Expanding the series gives

$$\epsilon - \epsilon_{\text{monomer}} = \frac{\kappa[\text{AX}](\epsilon' - \epsilon_{\text{monomer}}) + \kappa^2[\text{AX}]^2(2(\epsilon' - \epsilon_{\text{monomer}}) + \ldots}{1 + 2\kappa[\text{AX}] + 3\kappa^2[\text{AX}]^2 + \ldots} \quad (7)$$

$$\epsilon - \epsilon_{\text{monomer}} = (\epsilon' - \epsilon_{\text{monomer}}) \frac{\kappa[\text{AX}](1 + 2\kappa[\text{AX}] + 3\kappa^2[\text{AX}]^2) + \ldots}{1 + 2\kappa[\text{AX}] + 3\kappa^2[\text{AX}]^2 + \ldots} \quad (8)$$

$$\epsilon - \epsilon_{\text{monomer}} = \kappa[\text{AX}]\ (\epsilon' - \epsilon_{\text{monomer}}) \quad (9)$$

Correlating to the total monomer concentration gives $C_{\text{AX}} = \sum n[(\text{AX})_n]$, where

$$C_{\text{AX}} = [\text{AX}]\sum n\kappa^{n-1}[\text{AX}]^{n-1} = [\text{AX}]/(1 - \kappa[\text{AX}]^2) \quad (10)$$

Substituting this expression into eq 9 leads to

$$\epsilon - \epsilon_{\text{monomer}} = (\epsilon' - \epsilon_{\text{monomer}})\kappa C_{\text{AX}}\ (1 - \kappa[\text{AX}])^2 \quad (11)$$

Supplementary Material Available: Tables S1–S6, listing atomic coordinates, thermal parameters, bond lengths, bond angles, deviations of atoms from the porphyrin plane, and crystal data collection parameters (8 pages); Table S7, listing observed and calculated structures factors (19 pages). Ordering information is given on any current masthead page.

Notes

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Size and Shape Characteristics of Inorganic Molecular Ions and Their Relevance to Crystallization Problems

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Received January 3, 1991

The crystallization of molecular salts in coordination and organometallic chemistry has always been a critical step in the characterizational process because of the requirement for single crystals suitable for diffraction studies. Despite the general importance of this process, it has been little studied either from an experimental or theoretical point of view. Inorganic chemists have at their disposal a range of cations and anions with varying, but ill-defined, sizes and solubility properties and by a process of trial and error attempt to obtain crystals with the desired solubility properties and morphology. If inorganic chemists are to transform this "art" into procedures that enable them to truly design and fine tune at a molecular level those solid-state properties which have been defined as important, such as conductivity,[1] magnetic ordering,[2] and nonlinear optical properties,[3,4] then it will be necessary to understand in more detail the experimental and theoretical factors governing the crystallization process and organization of molecules in a crystal. This paper provides a tentative first step toward this goal by providing data on the molecular volumes, surface areas, and shapes of a wide range of ions used in coordination chemistry.

Basolo[5] has pioneered attempts to systematize the requirements for crystallizing coordination compounds with unusual geometries and coordination numbers. He proposed the empirical observation that "*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*". Further examples of this phenomenon have been cited by McDaniel.[6] The requirement of matching small cations and anions and large cations and anions has therefore passed into the folklore of inorganic chemistry but has not been substantiated by quantitative criteria. McDaniel has analyzed the role of large countercations based on his concept of "lattice inhibited" reactions. Using simple Born theory, he concluded, in contrast to Basolo's size-matching rule, that there is a lower critical limit for the size of the cation but no upper limit. Recently we have calculated the molecular volumes (V_m), surface areas (S_m), and shapes of a wide range of cations and anions, and the results are given in Tables I and II. The method used to calculate the volume is that of Gavezzotti.[7] The molecular volume is calculated by sampling a parallelepiped, which contains an ion constructed from van der Waals spheres centered on the atomic positions, with a large number of probe points (N) and counting the number (N_{occ}) of points inside at least one of the van der Waals

Table I. Size and Shape Parameters of Some Common Inorganic and Organometallic Cations

cation	V_m, Å^3	S_m, Å^2	F_s	F_c	F_d
Li^+	2	8			
Na^+	3	12			
K^+	10	22			
Cs^+	19	34			
$[NH_4]^+$	24	43	1.00	0.00	0.00
$[NH_3Me]^+$	41	64	0.39	0.61	0.44
$[NMe_4]^+$	91	123	1.00	0.00	0.00
$[Pt(NH_3)_4]^{2+}$	99	142	0.12	0.44	0.88
$[dienH_3]^+$	108	148	0.04	0.94	0.93
$[Cr(NH_3)_6]^{3+}$	126	176	0.93	0.07	0.04
$[Co(NH_3)_4(NO_2)_2]^+$	134	191	0.84	0.10	0.14
$[Me_2NHCH_2CH_2NHMe_2]^+$	140	182	0.09	0.81	0.85
$[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$	140	166	0.83	0.15	0.11
$[Fe(\eta\text{-}C_5H_5)_2]^+$	145	168	0.56	0.44	0.29
$[Hg(en)_2]^{2+}$	150	195	0.12	0.81	0.81
$[NEt_4]^+$	156	183	0.35	0.33	0.65
$[NBu_2H_2]^+$	157	206	0.09	0.87	0.85
$[Cr(\eta\text{-}C_6H_6)_2]^{3+}$	175	196	0.79	0.21	0.13
$[Cr(en)_3]^{3+}$	192	236	0.38	0.32	0.61
$[Co(pn)_3]^{3+}$	253	317	0.39	0.30	0.61
$[Cr(tn)_3]^{3+}$	256	303	0.39	0.38	0.58
$[PPh_3Me]^+$	271	310	0.39	0.32	0.60
$[AsPh_3Me]^+$	278	311	0.49	0.25	0.51
$[NBu_4]^+$	287	346	0.14	0.43	0.86
$[Fe(\eta\text{-}C_5Me_5)_2]^+$	309	362	0.89	0.06	0.11
$[PPh_4]^+$	317	349	0.90	0.08	0.07
$[AsPh_4]^+$	334	364	0.82	0.09	0.17
$[Co(PMe_3)_4]^{3+}$	338	425	0.83	0.16	0.10
$[Co(\eta\text{-}C_6Me_6)_2]^+$	361	397	0.81	0.10	0.19
$[Fe_4(\eta\text{-}C_5H_5)_4(\mu^3\text{-}S)_4]^+$	384	390	0.57	0.36	0.33
$[Ni(bpy)_3]^{3+}$	448	483	0.88	0.08	0.09
$[Ni_6(\eta\text{-}C_5H_5)_6]^+$	470	504	1.00	0.00	0.00
$[Ni(phen)_3]^{3+}$	485	514	0.60	0.26	0.36
$[PPN]^+$	490	543	0.70	0.27	0.20
$[Au(PPh_3)_3]^+$	761	836	0.60	0.23	0.38
$[Au(PPh_2Me)_4]^+$	795	879	0.78	0.22	0.12

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Table II. Size and Shape Parameters of Some Common Inorganic and Organometallic Anions

anion	V_m, Å^3	S_m, Å^2	F_s	F_c	F_d
$[NO_3]^-$	34	58	0.00	0.50	1.00
$[BF_4]^-$	38	63	1.00	0.00	0.00
$[ClO_4]^-$	47	74	1.00	0.00	0.00
$[SiF_5]^-$	52	77	0.70	0.30	0.18
$[PF_6]^-$	54	82	1.00	0.00	0.00
$[AsF_6]^-$	63	86	1.00	0.00	0.00
$[SbF_6]^-$	71	98	1.00	0.00	0.00
$[Au(CN)_2]^-$	73	100	0.00	1.00	1.00
$[CuCl_4]^-$ (distorted tetrahedron)	97	141	0.42	0.31	0.57
$[CuCl_4]^-$ (square planar)	98	138	0.00	0.51	1.00
$[NiCl_4]^{2-}$	100	139	1.00	0.00	0.00
$[FeCl_4]^-$	101	132	1.00	0.00	0.00
$[HFe(CO)_4]^{2-}$	103	133	0.76	0.12	0.24
$[PtCl_4]^{2-}$	104	137	0.00	0.50	1.00
$[I_3]^-$	107	133	0.00	1.00	1.00
$[HgCl_4]^{2-}$	107	148	1.00	0.00	0.00
$[TCNE]^-$	111	143	0.00	0.52	1.00
$[Ni(CN)_4]^{2-}$	111	144	0.00	0.54	1.00
$[Mn(CO)_5]^-$	119	150	0.75	0.25	0.14
$[CuCl_5]^{3-}$	120	168	0.81	0.19	0.10
$[AuBr_4]^{3-}$	130	158	0.00	0.50	1.00
$[Ni(CN)_5]^{3-}$ (trigonal bipyramid)	134	170	0.75	0.25	0.14
$[Ni(CN)_5]^{3-}$ (square pyramid)	135	172	0.68	0.16	0.32
$[OsCl_6]^{3-}$	139	173	1.00	0.00	0.00
$[FeCl_6]^{3-}$	142	185	1.00	0.00	0.00
$[Co(NH_3)_2(NO_2)_4]^-$	149	201	0.77	0.21	0.15
$[Fe(CN)_6]^{3-}$	155	190	1.00	0.00	0.00
$[Co(C_2O_4)_3]^{3-}$	168	212	0.23	0.47	0.75
$[TCNQ]^-$	182	218	0.00	0.84	1.00
$[Mo(CN)_8]^{4-}$ (dodecahedron)	203	234	0.81	0.19	0.11
$[Mo(CN)_8]^{4-}$ (square antiprism)	203	232	0.71	0.15	0.29
$[Fe_4(NO)_4(\mu^3\text{-}S)_4]^-$	207	229	0.90	0.09	0.07
$[Cr(NH_3)_2(SCN)_4]^-$	231	306	0.57	0.21	0.43
$[BPh_4]^-$	323	350	0.79	0.10	0.21
$[(Pt_3(CO)_6)_2]^{2-}$	358	384	0.55	0.23	0.45
$[Os_6(CO)_{18}]^{2-}$	467	453	0.97	0.01	0.02

Table III. Summary of Calculated Anion:Cation Volume Ratios for the Salts That Form the Basis of Basolo's Generalizations

anion	cation	V_m, Å^3	V_a/V_c
$[NiCl_4]^{2-}$		100	
	$[NMe_4]^+$	91	1.10
	$[NEt_4]^+$	156	0.65
	$[AsPh_3Me]^+$	278	0.36
$[CuCl_5]^{3-}$		120	
	$[dienH_3]^{3+}$	108	1.11
	$[Cr(NH_3)_6]^{3+}$	126	0.96
$[CuCl_4]^{2-}$		97	
(distorted tetrahedron)	$[NMe_4]^+$	91	1.07
	$[NBu_2H_2]^+$	157	0.62
$[CuCl_4]^{2-}$		98	
(square planar)	$[Pt(NH_3)_4]^{2+}$	99	0.99
$[Ni(CN)_5]^{3-}$		134	
	$[Cr(en)_3]^{3+}$	192	0.70
	$[Cr(tn)_3]^{3+}$	256	0.52
$[SiF_5]^-$		52	
	$[NEt_4]^+$	156	0.34
	$[AsPh_4]^+$	334	0.16
$[FeCl_6]^{3-}$		142	
	$[Co(pn)_3]^{3+}$	253	0.56
$[Mn(CO)_5]^-$		119	
	$[Ni(phen)_3]^{2+}$	485	0.25
$[HFe(CO)_4]^-$		103	
	$[PPN]^+$	490	0.21

spheres. If the volume of the parallelepiped is $V_{\|}$, then the molecular volume is given by

$$V_m = V_{\|}\frac{N_{occ}}{N}$$

The shape parameters are derived from the moments of inertia calculated without mass weighting.[8] The moments are the three eigenvalues of the symmetric matrix

$$\begin{bmatrix} \sum x^2 & \sum xy & \sum xz \\ \sum yx & \sum y^2 & \sum yz \\ \sum zx & \sum zy & \sum z^2 \end{bmatrix}$$

where the summations are over all atoms in the ion. The x, y, and z in this matrix refer to the cartesian coordinates of each atom in the ion after it has been translated such that its centroid lies at the origin. The largest of these eigenvalues is denoted M_1, the middle one M_2, and the smallest one M_3. With these moments, it is possible to define the following three indices:

$$F_s = M_3/M_1 \qquad \text{spherical index}$$

$$F_c = 1 - \frac{M_2 + M_3}{2M_1} \qquad \text{cylindrical index}$$

$$F_d = 1 - \frac{2M_3}{M_1 + M_2} \qquad \text{discoidal index}$$

The closer the values of the parameters are to unity, the closer the ion is to the geometry represented by the parameter. The interpretation of these calculations has been discussed more fully in the first paper of this series.[9] For the alkali-metal cations listed in Table I, the ionic radii have been used to calculate the ion volumes and surface areas.[10] Since the van der Waals radii have been used to calculate the volume of molecular ions, the radii used for the alkali metals will be underestimates but the difference between the volumes of the two classes is so large that it doesn't seriously affect the arguments presented below. The availability of this data provides a basis for discussing the role of ionic size and shape on the crystallization process and for testing Basolo's and McDaniel's empirical observations in a more quantitative manner.

Basolo noted that the complex ions $[NiX_4]^{2-}$ (X = Cl or Br) can be readily isolated as the NMe_4^+, NEt_4^+, and $AsMePh_3^+$ salts but not as simple alkali-metal salts. Analogous observations apply to other $[MX_4]^{n-}$ anions where M = Mn, Fe, Co, or Zn and n = 2. Similar considerations also apply to the $[MCl_6]^{3-}$ octahedral anions (M = Cr, Mn, or Fe), which are not stable in aqueous solution but can be stabilized in a crystal lattice with the $[Co(pn)_3]^{3+}$ counterion (pn = 1,2-diaminopropane).

The anion $[CuCl_5]^{3-}$ is not stable in solution, but it is produced as a crystalline solid with the counterion $[Cr(NH_3)_6]^{3+}$. This is an excellent illustration of the importance of the charge of the counterion since the corresponding NEt_4^+ salts contain $[CuCl_4]^{2-}$. The importance of the shape of the counterion has also been noted by Basolo and is illustrated by the observation that in $[Pt(NH_3)_4][CuCl_4]$ the anion and cation are both square planar, whereas in $[NMe_4]_2[CuCl_4]$ the cation and anion are both tetrahedral. The fact that $[dienH_3][CuCl_5]$ actually crystallizes as $[dienH_3][CuCl_4]Cl$ rather than as the $[CuCl_5]^{3-}$ salt is perhaps also related to shape effects.

The isolation of $[Ni(CN)_5]^{3-}$, both in trigonal-bipyramidal and square-pyramidal forms, as the $[Cr(en)_3]^{3+}$ salt or $[Cr(tn)_3]^{3+}$ salt (tn = 1,3-diaminopropane) underlines the size and charge effects, since the corresponding alkali-metal salts contain only the $[Ni(CN)_4]^{2-}$ ion.

Solid derivatives of the group 14 $[MX_5]^-$ ions have been obtained for Si, Ge, and Sn (X = F, M = Si and Ge; X = Cl, M = Ge and Sn, X = Br, M = Sn) but only when the counterion is NEt_4^+ or $AsPh_4^+$. With alkali-metal cations only the $[MX_6]^{2-}$ salts have been isolated.

These same principles seem to apply also to transition-metal carbonyl complexes, where for example $[Mn(CO)_5]^-$ has been

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Table IV. Packing Efficiencies of Several Hexafluorophosphate Salts with Spherical Cations

salt	packing efficiency, %	V_a/V_c	coordn no.
$[NMe_4][PF_6]$	66.9	1.7	8
$[Fe(\eta\text{-}C_5H_5)(CO)_3][PF_6]$	64.6	2.6	6
$[Fe(CO)_3(C_6Me_7)][PF_6]$	65.4	5.0	6
$[Co(\eta\text{-}C_6Me_6)_2][PF_6]$	68.9	6.7	6
$[Ni_6(\eta\text{-}C_5H_5)_6][PF_6]$	71.5	8.7	6
$[Co(NO)_2(PPh_3)_2][PF_6]$	67.8	10.2	6
$[Mn(CO)_2\{P(OMe)_2Ph\}_4][PF_6]$	68.0	12.2	4
$[Au(PMePh_2)_4][PF_6]$	69.9	14.7	4

isolated in a trigonal-bipyramidal form with $[Ni(phen)_3]^{2+}$ as the counterion. The large counterion PPN^+, i.e. $[(Ph_3P)_2N]^+$, has also been widely used to crystallize organometallic and carbonyl anionic complexes, e.g. $[PPN][HFe(CO)_4]$.

The volumes of many of the cations and anions that form the basis of Basolo's generalizations have been calculated and used to compute the volume ratios V_a/V_c (a = anion, c = cation) summarized in Table III. It appears from the calculated anion to cation volume ratios given in Table III that the stabilization of unusual anionic coordination compounds may be achieved if the volume of the cation is greater than or equal to that of the anion. For example, in the series $[NMe_4]_2[NiCl_4]$, $[NEt_4]_2[NiCl_4]$, and $[Ph_3AsMe]_2[NiCl_4]$ the volume of the cation increases by a factor of 3 relative to that of the anion. The largest anion/cation volume ratio for the salts isolated as solids and listed in Table III is 1.10, and the smallest is 0.16. Therefore, contrary to previous suggestions, it is not necessary to match the cation and anion sizes with any great precision in order to stabilize unusual coordination environments and the cation volume may exceed that of the anion by up to a factor of 6. However, an anion with an unusual coordination environment is not likely to be isolated if V_a/V_c greatly exceeds 1.0. For example, the calculated V_a/V_c ratios for Li_2NiCl_4 and K_2NiCl_4, which cannot be isolated, are 50 and 10, respectively. Therefore, optimum conditions for crystallization are achieved when the cation is approximately equal to or larger in volume than the anion. The analysis is thus consistent with McDaniel's concept of a lower critical cation volume, with the lower limit corresponding approximately to Basolo's size matching criterion.

The precise matching of the sizes of the cations and anions in molecular salts is not a dominating consideration in crystallization, since ions with quite different volumes can pack efficiently within a crystal by varying their coordination numbers. This effect may be illustrated by reference to the series of $[PF_6]^-$ salts with spherical cations, whose packing coefficients have been summarized in Table IV. Although the volume ratio (V_a/V_c) varies from 1.7 to 14.7, the packing efficiency within the unit cell calculated from the volumes given in Tables I and II and the literature unit cell volumes lies within the narrow range of 64.6–71.5%. It is apparent from Table IV that this is achieved by varying the coordination numbers of the cations and anions. Although the ions chosen in the table have relatively spherical geometries, similar considerations apply to ions with less symmetrical geometries. These results have encouraged us to develop a set of "radius ratio rules" for interpreting the structures of molecular salts, and these results will be described in subsequent publications.[11,12]

It is apparent from the results presented in this paper that the crystallization of salts using large countercations may be successful even when the V_a/V_c ratio falls to ca. 0.20, because the structure in the solid state can achieve a close-packed arrangement by varying the coordination number. The size effect may play an important role in the isolation process, however, if the cation is highly polarizing and is capable of forming a binary compound with a high lattice energy. For example, Li^+ salts of $[MX_n]^{n-}$ anions are thermodynamically unstable[6] because of the high lattice energy associated with LiX. For molecular cations M^+ with a volume greater than or equal to that of the anion, there is a significant contribution to the lattice energy from van der Waals forces and the thermodynamic driving force for forming M^+X^- is less critical.

The variation in coordination number may not be important for characterizational purposes but could influence the magnetic, conductivity, and nonlinear optical properties of the compound significantly.

The moments of inertia calculated for cations and anions provide objective criteria for evaluating their shape characteristics. For example, it is apparent from Table III that $[dienH_3]^{3+}$ is rather cylindrical in shape, whereas $[Cr(NH_3)_6]^{3+}$ is effectively spherical. Therefore, although these counterions have similar volumes ($[dienH_3]^{3+}$, 108 Å^3, $[Cr(NH_3)_6]^{3+}$, 126 Å^3), only the chromium complex stabilizes the $[CuCl_5]^{3-}$ ion.

The complex $[Pt(NH_3)_4][CuCl_4]$ provides a particularly interesting example of size and shape matching. The volumes of the cation and anion are equal to within 1 Å^3, and their shape parameters are both indicative of discoidal geometries if the $[CuCl_4]^{2-}$ ion adopts a square-planar geometry. In general, the packing efficiencies of discoidal molecules are greater than that of spherical molecules, which encourages the adoption of this geometry by $[CuCl_4]^{2-}$.

The availability of the size and shape factors in Tables I and II should encourage the study of more systems where the coordination geometry is influenced by the shape of the cation. The complementary problem of stabilizing unusual cation geometries by selecting the appropriate counteranions could also be addressed using the data provided. It is noteworthy that currently there are few well-documented examples of this phenomenon.

Acknowledgment. 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 AFOSR for financial support of this project.

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Chemistry of (Silica)zirconium Dihydride

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Received November 19, 1990

To most organometallic chemists, especially to those who use metals in "fine" synthesis, the notion of organozirconium chemistry is intimately tied to that of a "soft" ligand environment which usually involves "Cp" (or Cp*) or phosphine ligation.[1] In contrast, well-known processes for ethylene or propylene polymerization[2] or olefin isomerization[3] involve "hard", oxide-bound organozirconium compounds,[2,4] including hydrides[4] formed by hydrogenolysis[4-6] of oxide-bound alkyls; apart from catalyzed olefin isomerization, the chemistry of these oxide-bound hydrides is

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