly, the packing coefficient may be used to estimate the volume of a cation or anion not included in this work. For example, assuming a packing coefficient of 68.9% for a 1 : 1 salt composed of spherical ions should provide a volume for either the cation or anion with an accuracy of 10% if both the anion and cation are of comparable size and the volume of one of the ions is known.

Molecular Surface Area.—Gavezzotti[17] has calculated the surface areas of organic molecules, and demonstrated that the ratio of volume to surface area (the exposure ratio E_r), provides an important parameter for rationalising the structures of organic molecules. Therefore the surface areas of the cations and anions are included in Tables 1 and 2. Gavezzotti has observed that as molecular size increases, E_r increasingly drifts away from the value expected for a sphere ($R/3$ for a sphere of radius R). This deviation occurs because an increase in molecular size is achieved by increasing the number of atoms in the molecule which in turn makes the van der Waals surface less regular. These irregularities give a surface area larger than that expected for a sphere and this effect is magnified as the size of the molecule is increased. In Fig. 1 E_r is plotted against $\frac{1}{3}R_{eff}(V_m)$ for the ions in Tables 1 and 2. The values expected for a sphere are represented by the straight line. As expected, the exposure ratio increasingly drifts from the spherical value as the ion size is increased. Note that if these ions were true spheres then the magnitude of the volume would become greater than the magnitude of the surface area when R_{eff} is equal to 3 Å. Only one point on the graph, however, has an exposure ratio greater than unity (*i.e.* $V_m > S_m$) and it has a $R_{eff}(V_m)$ value of 4.81 Å. This point corresponds to the anion $[Os_6(CO)_{18}]^{2-}$ and its high exposure ratio is a consequence of both its large size and its closeness to the spherical ideal.

A more unexpected observation results when the surface areas of the ions are plotted against their volumes as shown in Fig. 2. If the ions were spheres we would expect the data points to lie on a $1/R$ curve whereas Fig. 2 displays a linear relationship. The correlation coefficient is 0.995 showing that the linear relationship is a good one. The line of best fit is $S_m = 29.8 + 1.04V_m$, *i.e.* the surface area may be derived from the volume by simply adding 30 Å^2 to it!

The ratio of the surface area to volume depends on the effective radius of the sphere, whereas the quantity $I = S_m/V_m^{2/3}$

Table 2 Size and shape parameters of some common inorganic and organometallic anions

Anion	V_m/Å^3	S_m/Å^2	I	$R_{eff}(V_m)$/Å	$R_{eff}(S_m)$/Å	R_{max}/Å	R_{eff}/R_{max}	F_s	F_c	F_d
$[NO_3]^-$	34	58	5.46	2.02	2.14	2.67	0.75	0.00	0.50	1.00
$[BF_4]^-$	38	63	5.55	2.09	2.24	2.70	0.78	1.00	0.00	0.00
$[ClO_4]^-$	47	74	5.64	2.24	2.42	2.90	0.77	1.00	0.00	0.00
$[SiF_5]^-$	52	77	5.51	2.32	2.48	2.95	0.79	0.70	0.30	0.18
$[PF_6]^-$	54	82	5.75	2.34	2.55	2.88	0.81	1.00	0.00	0.00
$[AsF_6]^-$	63	86	5.40	2.47	2.62	3.02	0.82	1.00	0.00	0.00
$[SbF_6]^-$	71	98	5.73	2.57	2.79	3.25	0.79	1.00	0.00	0.00
$[Au(CN)_2]^-$	73	100	5.75	2.59	2.82	4.67	0.55	0.00	1.00	1.00
$[CuCl_4]^-$ (distorted tetrahedron)	97	141	6.65	2.85	3.35	4.03	0.71	0.42	0.31	0.57
$[CuCl_4]^-$ (square planar)	98	138	6.48	2.86	3.31	4.07	0.70	0.00	0.51	1.00
$[NiCl_4]^{2-}$	100	139	6.45	2.88	3.33	4.03	0.72	1.00	0.00	0.00
$[FeCl_4]^-$	101	132	6.12	2.88	3.25	3.94	0.73	1.00	0.00	0.00
$[FeH(CO)_4]^{2-}$	103	133	6.07	2.90	3.25	4.32	0.67	0.76	0.12	0.24
$[PtCl_4]^{2-}$	104	137	6.18	2.92	3.30	4.08	0.72	0.00	0.50	1.00
$[I_3]^-$	107	133	5.90	2.94	3.25	5.03	0.59	0.00	1.00	1.00
$[HgCl_4]^{2-}$	107	148	6.55	2.94	3.43	4.24	0.69	1.00	0.00	0.00
$[tcne]^-$ [a]	111	143	6.21	2.98	3.37	4.51	0.66	0.00	0.52	1.00
$[Ni(CN)_4]^{2-}$	111	144	6.24	2.98	3.39	4.59	0.65	0.00	0.54	1.00
$[Mn(CO)_5]^-$	119	150	6.21	3.05	3.46	4.36	0.70	0.75	0.25	0.14
$[CuCl_5]^{3-}$	120	168	6.91	3.06	3.66	4.16	0.74	0.81	0.19	0.10
$[AuBr_4]^{3-}$	130	158	6.19	3.14	3.55	4.35	0.72	0.00	0.50	1.00
$[Ni(CN)_5]^{3-}$ (trigonal bipyramid)	134	170	6.52	3.17	3.68	4.59	0.69	0.75	0.25	0.14
$[Ni(CN)_5]^{3-}$ (square pyramid)	135	172	6.56	3.18	3.70	4.65	0.68	0.68	0.16	0.32
$[OsCl_6]^{3-}$	139	173	6.47	3.21	3.71	4.05	0.79	1.00	0.00	0.00
$[FeCl_6]^{3-}$	142	185	6.79	3.24	3.84	4.15	0.78	1.00	0.00	0.00
$[Co(NH_3)_2(NO_2)_4]^-$	149	201	7.15	3.29	4.00	4.19	0.78	0.77	0.21	0.15
$[Fe(CN)_6]^{3-}$	155	190	6.58	3.33	3.89	4.62	0.72	1.00	0.00	0.00
$[Co(C_2O_4)_3]^{3-}$	168	212	6.99	3.42	4.11	5.36	0.64	0.23	0.47	0.75
$[tcnq]^-$ [b]	182	218	6.78	3.52	4.17	6.26	0.56	0.00	0.84	1.00
$[Mo(CN)_8]^{4-}$ (dodecahedron)	203	234	6.77	3.64	4.31	4.86	0.75	0.81	0.19	0.11
$[Mo(CN)_8]^{4-}$ (square antiprism)	203	232	6.74	3.64	4.30	4.86	0.75	0.71	0.15	0.29
$[Fe_4(NO)_4(\mu_3\text{-}S)_4]^-$	207	229	6.54	3.67	4.26	5.90	0.62	0.90	0.09	0.07
$[Cr(NH_3)_2(SCN)_4]^-$	231	306	8.12	3.81	4.93	6.79	0.56	0.57	0.21	0.43
$[BPh_4]^-$	323	350	7.43	4.26	5.28	6.66	0.64	0.79	0.10	0.21
$[\{Pt_3(CO)_6\}_2]^{2-}$	358	384	7.62	4.40	5.53	6.44	0.68	0.55	0.23	0.45
$[Os_6(CO)_{18}]^{2-}$	467	453	7.52	4.81	6.01	6.02	0.80	0.97	0.01	0.02

[a] tcne = Tetracyanoethylene. [b] tcnq = Tetracyanoquinodimethane.

Table 3 Packing coefficients of some inorganic and organometallic salts

Salt	Coefficient	Salt	Coefficient
$[Pt(NH_3)_4][tcnq]_2$	76.1	$[Pt_4H_7(PBu^t_3)_4][BPh_4]$	68.7
$[H_2tmen][PtCl_4]$[a]	74.7	$[Co(CO)_2\{P(OMe)_3\}_2][BPh_4]$	68.7
$[Cr(\eta\text{-}C_6H_6)_2][tcnq]$	73.2	$[Fe(\eta^5\text{-}C_{11}H_{11})_2][PF_6]$[d]	68.6
$[Ni_6(\eta\text{-}C_5H_5)_6][PF_6]$	71.5	$[RhO_2(PMe_2Ph)_4][BPh_4]$	68.6
$[AsPh_4][SiF_5]$	71.4	$[Co(C_2Ph_2)(PMe_3)_3][BPh_4]$	68.5
$[NMe_4][BPh_4]$	71.2	$[Ru_2(OH)_3(PMe_2Ph)_6][BPh_4]$	68.5
$[Hg(en)_2][ClO_4]_2$	71.2	$[NBu_4][AuBr_4]$	68.4
$[V(\eta\text{-}C_5H_5)_2(CO)_2][BPh_4]$	70.8	$[NH_3Me][ClO_4]$	68.4
$[NEt_4][tcnq]_2$	70.7	$[Co(CO)_2(PMe_3)_3][BPh_4]$	68.4
$[Fe(\eta\text{-}C_5H_5)_2][I_3]$	70.7	$[Mn(CO)_2\{P(OMe)_3\}_2][PF_6]$	68.0
$[PPh_4][tcnq]_2$	70.6	$[Fe(\eta\text{-}C_5H_5)_2][FeCl_4]$	67.8
$[AsPh_4][I_3]$	70.6	$[Co(NO_2)(PPh_3)_2][PF_6]$	67.8
$[PPh_4][OsCl_6]$	70.5	$[PPh_4]_2[Hg(SCN)_4]$	67.7
$[Ru(cod)(PMe_2Ph)_3][PF_6]$[b]	70.2	$[Co(PMe_3)_4][BPh_4]$	67.7
$[PPh_4][Br_3]$	70.1	$[Ru(N_3)(N_2)(en)_2][PF_6]$	67.4
$[Cu(btz)_2][BPh_4]$[c]	69.9	$[Cu(tmen)_2][BPh_4]$	67.1
$[Au(PMePh_2)_4][PF_6]$	69.9	$[Ni_2(napy)_4Br_2][BPh_4]$[e]	67.0
$[ZrH(\eta\text{-}C_5H_5)_2(PMe_3)_2][BPh_4]$	69.9	$[PPh_4]_2[Pt_6(CO)_{12}]$	66.9
$[Ni(phen)_3][I_3]_2$	69.5	$[NMe_4][PF_6]$	66.9
$[Au(PPh_3)_3][BPh_4]$	69.5	$[NBu_4][AuPh_4]$	66.5
$[NBu_4][I_3]$	69.2	$[Fe(CO)_3(\eta^5\text{-}C_6Me_7)][PF_6]$[f]	65.4
$[NH_4][BPh_4]$	69.1	$[FeL^1][PF_6]$[g]	65.2
$[NEt_4][I_3]$	69.0	$[Fe(\eta\text{-}C_5H_5)(CO)_3][PF_6]$	64.6
$[NH_4][tcnq]$	69.0	$[NBu_4]_3[Mo(CN)_8]$	64.6
$[Co(\eta\text{-}C_6Me_6)_2][PF_6]$	68.9	$[FeL^2][PF_6]$[e]	64.4

[a] tmen = *N,N,N′,N′*-Tetramethylethylenediamine. [b] cod = Cycloocta-1,5-diene. [c] btz = 2.2′-Bi(4,5-dihydro-6*H*-1,3-thiazine). [d] $C_{11}H_{11}^-$ = 1,3-Dimethylindenyl. [e] napy = 1,8-Naphthyridine. [f] $C_6Me_7^-$ = Heptamethylcyclohexadienyl. [g] H_2L^1 = Schiff-base obtained by condensation of triethylenetetramine with two equivalents of 3-chloropentane-2,4-dione. [h] H_2L^2 = Schiff-base obtained by condensation of triethylenetetramine with two equivalents of pentane-2,4-dione.

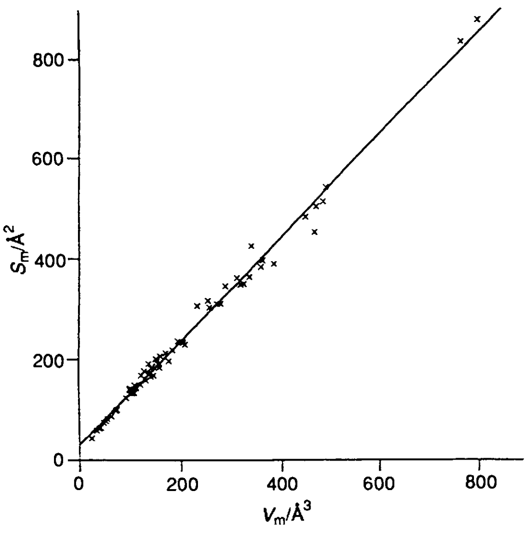

Fig. 2 Plot of S_m *versus* V_m

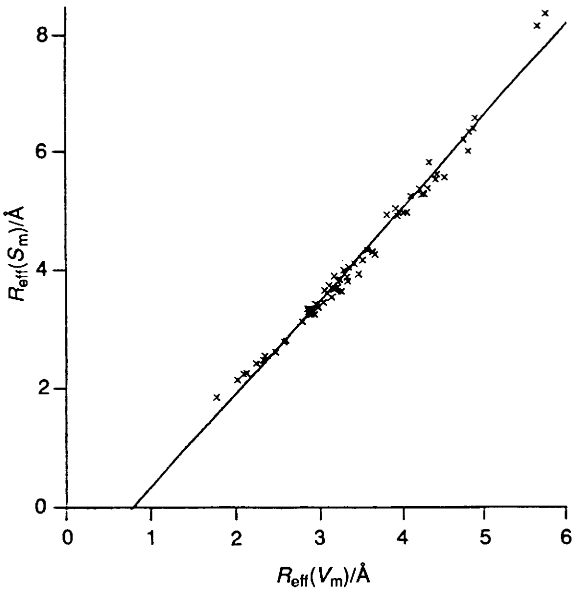

Fig. 3 Plot of $R_{eff}(S_m)$ *versus* $R_{eff}(V_m)$

is dimensionless and provides some indication of the non-spherical nature of the molecule. Values of I for some anions and cations are included in Tables 1 and 2 and lie in the range 5.22–10.21. These values can be compared with the calculated values of I for a sphere (4.84), icosahedron (5.15), octahedron (5.72) and tetrahedron (7.21). Clearly the molecular ions cannot be treated as strictly spherical.

Effective and Maximum Radii.—The approximately spherical nature of the molecular ions provides a basis for calculating an effective radius based either on the calculated volume or surface area. These are summarised in Tables 1 and 2 under the headings $R_{eff}(V_m)$ and $R_{eff}(S_m)$. Since a sphere achieves the minimum surface area for a given volume, any deviation from sphericality in an ion would make $R_{eff}(S_m)$ greater than $R_{eff}(V_m)$. Tables 1 and 2 show that $R_{eff}(S_m)$ is greater than $R_{eff}(V_m)$ in all cases, a result which is expected for all molecules. The quantities $R_{eff}(S_m)$ and $R_{eff}(V_m)$ correlate well with a correlation coefficient of 0.992 as shown in Fig. 3. It is interesting to note that R_{max} is greater than $R_{eff}(S_m)$ and $R_{eff}(V_m)$ for all ions except $[Co(NH_3)_6]^{3+}$. This anomaly occurs because the $[Co(NH_3)_6]^{3+}$ ion is compact but has a very bumpy van der Waals surface due to the large number of surface hydrogen atoms.

In the subsequent papers in this series, we shall use $R_{eff}(V_m)$ for discussing size effects and refer to it simply as R_{eff}. For the cations R_{eff} varies from 1.78–5.75 Å, *cf.* the ionic radii of Li^+ (0.68) and Cs^+ (1.67 Å) and for the anions the range is 2.02–4.81 Å, *cf.* F^- (1.33) and I^- (2.20 Å).

The ratio R_{eff}/R_{max} provides an indication of the possibility of interpenetration between an ion and its counter-ion in the solid state, if the ion is approximately spherical. For example, $[BPh_4]^-$ has $R_{eff}/R_{max} = 4.24/6.66 = 0.64$ and an examination of $[BPh_4]^-$ salts has shown a significant degree of cation–anion interpenetration. This contrasts with $[PF_6]^-$ where $R_{eff}/R_{max} = 0.81$ and the extent of interpenetration is minimal.

Moments of Intertia.—The moments of intertia provide a means of classifying the shapes of cations and anions. Spherical top ions have $M_1 \approx M_2 \approx M_3$, discoidal ions have $M_1 \approx M_2 > M_3$ whilst cylindrical ions have $M_1 > M_2 \approx M_3$. The three indices F_s, F_d and F_c are derived from the above relationships and the closer the values of the indices are to unity, the closer the ion is to the geometry represented by the index.

The relevance of the indices F_s, F_d and F_c are best illustrated by some specific examples. The flat $[NO_3]^-$ anions has $F_s = 0.00$, $F_c = 0.50$ and $F_d = 1.00$; whereas the linear (cylindrical) anion $[Au(CN)_2]^-$ has $F_s = 0.00$, $F_c = 1.00$ and $F_d = 1.00$. In contrast spherical top molecules such as $[BF_4]^-$ and $[PF_6]^-$ have $F_s = 1.00$, $F_c = 0.00$ and $F_d = 0.00$. For less symmetrical anions, the values of the indices give a reasonable description of the shape, for example $[Mn(CO)_5]^-$ and $[SiF_5]^-$ are basically spherical, but have a pronounced cylindrical distortion, $F_s = 0.75$, $F_c = 0.25$ and $F_d = 0.14$ and $F_s = 0.70$, $F_c = 0.30$ and $F_d = 0.18$ respectively. The anion $[Co(C_2O_4)_3]^{3-}$ has $F_s = 0.23$, $F_c = 0.47$ and $F_d = 0.75$ has an octahedral inner co-ordination sphere but the overall shape of the ion is distinctly discoidal. The metallocene cation $[Fe(\eta\text{-}C_5H_5)_2]^+$ with $F_s = 0.56$, $F_c = 0.44$ and $F_d = 0.29$ is quite cylindrical in character but the related cations $[Cr(\eta\text{-}C_6H_6)_2]^+$ ($F_s = 0.88$, $F_c = 0.12$ and $F_d = 0.07$) and $[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$ ($F_s = 0.83$, $F_c = 0.15$ and $F_d = 0.11$) are both far more spherical but still retain a cylindrical component to their shape. The decamethylferrocenium ion $[Fe(\eta\text{-}C_5Me_5)_2]^+$ with $F_s = 0.89$, $F_c = 0.06$ and $F_d = 0.11$ is also spherical but has a small discoidal component to its shape.

Several of the anions in Table 2 possess more than one possible geometry and the moments of inertia are listed for both geometries. The values show that the moments differ significantly between the different conformations, *i.e.* the moments are very sensitive to small changes in shape. For example crystal structures of $[Mo(CN)_8]^{4-}$ show that it can have either a dodecahedral or square-antiprismatic geometry. The dodecahedral geometry has $F_s = 0.81$, $F_c = 0.19$ and $F_d = 0.11$, indicating a spherical geometry with a cylindrical distortion whilst the square-antiprismatic geometry has $F_s = 0.71$, $F_c = 0.15$ and $F_d = 0.29$, showing that it is less spherical than the dodecahedron and that it has a distinct discoidal component. The sensitivity of the moments to small changes in shape has been used to map out rearrangement pathways of co-ordination compounds.[29]

The shape parameters given in Table 1 suggest a significant variation in sphericality for the quaternary ammonium salts. Although $[NMe_4]^+$ and $[NH_4]^+$ are both spherical, the higher homologues have geometries which display substantial discoidal and cylindrical distortions. For example, $[NEt_4]^+$ and $[NBu_4]^+$ are relatively discoidal whereas $[NH_2Bu_2]^+$ is relatively cylindrical. Similarly, the shape parameters for $[Ni(bipy)_3]^{2+}$ indicate that it is close to spherical, but $[Cr(en)_3]^{3+}$ and $[Ni(phen)_3]^{2+}$ are both significantly less spherical and have discoidal components to their shape. These shape parameters may in the future provide a more rational

Table 4 Co-ordination number (c.n.), *a*/*c* ratios and shape parameters for a selection of $[PF_6]^-$ salts

Cation	*a*/*c*	c.n.	Lattice type	F_s	F_c	F_d
$[NMe_4]^+$	0.86	8:8	CsCl	0.99	0.01	0.00
$[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$	0.75	6:6	NiAs	0.83	0.15	0.11
$[Ru(N_3)(N_2)(en)_2]^+$	0.68	5:5	Five-co-ordinate	0.26	0.68	0.63
$[Fe(CO)_3(\eta^5\text{-}C_6Me_7)]^+$	0.60	6:6	*anti*-NiAs	0.59	0.22	0.40
$[Fe(\eta^5\text{-}C_{11}H_{11})_2]^+$	0.58	5:5	NaCl	0.55	0.30	0.40
$[Co(\eta\text{-}C_6Me_6)_2]^+$	0.56	6:6	NaCl	0.77	0.13	0.22
$[Ni_6(\eta\text{-}C_6H_6)_6]^+$	0.50	6:6	NaCl	1.00	0.00	0.00
$[Ru(cod)(PMe_2Ph)_3]^+$	0.48	5:5	NiAs	0.46	0.44	0.45
$[Co(NO)_2(PPh_3)_2]^+$	0.47	6:6	NaCl	0.46	0.50	0.41
$[Mn(CO)_2\{P(OMe)_2Ph\}_4]^+$	0.45	4:4	Layer	0.58	0.37	0.31
$[Au(PMePh_2)_4]^+$	0.42	4:4	Layer	0.77	0.23	0.13

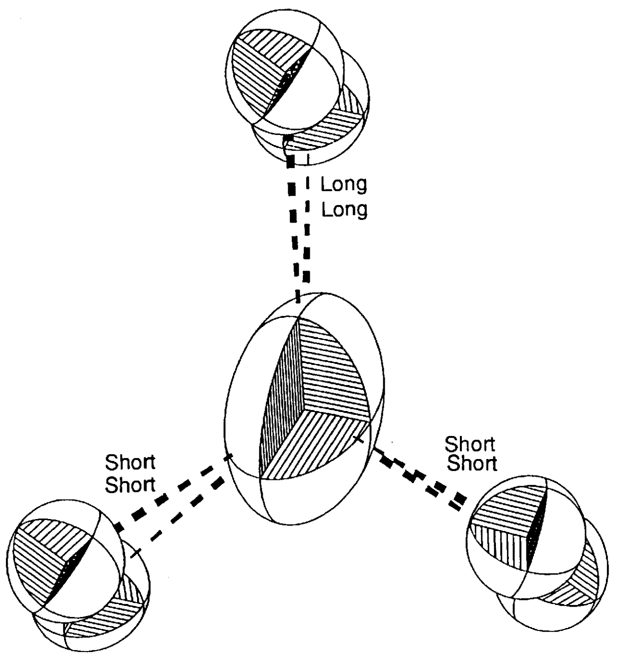

Fig. 4 The co-ordination geometry around the $[Fe(CO)_3(\eta^5\text{-}C_6Me_7)]^+$ cation which is represented by an ellipsoid which reflects the cation's moments of inertia. The $[PF_6]^-$ ions adopt a trigonal prismatic arrangement around the cation, but the distortions in the cation–anion distances reflect the discoidal nature of the cation

basis for choosing specific counter-ions for stabilizing unusual co-ordination geometries.

Summary and Applications

In this paper the surface areas, volumes and effective radii for a wide range of ions commonly encountered in co-ordination and organometallic chemistry have been calculated. In addition the calculated moments of inertia have provided a crude analysis of the shapes of the ions which emphasises their spherical, discoidal and cylindrical nature. General relationships between the calculated parameters have been discussed in this paper. The utility of these data for understanding the crystallization and crystal structures of molecular inorganic salts will be briefly described below.

Basolo[3] has pioneered attempts to systematise the requirements for crystallizing co-ordination compounds with unusual co-ordination geometries and numbers from aqueous solutions. He proposed the following empirical relationship. 'Solid salts separate from aqueous solution easiest for combinations of either small cation–small anion or large cation–large anion, preferably with systems having the same but opposite charges on the counterions.' The availability of the data presented in Tables 1 and 2 provide a more quantitative test of the size criteria associated with the generalization. For example, Basolo noted that the complex ions $[NiX_4]^{2-}$ (X = Cl or Br) can be reasily isolated as the $[NMe_4]^+$, $[NEt_4]^+$ and $[AsMePh_3]^+$ salts but not as simple alkali-metal salts. The calculated volume for $[NiCl_4]^{2-}$ is 100 Å^3 (Table 2) and those for $[NMe_4]^+$, $[NEt_4]^+$ and $[AsMePh_3]^+$ are 91, 156 and 278 Å^3 respectively (Table 1). These results suggest that the critical factor for crystallization is not so much an exact matching of cation and anion size, but rather a threshold volume for the cation has to be exceeded. This threshold volume is approximately equal to the volume of the anion. This conclusion is supported by a more detailed analysis[30] which has calculated the volume ratios for $[NiCl_4]^{2-}$, $[CuCl_5]^{3-}$, $[CuCl_4]^{2-}$ (tetrahedral and square planar), $[Ni(CN)_5]^{3-}$, $[SiF_5]^-$, $[FeCl_6]^{3-}$, $[Mn(CO)_5]^-$ and $[FeH(CO)_4]^-$ salts. This analysis has also shown that salts may be successfully crystallized even when the volume of the cation exceeds that of the anion by a factor of 6.

The packing modes of a wide range of PF_6^- salts have been analysed. The co-ordination numbers of the cations and anions have been related to the ratio of their effective radii (*a*/*c* ratio). The results are summarised in Table 4. The *a*/*c* ratio varies from 0.86 to 0.42 and correlates with the co-ordination numbers very well for those cations which have a high spherical index F_s derived from the moments of inertia calculation. The structures of these salts correspond closely with those observed in simple inorganic salts, *e.g.* CsCl, NiAs and NaCl in eight- and six-co-ordination. The 4:4 co-ordination observed in $[Mn(CO)_2\{P(OMe)_2Ph\}_4][PF_6]$ and $[Au(PMePh_2)_4][PF_6]$ is based on a square-planar layer structure rather than the ZnS structures however. For those cations with distinctly non-spherical shapes the calculated moments of inertia provide an interesting insight into their packing modes. The cation shape can be represented by an ellipsoid with axes lengths, R_i, proportional to the moments of inertia M_i according to equation (12) and drawn using a thermal ellipsoid plotting

$$R_i \propto [3M_i/(M_1 + M_2 + M_3)]R_{\text{eff}}\ (i = 1, 2 \text{ or } 3) \quad (12)$$

program.[31] Such a plot, showing the arrangement of six anions around the cation for the salt $[Fe(CO)_3(\eta^5\text{-}C_6Me_7)][PF_6]$ is illustrated in Fig. 4. The calculated moments of inertia suggest that the cation is discoidal in shape (F_d = 0.40). The trigonal-prismatic co-ordination is clearly visible, but it is noteworthy that two of the PF_6^- anions lie in the plane of the two long equatorial axes of the oblate spheroid and the remaining four lie much closer to the short polar axis. This arrangement is reflected in the calculated cation–anion centroid distances: 6.07, 6.12 × 2, 6.27, 6.63 and 6.77.

This mode of analysis has proved to be particularly useful for interpreting the structures of $[PF_6]^-$ salts.[32] Similar techniques have been applied to $[BPh_4]^-$ salts where interpenetration effects are more significant[33] and 'soft salts' based on the combination of cluster cations and anions.[28]

Acknowledgements

Professor A. Gavezzotti is thanked for the provided programs used in the initial stages of the research. A. L. R. would like to thank the British Council and the Association of Commonwealth Universities for his Commonwealth Scholarship. Thanks are also due to the Air Force Office of Scientific Research for financial support for this project.

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Received 6*th June* 1991; *Paper* 1/02703D