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Geometry variation of complex ions in crystals†

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The geometries of a series of metal complex and other inorganic ions have been retrieved from crystal structures of their salts in the Cambridge Structural Database. These ions show substantially higher variation (σ) in their bond lengths and angles than would be expected on the basis of normal crystallographic estimates of precision (standard uncertainty). There is clear evidence of a link between σ and the softness of systems. Thus M–Cl bond length σ values are small for species such as $[SnCl_6]^{2-}$ or $[MoCl_6]^{3-}$ ($\sigma = 0.016$ and 0.010 Å respectively) while at the other extreme $[TeCl_6]^{2-}$ or $[BiCl_6]^{3-}$ have $\sigma = 0.083$ and 0.094 Å respectively. Baseline uncertainty levels are apparent in even very well behaved systems such as $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$ (bond length and bond angle σ values of *ca.* 0.01 Å and 1.0° respectively). There is no evidence that the geometries of the complex ions studied here are substantially more variable than those of similar neutral molecules. There is some evidence that the "organic" or non-metal aspects of molecular geometry are less variable than the metal-containing aspects.

Introduction

The intramolecular geometric information obtained from single crystal diffraction studies is often used to interpret and understand molecular phenomena which take place in environments differing significantly from that of the molecule in the crystal. However, the molecular geometry found in the crystal may differ from that determined experimentally or computationally for non-crystalline phases. In part these differences arise because crystallography yields interatomic distances and other aspects of geometry that are subject to different averaging and systematic errors than is obtained by other techniques whether experimental or computational. However, it has often been claimed that the geometric results of a crystal structure analysis are subject to distortion arising from "crystal packing forces". It has been noted that the geometry of a molecule or molecular fragment in two different crystal environments may differ by an amount far beyond the experimental uncertainties.[2] These observations raise the issue of the flexibility of molecular structure and the transferability of bond length, angle and other geometric parameters from one situation to another. These concepts underpin much of modern structural chemistry and are implicit in the compilation and use of collections of structural data such as those in ref. 3.

The environment of a molecule may be empty (as in an ideal gas), it may be a host condensed phase (as in liquid and solid solutions), or it may be composed of other copies of the molecule under investigation (as in pure liquids, crystalline or amorphous phases). In the crystalline state different environments are available for a given molecular species through the existence of polymorphs, phases with more than one molecule in the crystallographic asymmetric unit, solvates, inclusion compounds and other crystalline phases composed of more than one type of molecule. Such differences in environment can in principle induce variations in the structure of a molecule or molecular fragments. These differences are usually small enough not to wipe out the identity of the molecule, but may be sufficiently large to blur its inherent geometry to an extent which can be determined experimentally and interpreted in terms of the flexibility of the fragment.

Error estimates are ubiquitous in the literature of crystallography. Almost all published atomic coordinates and temperature factors, and derived quantities such as bond lengths and angles, are accompanied by standard uncertainties (s.u.'s) which represent the precision of the crystallographically determined parameter.[4] It is generally recognised that no physical measurement is complete without a reliable indication of its precision. This may be more important in diffraction studies when many results are based on the findings of just one experiment. Studies by Taylor and Kennard[5] and organised by the IUCr[6] have shown the s.u.'s of non-hydrogen atoms are often underestimated by a factor of 1.4–1.5; and that the s.u.'s of heavy-atom positions are usually less reliable than those of light-atom positions and that the s.u.'s of cell parameters may be grossly underestimated,[7] by a factor of up to 5 for cell lengths and 2.5 for cell angles. Additional support for some of these observations has been provided by Allen, Cole and Howard through their work on predicting the mean isotropic coordinate s.u. based on crystallographic *R*-factor, atomic number and chemical composition of the molecular structure.[8]

It is usually implicitly assumed that the structure of a molecule in the crystalline state is close to that of the gas-phase molecule. Indeed careful studies by Allen, Harris and Taylor[9] showed that such assumptions were useful and not misleading in a range of systems. That this assumption will fail in some cases is well known however. Perhaps the classic example of the problem of molecule geometry and crystalline environment is that of biphenyl and its derivatives. Biphenyl has been shown to be twisted by 42–45° about the exocyclic C–C bond (φ) in the gas phase,[10] while the crystal structure analysis indicates a planar conformation, strengthened by the fact that the molecule lies astride an inversion centre. Further analysis[11] of biphenyl fragments with hydrogen atoms in all four *ortho* positions showed few structures to have φ close to 45° and that most have much smaller values. The herringbone packing arrangement of nearly planar molecules that is found in the structure of biphenyl itself is very favourable. It appears that these *o*-unsubstituted biphenyl derivatives show that the crystal packing effects of the solid state can *systematically* favour a molecular conformation that does not correspond to an intramolecular energy minimum. While this may be an unusual case it serves to reinforce the point that there may be systematic distortion of molecular geometry in the solid state as well

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† Structural systematics. Part 8.[1] Electronic supplementary information (ESI) available: bond parameters and their statistics. See http://www.rsc.org/suppdata/dt/b1/b100108f/

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as "random" distortions which do not distort the average geometry substantially away from its ideal gas-phase value.

Kitaigorodskii[12] offered four approaches to answer the question, "what is the difference between the geometry of molecules in a crystal and the geometry of the free molecule?" (a) Comparison of molecular structure in the gaseous and crystalline states; (b) comparison of geometries of crystallographically independent molecules in the same crystal; (c) analysis of the structure of a molecule whose symmetry in the crystal is lower than the symmetry of the free molecule; (d) comparison of molecules in different polymorphs.

We performed[2] a detailed assessment of the flexibility of metal complexes in crystals using methods (b), (c) and (d) outlined above and a combination of methods (b) and (c) based on structures in the Cambridge Structural Database. In these studies the geometrical variations in a number of transition metal systems, showed that sample standard deviations, σ, were typically *ca.* 0.01–0.02 Å for all M–X bonds (X = Cl, N, O, C, P ligands), and similar results were produced by each method of analysis. Bond angles showed σ values typically in the range 1–4°. Torsion angles were more flexible, with σ commonly up to 10° and sometimes much larger (up to 40°). It was deduced that "crystal packing effects" were the largest source of these variations. The experimental uncertainties (*i.e.* crystallographic precision, even when allowing for their underestimation by a factor of 1.5) associated with each structure determination apparently made only minor contributions to the overall σ. Using the same methodology, on an in-house data set, Cotton and Yokochi demonstrated broadly similar behaviour in a set of "paddlewheel" multiply-bonded dimetal complexes.[13] These species showed much smaller σ values (<0.01 Å) for the metal–metal bond lengths than we had observed (*ca.* 0.03 Å) indicating that the large value observed in our study may reflect the softness of the single M–M bonds which dominated our dataset rather than being a general feature of metal–metal bonding. In related work Englert and colleagues carried out a series of studies on tungsten, indium and cobalt complexes which show considerable variation in structure as a function of solvation and other aspects of the crystal environment.[14] Careful study of several solvates of a platinum(II) complex[15] and a series of studies using crystallographic and theoretical approaches in tin chemistry[16] have highlighted the effects of crystal packing on molecular geometry in specific systems.

In our work[2] and that of others[13] a link between the σ value for a given parameter and its force constant k, was not easily established. Cotton and Yokochi concluded that a "general trend" was established, as one would expect, with stiff bonds being less distorted by crystal environment than soft bonds. The σ value that is determined in such studies is the result of the forces exerted by the crystal environment convoluted with the softness of the molecular structure in some way. Since it is not possible to evaluate even the average distorting force in a given set of environments from which parameters have been retrieved it is unlikely that a formal correlation between σ and k will be established. However, at least in extreme cases some qualitative link may be expected. Thus for much organic chemistry, where C–C and similar force constants are high, the effects of the crystal environment (and hence the σ values) are likely to be small. Grabowski has shown that, as an example of a hard system, there is little variation of the bond lengths of the NO_2 group.[17] However the case of *o*-xylene[18] indicates that even in organic crystals there is evidence that measurable distortions from gas-phase geometry (*i.e.* bond lengths and angles) may be observed.

Many small polyatomic ions would be expected to possess high symmetry in an isotropic environment but exhibit deviations from this symmetry in the crystalline state as a result of the anisotropy of their environment. About one quarter of known "molecular" crystal structures are salts and in many cases these salts contain polyatomic ions of moderately high symmetry and simple stoichiometry (*e.g.* of the form $[ECl_n]^{x-}$). Such ions offer the opportunity to study a wide range of chemistry, from d-block metal mononuclear complexes and clusters to high oxidation state p-block chemistry. Here we report studies of the variation in geometry of common complex ions studied crystallographically in a range of salts. Our objectives are: (i) to quantify the variation in their geometries arising from experimental and crystal environment sources. (ii) To establish the reliability of molecular geometry in these and related cases as determined by X-ray crystallography, particularly in light of the use of crystallographic data to validate and calibrate other structural methods, whether experimental or computational. (iii) To investigate the distortions that occur in such ions and the link between their range and the nature of the ion. (iv) To test Kitaigorodskii's dictum that "the crystalline field does not change the bond lengths of organic molecules"[12] and the validity of its extension to ions containing inorganic elements.

Experimental

The methods used are based on those we and others have used previously.[2,13,15] The total variance, σ, of a particular geometric parameter in a given ion is composed of two terms as in eqn. (1).

$$\sigma^2 = \sigma_{\mathrm{env}}^2 + \sigma_{\mathrm{e}}^2 \qquad (1)$$

Here σ_{env}^2 is due to effects caused by the chemical environment and σ_{e}^2 is the variance arising from the crystallographic experiment.

As noted by Taylor and Kennard[19] this method may be used to distinguish between "hard" and "soft" parameters. If the parameter is "hard" it will be relatively insensitive to changes in its environment and so eqn. (2) holds.

$$\sigma^2 \approx \sigma_{\mathrm{e}}^2 \qquad (2)$$

For a "soft" parameter the chemical variance term, σ_{env}^2 will be the major contributor to σ^2. The σ_{env}^2 term may be further subdivided into terms arising from inter- and intra-molecular factors. The latter are the intramolecular steric and electronic factors which are usually considered to determine the "inherent" molecular geometry and whose associated variance will be denoted as σ_{c}^2. The variance due to intermolecular effects, σ_{p}^2, is caused by the crystal packing forces exerted on the molecule in its crystal environment (Kitaigorodskii's "crystalline field").[12] Hence, the overall expression is as in eqn. (3).

$$\sigma^2 = \sigma_{\mathrm{c}}^2 + \sigma_{\mathrm{p}}^2 + \sigma_{\mathrm{e}}^2 \qquad (3)$$

For individual crystal structure analyses σ_{e} may be estimated as the standard uncertainty obtained from the variance–covariance matrix produced by the crystallographic least-squares refinement from which the parameter is derived. In this work we will use a (conservative) estimate $s_{\mathrm{e}} \approx \sigma_{\mathrm{e}}$ as described below.

In this work, since the parameter under investigation will belong to the same ion in different crystal structures, the intramolecular environment is identical in all cases, and hence $\sigma_{\mathrm{c}}^2 = 0$. The elimination of this factor from eqn. (3) means that the total variance of the parameter under investigation is composed of just two terms. Hence, from σ^2 and having an estimate of σ_{e}^2 (*i.e.* s_{e}^2), σ_{p} may be estimated as in eqn. (4).

$$\sigma_{\mathrm{p}}^2 = \sigma^2 - s_{\mathrm{e}}^2 \qquad (4)$$

Alternatively the ratio S defined as in eqn. (5) below may be

$$S = \sigma / s_{\mathrm{e}} \qquad (5)$$

used to indicate those cases in which substantial distortions to the molecular geometry occur whether as a consequence of variation in crystal environment or due to other systematic effects. We shall refer to S as the softness of a given parameter in the discussion below.

A value of 1 for S implies that a parameter is completely insensitive to its crystallographic environment (and that it is not subject to any uncertainty above that implied by the standard crystallographic estimates).

Data retrieval

Crystal structures containing the required ion were retrieved from the Cambridge Structural Database (CSD), using the QUEST programme.[20] Crystallographic data retrieved were screened manually and automatically using the CSD programme VISTA and only structures which fulfilled all of the following criteria were retained for further analyses: a) a crystallographic R-factor ≤ 0.07 for metal containing ions and $R \leq 0.05$ for non-metal containing ions; b) there was no disorder present in the crystal structure, *i.e.* the 'NO DISORDER' flag was set to on; c) all structure determinations were carried out at room temperature (due to the relative paucity of low temperature data in the CSD and in order to minimise apparent variation in geometry resulting from librational effects of varied magnitude due to different temperatures being used for different structure determinations); d) for multiple structure determinations the one with the highest precision was kept. Data were retrieved using a variety of constraints so as to ensure that exactly the correct ion was retrieved. All data were input in to the procedure MISSYM[21] in the PLATON[22] package to check if the reported unit cell and non-hydrogen atomic coordinates did not apparently conform to a higher symmetry space group. When entries were highlighted as possibly having unreported extra symmetry, they were deleted from the data sets.

Data analysis

After screening, data were analysed using the statistical analysis programme SYSTAT.[23] Symmetry equivalent bond lengths and angles were removed and bond and torsion angles constrained by crystallographic symmetry to 0° or 180° were also removed. For a given ion the unweighted mean ($\langle p \rangle$) of a parameter for which n individual observations p_i were available, and the sample standard deviation (σ) were calculated as in eqns. (6) and (7).

$$\langle p \rangle = \Sigma\, p_i/n \qquad (6)$$

$$\sigma^2 = \Sigma\,(p_i - \langle p \rangle)^2/(n-1) \qquad (7)$$

Individual structures were subsequently removed from the dataset if they had p_i outside the range $\langle p \rangle \pm 4\sigma$ for any parameter, and $\langle p \rangle$ and σ were then recalculated. The standard error of σ, SE(σ) was calculated as below:

$$\mathrm{SE}(\sigma) = \sigma/\sqrt{(2n)} \qquad (8)$$

When pooling σ values for a set of n similar ions (*e.g.* all cases of the sort $[\mathrm{MCl_4}]^{2-}$) differences $\Delta_{ij} = p_{ij} - \langle p_j \rangle$ were calculated, where p_{ij} is the value of the i^{th} observation of a parameter p in the j^{th} of m sets whose unweighted mean is $\langle p_j \rangle$. The pooled standard deviation σ was then calculated using eqn. (9) below.

$$\sigma^2 = [\Sigma(\Delta_{ij})^2/(n-m)] \qquad (9)$$

Where n is the total number of parameter values in the data set. It was not assumed in any case that the distribution was normal.

For bond angles with values close to 180° (*e.g trans* bonds angles in square planar and octahedral ions) a different approach was taken, since they are necessarily ≤180°. The variance of these values was obtained by analysis of the combined distribution of angles b_i and $360 - b_i$, where b_i are the values retrieved from the CSD. A similar approach was used for torsion angles with mean values close to ±180°.

Estimation of σ_e

Since standard uncertainties for the parameters are not easily retrieved from the CSD a value representative of the highest s.u. observed for the parameter in a range of structures in each data set was selected from the original literature source and multiplied by a correction factor of 1.5 to give s_e.[5] In addition, the method of Allen *et al.*[8] for predicting the isotropic error in any atom position based on R-factor, atomic weight of atom in question, number of carbon atoms in formula unit was used to obtain the s.u. on a bond length. There was found to be a good agreement between the two methods for calculating s_e. These s_e values are therefore intended to be *upper bound* estimates of σ_e.

Results

The variation of bond lengths, bond angles and torsion angles in a series of metal-containing and other ions in their crystalline salts is summarised in Tables 1–4, further data for these and some other less common ions is given in the Electronic Supplementary Information (ESI) for this paper.† These Tables provide values of σ for the bond parameters together with the number of observations and the mean values for these parameters. The ESI data include s_e and S values, and measures of skewness and kurtosis for these datasets.

Table 1 reports results for perchloro- and perbromometallate anions, a numerous and diverse set of species. The ions are of square planar, tetrahedral or octahedral form with ideal symmetry D_{4h}, T_d and O_h respectively. The variation of bond lengths and other parameters described by σ therefore circumscribes both the deviations from these ideal symmetries and the variations between ions in different crystal structures. In Tables 2–4 similar comments apply. Fig. 1 shows the bond length distributions for square planar $[\mathrm{PtCl_4}]^{2-}$, tetrahedral $[\mathrm{CoCl_4}]^{2-}$, and more irregular but generally tetrahedral $[\mathrm{HgCl_4}]^{2-}$ anions. The variation in the spread of bond lengths shown in Fig. 1 is implied by the M–Cl bond length σ values for these ions (0.010, 0.018, 0.044 Å respectively). As discussed in more detail below these plots are typical of the least variable M–L bond lengths (case (a) in Fig. 1), ions of moderately variable geometry (case (b)) and ions of highly variable geometry (case (c)).

Fig. 2 shows the σ values for the perchloro- and perbromometallates with the σ values for M–X lengths plotted against those for X–M–X angles (X = Cl or Br; only *cis* angles for nominally D_{4h} and O_h ions). It is clear that in all cases in Table 1 the σ values are considerably larger than the (conservatively) estimated s_e values, giving softness parameter, S, values for bond lengths in the range 2.4–31.3 with most in the range 3–6 (see ESI). For bond angles the corresponding S ranges are 1.9 to 82.6 with most in the range 3–15. In effect there appears to be a lower bound on σ for M–Cl (or M–Br) bond lengths which is *ca.* 0.01 Å and for bond angles which is *ca.* 1°. These limiting values are approached by the complex ions of square planar d^8 metals [Pt(II), Au(III), Pd(II)] and the octahedral d^0, d^3, low-spin d^6, and d^{10} metals (Ta(V), Re(IV), Mo(III), Pt(IV), Sn(IV) and Sb(V)). In contrast the values for tetrahedral M(II) tetrachlorides (M = Mn, Fe, Co, Ni, Zn, Cd) are consistently higher with σ(M–Cl) typically ≥0.02 Å and σ(Cl–M–Cl) ≥ 3°. The propensity for this class of anion for forming hydrogen bonds with OH or NH donors has been noted[24] and exploited both for square planar[25] and tetrahedral anions.[26,27] The values for tetrahedral $[\mathrm{MX_4}]^-$ (X = Cl, Br) species are intermediate in behaviour between the lower bound values noted above and the

Table 1 Metal chloride and bromide anions, bond parameters and their standard deviations

Ion (symmetry)	Parameter, *p*	σ	*n*	$\langle p \rangle$
$[CdCl_4]^{2-}$ (T_d)	M–Cl	0.020	27	2.453
	Cl–M–Cl	4.27	43	109.55
$[CoCl_4]^{2-}$ (T_d)	M–Cl	0.018	87	2.273
	Cl–M–Cl	3.29	148	109.63
$[FeCl_4]^{2-}$ (T_d)	M–Cl	0.023	23	2.310
	Cl–M–Cl	4.92	40	109.48
$[HgCl_4]^{2-}$ (T_d)	M–Cl	0.044	44	2.479
	Cl–M–Cl	6.49	66	106.19
$[MnCl_4]^{2-}$ (T_d)	M–Cl	0.018	25	2.360
	Cl–M–Cl	4.05	41	109.46
$[NiCl_4]^{2-}$ (T_d)	M–Cl	0.013	25	2.260
	Cl–M–Cl	4.28	48	109.42
$[ZnCl_4]^{2-}$ (T_d)	M–Cl	0.023	218	2.27
	Cl–M–Cl	3.14	331	109.45
$[AlCl_4]^{1-}$ (T_d)	M–Cl	0.018	220	1.174
	Cl–M–Cl	1.30	333	109.47
$[GaCl_4]^{1-}$ (T_d)	M–Cl	0.021	61	2.157
	Cl–M–Cl	1.80	95	109.46
$[FeCl_4]^{1-}$ (T_d)	M–Cl	0.016	180	2.178
	Cl–M–Cl	1.68	293	109.47
$[PdCl_4]^{2-}$ (D_{4h})	M–Cl	0.011	29	2.305
	Cl–M–Cl *cis*	0.97	28	90.01
	Cl–M–Cl *trans*	1.84	20	178.95
$[PtCl_4]^{2-}$ (D_{4h})	M–Cl	0.010	65	2.301
	Cl–M–Cl *cis*	1.00	71	90.03
	Cl–M–Cl *trans*	2.42	64	178.16
$[AuCl_4]^{1-}$ (D_{4h})	M–Cl	0.010	70	2.277
	Cl–M–Cl *cis*	0.57	65	90.01
	Cl–M–Cl *trans*	1.71	68	179.15
$[SbCl_6]^{-}$	M–Cl	0.017	261	2.356
	Cl–M–Cl *cis*	0.89	529	90.00
	Cl–M–Cl *trans*	1.49	254	178.75
$[TaCl_6]^{-}$	M–Cl	0.021	17	2.327
	Cl–M–Cl *cis*	1.06	40	90.00
	Cl–M–Cl *trans*	1.94	22	178.53
$[SnCl_6]^{2-}$	M–Cl	0.016	73	2.428
	Cl–M–Cl *cis*	1.00	156	90.00
	Cl–M–Cl *trans*	1.10	29	179.04
$[TeCl_6]^{2-}$	M–Cl	0.083	50	2.540
	Cl–M–Cl *cis*	1.36	100	90.00
	Cl–M–Cl *trans*	2.19	40	178.81
$[PtCl_6]^{2-}$	M–Cl	0.009	60	2.316
	Cl–M–Cl *cis*	0.91	121	90.00
	Cl–M–Cl *trans*	0.92	36	179.48
$[ReCl_6]^{2-}$	M–Cl	0.008	15	2.360
	Cl–M–Cl *cis*	0.61	32	89.98
	Cl–M–Cl *trans*	0.71	24	179.52
$[InCl_6]^{3-}$	M–Cl	0.027	14	2.517
	Cl–M–Cl *cis*	1.93	29	90.00
	Cl–M–Cl *trans*	3.22	12	177.38
$[BiCl_6]^{3-}$	M–Cl	0.094	16	2.718
	Cl–M–Cl *cis*	2.99	32	90.12
	Cl–M–Cl *trans*	4.14	18	176.75
$[MoCl_6]^{3-}$	M–Cl	0.010	9	2.452
	Cl–M–Cl *cis*	1.35	11	90.15
	Cl–M–Cl *trans*	1.13	5	177.84
$[CuCl_4]^{2-}$ *all*	Cu–Cl	0.028	292	2.253
	Cl–Cu–Cl	24.79	476	113.07
$[CuCl_2]^{1-}$	M–Cl	0.022	28	2.086
	Cl–M–Cl	8.10	24	177.53
$[AlBr_4]^{1-}$ (T_d)	M–Br	0.012	4	2.257
	Br–M–Br	0.72	6	109.47
$[FeBr_4]^{1-}$ (T_d)	M–Br	0.011	28	2.328
	Br–M–Br	1.23	42	109.47
$[GaBr_4]^{1-}$ (T_d)	M–Br	0.013	8	2.318
	Br–M–Br	2.07	12	109.46
$[TlBr_4]^{1-}$ (T_d)	M–Br	0.018	4	2.552
	Br–M–Br	2.14	3	109.73
$[CdBr_4]^{2-}$ (T_d)	M–Br	0.045	16	2.580
	Br–M–Br	3.53	24	109.36
$[CuBr_4]^{2-}$ (T_d)	M–Br	0.025	11	2.38
	Br–M–Br	10.66	17	110.19
$[HgBr_4]^{2-}$ (T_d)	M–Br	0.019	12	2.594
	Br–M–Br	2.75	16	109.61
$[ZnBr_4]^{2-}$ (T_d)	M–Br	0.016	7	2.402
	Br–M–Br	1.70	11	109.53

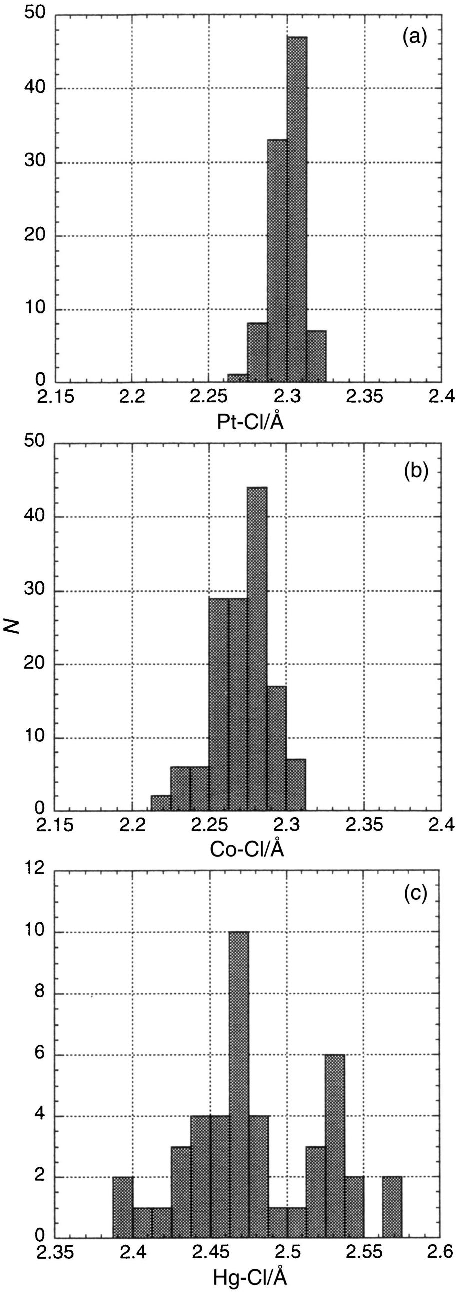

Fig. 1 Histogram of M–Cl bond distances (Å) observed in (a) $[PtCl_4]^{2-}$, (b) $[CoCl_4]^{2-}$ and (c) $[HgCl_4]^{2-}$ anions.

higher values typical of the dianions. Thus the σ values are in the range 0.011–0.021 Å for M–X lengths and in the range 0.72–2.14° for X–M–X angles.

Among the chloride anions in Table 1 there are some pathological cases. These show very high σ values for M–Cl lengths, Cl–M–Cl angles or both: $[CuCl_4]^{2-}$, $[HgCl_4]^{2-}$, $[CuCl_2]^{-}$, $[TeCl_6]^{2-}$, and $[BiCl_6]^{3-}$. The first of these, $[CuCl_4]^{2-}$, is a well studied case[28–30] in which the anion adopts a wide range of geometries between nearly regular tetrahedral (T_d) and square planar (D_{4h}) symmetry reflecting the delicate balance between electronic and steric requirements in this d^9 metal complex. As a consequence σ for the Cl–Cu–Cl angle is abnormally large. The $[HgCl_4]^{2-}$ ion is also a familiar case with many ions reflecting the preference of the Hg(II) centre for linear two-coordination and having substantial variations in both bond lengths and bond angles. The Te(II) and Bi(III) cases are classic 14e VSEPR systems[31,32] in which the lone pair (formally s^2 in character) expresses its influence primarily in wildly variable bond lengths. The environmental factors at work in this class of ions has been discussed.[33] It seems that those $[TeCl_6]^{2-}$ and $[BiCl_6]^{3-}$ ions that

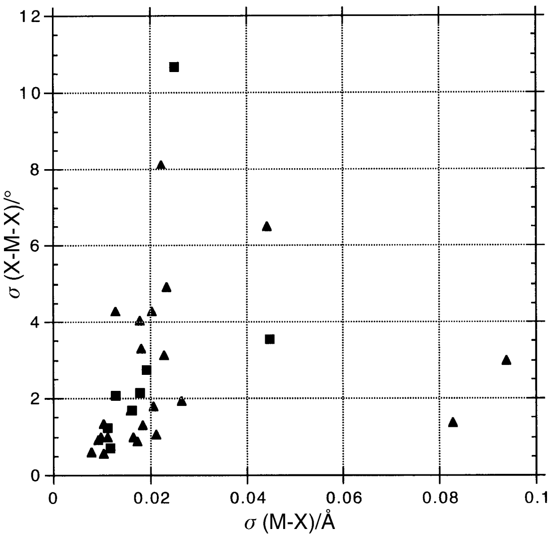

Fig. 2 Graph of σ(M–X) (Å) *vs.* σ(*cis* X–M–X) (°) for perhalogenometallate anions (▲ = chlorides, ■ = bromides). The point for $[CuCl_4]^{2-}$ has been omitted and has σ(M–Cl) = 0.028 Å, σ(Cl–M–Cl) = 24.8°.

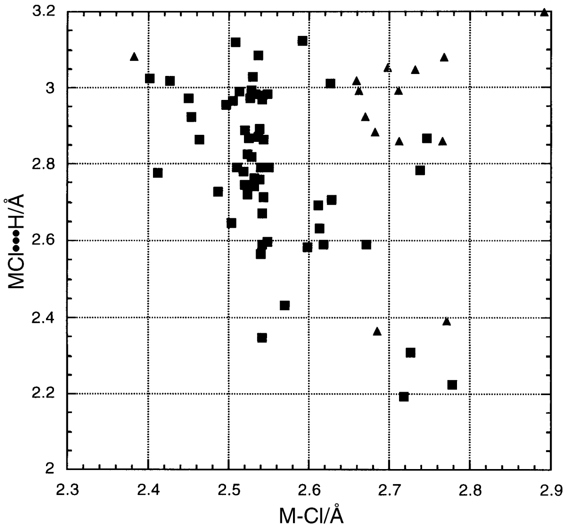

Fig. 3 Graph of M–Cl bond length (Å) *vs.* M–Cl · · · H hydrogen bond length (Å) for $[BiCl_6]^{3-}$ (■) and $[TeCl_6]^{2-}$ (▲) salts.

are in structures with only very weak hydrogen bond donors (*e.g.* CH) in general have rather close to O_h symmetry while cases where there are stronger donors (*e.g.* NH) show much larger bond length variations (see Fig. 3) with the shortest EH · · · Cl (E = N, *etc.*) distances usually (but not rigorously) being associated with the longer Te– or Bi–Cl distances. The "linear" $[CuCl_2]^-$ ion shows substantial angular variation but not abnormally large Cu–Cl variation. This presumably reflects the low force constant for bond angle deformation when Cl–M–Cl is *ca.* 180°. In general the *trans* Cl–M–Cl bond angles are more variable than the *cis* angles in the square planar complexes although this trend is somewhat less clear-cut in the octahedral MCl_6 anions.

The bromide anions in Table 1 behave broadly as do the chlorides given the lesser chemical diversity they represent (all the sufficiently common ions are formally tetrahedral). Thus most of these ions have σ values for M–Br bond lengths and Br–M–Br angles that are in the range 0.01–0.02 Å and 1–3° respectively. The $[CuBr_4]^{2-}$ anion shows great variability in Br–Cu–Br angles as does its chloride analogue.

Table 2 reports values for a series of mononuclear d-, s- and p-block metal complex ions: $[M(CN)_4]^{2-}$ (M = Ni, Pt), $[M(OH_2)_4]^{2+}$ (M = Mg, Co, Ni, Cu, Zn), $[M(mnt)_2]^{x-}$ [x = 1 or 2, mnt = 1,2-$S_2C_2(CN)_2$), M = Au, Ni, Cu], $[FeCp_2]^+$, $[Cr(\eta\text{-}C_6H_6)_2]^+$, $[Co(CO)_4]^-$, $[Rh(CO)_2Cl_2]^-$, $[Li(thf)_4]^+$, [K(18-crown-6)]$^+$ and $[SbPh_4]^+$. The tetracyanometallates show M–C bond length and C–M–C bond angle variation (σ) much larger than expected from estimates of experimental precision (s_e) particularly so for Ni–C distances [hence S values = 2.3 and 4.8 for M–C lengths and 10 and 6 for *cis* C–M–C angles (M = Pt and Ni respectively)]. The intra-ligand (*i.e.* "organic") aspects of structure show less pronounced excess variation for both $[Pt(CN)_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ salts (S = 1.5 and 2.1 respectively for C–N bond lengths).

The hexaaqua dications of Cu (see Table 2) show the effects of the Jahn–Teller distortions giving enormous variation in Cu–O distances (arguably of course these cations should be treated as having D_{4h} symmetry in which case the equatorial Cu–O distances have σ = 0.018 Å with mean 1.960 Å and the axial distances have much larger variability, with σ = 0.073 Å and mean 2.347 Å). The other dications (Co, Ni, Zn) represent a reasonably homogeneous set with σ for M–O and *cis* O–M–O in the ranges 0.018–0.032 Å and 1.7–2.8° (and S > 3.5 and >8 respectively).

The $[M(mnt)_2]^{x-}$ data sets in Table 2 imply rather small variability in the M–S distances and S–M–S angles only marginally higher than the conservatively estimated s_e values for these parameters. In general intra-ligand parameter σ values are of the same order as the estimates of σ_e implying that the ligand (and to a degree metal–ligand) geometries in this case do obey the Kitaigorodskii dictum.

The organometallic d-block metal complexes $[FeCp_2]^+$, $[Cr(\eta\text{-}C_6H_6)_2]^+$, $[Co(CO)_4]^-$, and $[Rh(CO)_2Cl_2]^-$ in Table 2, show σ values for bond length (and metal–centroid distances for the η-ligands) of similar magnitude to earlier cases in Table 1 and elsewhere,[2] *viz.* in the range 0.012–0.028 Å. The L–M–L angles behave similarly and have σ values between 0.66° (for *cis* Cl–Rh–Cl angles) and 3.3°.

The s-block metal complexes in Table 2 ($[Mg(OH_2)_6]^{2+}$, $[Li(thf)_4]^+$, [K(18-crown-6)]$^+$) show rather larger σ values for M–O bond lengths (from 0.025 to 0.065 Å) and O–M–O angle variation at about the same level seen for other cases (σ values from 1.3 to 4.3°). Finally the p-block metalloid case here $[SbPh_4]^+$ again shows similar σ values to those above (Sb–C 0.018 Å, C–Sb–C 3.22°) but slightly above those for $[PPh_4]^+$ (see Table 4 below). This latter observation is consistent with expectation of somewhat more easily deformed (and of course longer) Sb–C bonds than P–C.

Table 3 reports σ values for a series of di-, tri- and tetranuclear metal complexes with varying amounts of metal–metal bonding. The $[Re_2Cl_8]^{2-}$ species contain a strong quadruple metal–metal bond for which a small σ value is observed (0.007 Å, *cf.* 0.0062 Å in ref. 13). Rather larger values are observed for the M · · · M distances for other ions especially $[Mo_2Cl_9]^{3-}$ and $[Fe_4S_4Cp_4]^+$. The dimolybdenum ion has been the subject of some careful studies in which the effect of environment on the length of the metal–metal "bond" is pronounced.[34] Similarly the variability of the Fe · · · Fe distances in the individual $[Fe_4S_4Cp_4]^+$ system has been noted[35,36] and may be ascribed to the weak and variable Fe–Fe bonding in these clusters. In these cases the deformability of the metal–metal distances is a consequence of a rather flexible electronic structure. The bridging ligands seem to exert the primary influence on the geometry of the ion and their bond lengths are much less easily distorted. Thus, M–L σ values are *ca.* 0.02 Å, *cf.* M–M σ values 0.07–0.32 Å. It is notable that the other tetranuclear species in this Table ($[Mo_4(OH)_4(CO)_{12}]^{4-}$ and $[Fe_4S_4(NO)_4]^-$) show much less variability in their M · · · M distances. In the former case there is no metal–metal bonding while the latter formally has more nearly electron precise 2c–2e Fe–Fe bonds. The case of $[Cu_2Cl_6]^{2-}$ is notable[28] in that the local geometry at copper once again varies between nearly tetrahedral and square planar (see ref. 27 for discussion of the effects of crystal environment in some specific cases). In all cases in Table 3, the M–L distances and angles in

Table 2 Mononuclear metal complex ions: bond parameters and their standard deviations

Ion	Parameter, *p*	*σ*	*n*	⟨*p*⟩
$[Ni(CN)_4]^{2-}$	M–C	0.038	24	1.873
	C≡N	0.023	24	1.136
	C–M–C *cis*	1.25	24	90.0
	C–M–C *trans*	1.12	22	178.94
	M–C≡N	2.94	27	177.47
$[Pt(CN)_4]^{2-}$	M–C	0.019	36	1.988
	C≡N	0.016	36	1.144
	C–M–C *cis*	2.05	38	90.0
	C–M–C *trans*	1.36	24	178.94
	M–C≡N	1.35	38	177.57
$[Co(H_2O)_6]^{2+}$	M–O	0.032	41	2.084
	O–M–O *cis*	2.73	87	89.98
	O–M–O *trans*	3.07	24	179.05
$[Cu(H_2O)_6]^{2+}$	M–O	0.192	18	2.089
	O–M–O *cis*	2.72	36	90.0
	O–M–O *trans*	0.03	6	179.97
$[Ni(H_2O)_6]^{2+}$	M–O	0.018	26	2.051
	O–M–O *cis*	1.74	54	89.93
	O–M–O *trans*	2	16	179.99
$[Mg(H_2O)_6]^{2+}$	M–O	0.025	60	2.066
	O–M–O *cis*	2.12	117	92.0
	O–M–O *trans*	3.53	44	178.71
$[Zn(H_2O)_6]^{2+}$	M–O	0.031	16	2.084
	O–M–O *cis*	2.25	33	90.0
	O–M–O *trans*	3.58	12	179.20
$[Au(mnt)_2]^{1-}$	M–S	0.006	14	2.310
	S–C	0.018	14	1.742
	C=C	0.012	7	1.333
	C–C	0.020	14	1.437
	C≡N	0.014	14	1.143
	S–M–S	0.22	7	90.48
	S–C–C	1.24	14	115.11
	S–C=C	0.93	14	123.97
	M–S–C	0.58	14	100.74
	C–C≡N	0.99	14	177.306
	C–C–C	1.50	14	120.87
	S′–M–S	0.68	7	89.52
	M–S–C–C	2.39	32	1.44
$[Ni(mnt)_2]^{1-}$	M–S	0.005	24	2.145
	S–C	0.011	24	1.715
	C=C	0.014	12	1.359
	C–C	0.010	24	1.437
	C≡N	0.008	24	1.132
	S–M–S	0.21	12	92.58
	S–C–C	0.82	24	118.18
	S–C=C	1.01	24	120.48
	M–S–C	0.37	24	103.23
	C–C≡N	0.75	24	178.61
	C–C–C	0.83	24	121.33
	S′–M–S	0.70	12	87.44
	M–S–C–C	1.48	48	0.64
$[Cu(mnt)_2]^{2-}$	M–S	0.014	12	2.261
	S–C	0.011	12	1.735
	C=C	0.011	6	1.350
	C–C	0.016	12	1.439
	C≡N	0.008	12	1.133
	S–M–S	0.95	6	92.09
	S–C–C	0.78	12	116.46
	S–C=C	0.78	12	123.29
	M–S–C	0.71	12	100.61
	C–C≡N	1.24	12	178.21
	C–C–C	0.94	12	120.20
	S′–M–S	3.91	6	93.97
	M–S–C–C	4.21	32	0.56
$[Li(thf)_4]^{+}$	Li–O	0.057	28	1.925
	O–Li–O	4.30	42	109.35
$[SbPh_4]^{+}$	Sb–C	0.018	19	2.095
	C–Sb–C	3.22	30	109.25
$[FeCp_2]^{+}$	Fe–C	0.020	110	2.067
	Fe–X	0.013	22	1.698
	X–Fe–X	1.10	11	178.34
[K(18-crown ether)]$^{+}$	K–O	0.065	192	2.833
	O–M–O_{acute}	1.34	192	59.29
	O–C–C–O	5.40	192	64.00
$[Cr(\eta\text{-}C_6H_6)_2]^{+}$	Cr–C	0.015	72	2.131
	Cr–X	0.012	12	1.615
	X–Cr–X	1.11	6	179.30

Table 2 (*Contd.*)

Ion	Parameter, *p*	σ	*n*	$\langle p \rangle$
$[\mathrm{Co(CO)_4}]^-$	M–C	0.028	60	1.746
	C≡O	0.013	60	1.152
	C–M–C	3.18	98	109.51
	M–C≡O	2.56	116	177.88
$[\mathrm{Rh(CO)_2Cl_2}]^{2-}$	Rh–C	0.015	12	1.813
	Rh–Cl	0.0122	12	2.342
	C≡O	0.040	12	1.119
	Rh–C≡O	2.72	24	177.58
	Cl–Rh–Cl	0.66	6	91.46
	C–Rh–C	1.14	6	90.73
	C–Rh–Cl *trans*	2.71	48	177.55
	C–Rh–Cl *cis*	1.07	12	99.00

Table 3 Polynuclear metal complexes, bond parameters and their standard deviations

Ion	Parameter, *p*	σ	*n*	$\langle p \rangle$
$[\mathrm{Mo_2Cl_9}]^{3-}$	Mo–Mo	0.074	6	2.705
	Mo–$\mathrm{Cl_t}$	0.024	36	2.416
	Mo–$\mathrm{Cl_{br}}$	0.020	36	2.464
	Cl–Mo–Cl	1.70	36	90.72
	Mo–Cl–Mo	2.03	18	66.58
	$\mathrm{Cl_t}$–Mo–$\mathrm{Cl_{br}}$ *trans*	1.11	36	177.64
	$\mathrm{Cl_t}$–Mo–$\mathrm{Cl_{br}}$ *cis*	1.33	72	88.27
$[\mathrm{Re_2Cl_8}]^{2-}$	Re–Re	0.007	6	2.228
	Re–Cl	0.009	30	2.325
	Cl–Re–Cl *trans*	1.21	12	153.76
	Cl–Re–Cl *cis*	0.66	24	87.05
$[\mathrm{Re_3Cl_{12}}]^{3-}$	Re–Re	0.026	17	2.462
	Re–$\mathrm{Cl^b}$	0.008	33	2.400
	Re–$\mathrm{Cl^t}$	0.017	34	2.313
	Re–$\mathrm{Cl^{t,eq}}$	0.016	17	2.578
	$\mathrm{Cl^{ax}}$–Re–$\mathrm{Cl^{ax}}$ *trans*	0.50	17	158.74
	$\mathrm{Cl^{eq,t}}$–Re–$\mathrm{Cl^{t,ax}}$ *trans*	0.87	34	79.41
	$\mathrm{Cl^{eq,t}}$–Re–$\mathrm{Cl^b}$	1.47	99	90.40
	Re–$\mathrm{Cl^b}$–Re	0.44	17	61.73
$[\mathrm{Cu_2Cl_6}]^{2-}$	Cu–$\mathrm{Cl^t}$	0.013	32	2.198
	Cu–$\mathrm{Cl^b}$	0.014	32	2.304
	Cl–Cu–Cl	2.55	18	99.23
	Cu–Cl–Cu	1.59	18	93.94
$[\mathrm{Mo_4(OH)_4(CO)_{12}}]^{4-}$	Mo–O	0.014	40	2.240
	Mo–C	0.033	60	1.888
	Mo–O–Mo	1.13	20	103.39
	Mo···Mo	0.024	20	3.516
	C–Mo–C	2.59	60	84.64
	C≡O	0.057	60	1.207
	Mo–C≡O	4.10	60	174.11
$[\mathrm{Fe_4S_4(Cp)_4}]^+$	Fe–S	0.024	12	2.213
	Fe–C	0.033	20	2.117
	Fe–X	0.012	4	1.757
	S–Fe–X	1.09	12	125.05
	Fe–S–Fe	9.69	24	87.48
	S–Fe–S	8.56	24	89.66
	Fe···Fe	0.318	18	3.032
$[\mathrm{Fe_4S_4(NO)_4}]^-$	Fe–S	0.009	36	2.227
	Fe–N	0.010	12	1.651
	N=O	0.015	12	1.174
	Fe–N=O	1.96	12	176.78
	S–Fe–N	2.10	36	114.73
	Fe–S–Fe	0.42	33	74.29
	S–Fe–S	0.51	36	103.72
	Fe···Fe	0.009	18	2.689

general show the usual substantial values of σ (on the order of 0.01–0.02 Å and 1–2°).

Table 4 lists σ values for a series of non-metal containing ions for comparison with the metal species of Tables 1–3. In most cases although the σ values for bond lengths are in the range 0.01–0.03 Å the estimated contributions of σ_e to these values is rather larger than for the heavy atom containing distances in Tables 1–3. As a consequence *S* values come close to 1 in a number of instances. The implication is that we can be less sure that Kitaigorodskii's dictum fails in such cases. Furthermore, in some cases, most notably $[\mathrm{PF_6}]^-$, $[\mathrm{NMe_4}]^+$ and $[\mathrm{ClO_4}]^-$ there is clear evidence for the effects of librational effects on bond lengths. Thus histograms for these bond length distributions show elongated tails to short distances (see Fig. 4 for the $\mathrm{PF_6}^-$ case) and correspondingly negative coefficients of skewness. Surprisingly the $[\mathrm{BF_4}]^-$ ion does not show such effects in this dataset. The $\mathrm{I_3}^-$ ion is a notable and well documented[37,38] exception to the above comments on Table 4 and shows very large I···I distance variation ($\sigma = 0.468$ Å) although a normal degree of bond

Table 4 Non-metal containing ions, bond parameters and their standard deviations

Ion	Parameter, *p*	σ	*n*	$\langle p \rangle$
$[I_3]^-$	I–I	0.468	417	2.921
	I–I–I	3.27	394	178.01
$[PF_6]^-$	P–F	0.037	2703	1.551
	F–P–F *cis*	2.20	5553	90.0
	F–P–F *trans*	2.09	1485	177.66
$[BF_4]^-$	B–F	0.030	944	1.350
	F–B–F	2.81	1484	109.43
$[Ph_3P{=}N{=}PPh_3]^+$	P–N	0.011	322	1.576
	P–N–P	8.30	161	143.24
	C–P–C	1.17	966	107.53
$[PPh_4]^+$	P–C	0.013	1429	1.791
	C–P–C	1.82	2210	109.45
$[BPh_4]^-$	B–C	0.022	616	1.655
	C–B–C	3.15	952	109.49
$[SO_3CF_3]^-$	S=O	0.030	630	1.420
	C–F	0.039	630	1.308
	S–C	0.038	210	1.795
	F–C–F	2.98	630	107.17
	O=S=O	2.23	630	114.74
$[NMe_4]^+$	N–C	0.039	698	1.482
	C–N–C	2.71	1044	109.44
$[NEt_4]^+$	N–C	0.024	1195	1.516
	C–N–C	2.81	1839	109.47
$[NPr_4]^+$	N–C	0.027	90	1.527
	C–N–C	2.53	140	109.49
$[NBu_4]^+$	N–C	0.022	667	1.525
	C–N–C	2.60	1024	109.48
$[ClO_4]^-$	Cl–O	0.029	3096	1.406
	OClO	1.78	4644	109.46
$[2,4,6\text{-}(NO_2)_3C_6H_2O]^-$	N–O	0.019	606	1.217
	$C–O^-$	0.015	101	1.248
	C–N	0.013	303	1.453
	C–C	0.037	606	1.399
	O–N–O	1.43	303	122.59
	O–N–C	1.18	606	118.67
	O–C–C	1.52	202	124.23
	N–C–C	1.76	606	118.28
	C–C–C	4.56	606	119.95
$[H_3CCO_2]^-$	C–O	0.025	62	1.250
	C–C	0.019	31	1.511
	O–C–O	2.22	31	123.72
	O–C–C	1.86	31	117.93
$[F_3CCO_2]^-$	C–O	0.029	40	1.223
	C–C	0.022	20	1.514
	C–F	0.058	60	1.294
	O–C–O	1.96	20	128.57
	O–C–C	2.34	40	115.67
	F–C–F	5.06	60	104.96
$[SO_4]^{2-}$	S–O	0.015	357	1.470
	O–S–O	1.22	716	109.46

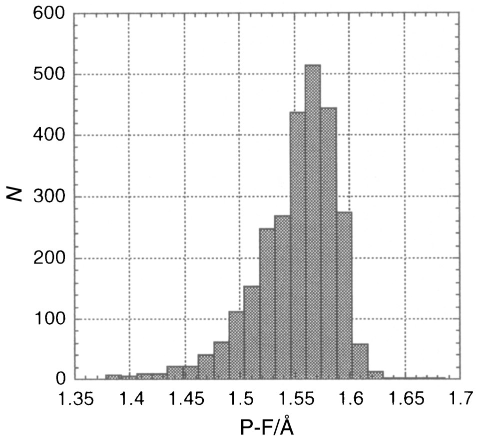

Fig. 4 Histogram of bond distances (Å) observed in $[PF_6]^-$ anions.

angle variability ($\sigma = 3.3°$). Once again the influence of the interaction of the anion with its crystal environment through hydrogen bonding has been emphasised.[39]

Conclusions

Kruskal–Wallis statistics[40] for the perchlorometallate datasets in Table 1 indicate that they are not drawn from the same population, *i.e.* that there is good evidence that they are due to bonds with distinctly different σ values for bond lengths and angles. When the pathological cases noted above (for Cu, Hg, Te and Bi salts) are removed, further Kruskal–Wallis analysis allows us to identify 4 essentially homogenous data sets: square planar $[MCl_4]^{n-}$, tetrahedral $[MCl_4]^{2-}$, tetrahedral $[MCl_4]^-$ and octahedral $[MCl_6]^{n-}$ ions. Here the null hypothesis that the Δ_{ij} values within these grouped datasets are drawn from the same distribution cannot be rejected at the 99% confidence level. Pooled estimates of σ for each of these data sets (and for the tetrahedral $[MBr_4]^-$ anions as well as two other homogenous data sets) are given in Table 5. These reflect the general observations made above.

The implied emphasis on distortion of molecular geometry by crystal environment in the above discussion should not be taken to mean that the large σ and *S* values observed are caused solely by the crystal packing effects. It is important to note that other sources of apparent variation in molecular dimensions

Table 5 Statistics for pooled results

Ion (symmetry)	Parameter	Remarks	σ	n	SE(σ)
$[MCl_4]^{2-}$ (T_d)	M–Cl	no Hg	0.0218	418	0.0008
	Cl–M–Cl	no Cu	3.87	710	0.10
$[MCl_4]^{-}$ (T_d)	M–Cl		0.0177	461	0.0006
	Cl–M–Cl		1.53	721	0.04
$[MCl_4]^{n-}$ (T_d)	M–Cl	no Hg	0.0200	879	0.0005
	Cl–M–Cl	no Cu	2.93	1431	0.05
$[MCl_4]^{n-}$ (D_{4h})	M–Cl	no Cu	0.0097	164	0.0005
	Cl–M–Cl *cis*	no Cu	0.82	196	0.04
	Cl–M–Cl *trans*	no Cu	2.46	156	0.14
$[MCl_6]^{n-}$ (O_h)	M–Cl	no Bi or Te	0.0144	171	0.0008
	Cl–M–Cl *cis*		1.34	481	0.04
	Cl–M–Cl *trans*		1.27	150	0.07
$[MBr_4]^{n-}$ (T_d)	M–Br	no Cd	0.0163	66	0.0014
	Br–M–Br	no Cu	2.32	105	0.16
$[M(H_2O)_6]^{2+}$	M–O	no Cu	0.0268	143	0.0016
	O–M–O *cis*		2.33	327	0.09
	O–M–O *trans*		2.03	93	0.15
$[M(mnt)_2]^{x-}$	M–S		0.0081	82	0.0006
	S–C		0.0138	82	0.0011
	C–C		0.0126	42	0.0014
	C=C		0.0144	81	0.0011
	C≡N		0.0121	82	0.0009
	S–M–S		0.42	41	0.05
	S–C–C		1.07	82	0.08
	S–C=C		0.87	82	0.07
	M–S–C		0.51	81	0.04
	C–C≡N		1.01	83	0.08
	C–C–C		1.01	81	0.08
	S′–M–S		1.57	41	0.17
	M–S–C–C		1.32	88	0.10

must contribute some of the excess variability in bond parameters noted in Tables 1–5. These effects have been discussed and noted by a number of authors including ourselves[2,15] and include the following: unresolved twinning, the effects of disorder (when not resolved or adequately treated); the mis-assignment of space group, poor absorption corrections; anharmonicity of atomic vibrational motion; librational shortening of bonds; temperature variation between structure determinations; compositional disorder in which, for example, chloride and methyl occupy the same site in the crystal. This is a formidable list of potential contributors to the observed σ values. The magnitude of the contributions may vary widely between individual crystal structures contributing to the dataset used in this paper. However it would be surprising if the dominant effect were not the "packing effects" assumed in the discussion above given the *chemical* effects noted. It is striking that σ_p values for Pt–Cl bond lengths estimated by detailed and careful study of one complex in a variety of solvated crystal forms[15] [σ_p(Pt–Cl) = 0.008 Å] and in this work [for $[PtCl_4]^{2-}$, σ_p = 0.0088(9) Å] are the same.

The key advance in this work compared with our previous study is the opportunity to monitor chemical effects on molecular flexibility by study of specific chemical entities rather than similar fragments from a series of related but not identical systems. The outcome of this study is summarised below.

(1) The data presented offer clear evidence for a link between σ and the softness of systems when a big enough range of chemistry is spanned. Thus for example M–Cl bond length σ values are small for species such as $[SnCl_6]^{2-}$ or $[MoCl_6]^{3-}$ (σ = 0.016(1) and 0.010(2) Å respectively). In contrast some classes of anions, most notably $[TeCl_6]^{2-}$ or $[BiCl_6]^{3-}$ have much larger values (σ = 0.083(8) and 0.094(17) Å respectively). Nevertheless this is still some way short of a quantitative relationship between σ and force constant.

(2) Baseline uncertainty levels are apparent in even very well behaved systems such as $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$ (bond length and bond angle σ *ca.* 0.01 Å and 1.0° respectively). This may represent the limiting case for collections of structural data that is achievable, at least for routine room temperature X-ray crystal structure analyses in the period up to the mid-1990s using 4-circle X-ray diffractometry serial detector technology.

(3) There is no evidence that the geometries of the complex ions studied here are substantially more variable than those of similar neutral molecules. Thus the pooled estimates of σ for M–Cl bond lengths and angles in the present study (see Table 5) are similar to those previously estimated by a variety of methods [M–Cl length σ values: 0.0113(7), 0.0112(5) and 0.0193(3) Å; *cis* Cl–M–Cl 1.43(6)°].[2]

(4) There is some evidence that the "organic" or non-metal aspects of molecular geometry are less variable than the metal-containing aspects. This would be in accord with expectations of lower force constants for bonds of the latter sort and with Kitaigorodskii's dictum (see above).

Crystallographic analysis of any one given crystal gives an image of molecular structure which should be regarded as a snapshot of one part of the range of geometries available to that molecular entity. In the studies we have done (see ref. 2 and the present work) the numbers of structures may approach sufficient diversity to allow a qualitative sense of how molecular geometry is blurred in solution. Thus the ensemble of crystal environments represented in these datasets may mimic the ensemble of solvent environments and ion-pairing, *etc.* that might occur in solutions of these ions. A more quantitative test of this assertion will have to await for example, molecular dynamics simulations of the structures of such ions in solution and other experimental tests.

As we have noted, crystallographically determined intramolecular geometry is often used in calibration of both experimental (*e.g.* EXAFS spectroscopic) and computational procedures for the determination of molecular geometry. Our work implies that when the crystallographic and other procedures agree to rms and mean deviations on the order of 0.01 or 0.02 Å for bond lengths and 1 or 2° for bond angles then this calibration or validation process is essentially complete.

The softness ratio, S (= σ/s_e) is substantial in many cases and particularly in nearly all metal–ligand and metal–metal bond lengths or angles involving these bonds. Only in some particular cases do the s_e and σ values become close enough that the approximations made here to provide the s_e values become unsatisfactory and hence the S values unreliable. In short, the usual crystallographic estimates of precision while they may underestimate true levels of precision by factors of *ca.* 1.5[5,6] apparently underestimate by much larger amounts the variation of molecular geometry (lengths and angles) as determined by routine application of single crystal X-ray diffractometry for almost all metal–ligand and metal–metal bonds. The σ values presented in this paper may be taken as representing the "inherent uncertainty" for X-ray crystallographically determined metal–ligand bond distances and valence angles. As such it appears that this "inherent uncertainty" is at least 0.01 Å and for angles 1 or 2°. These values are of course standard deviations. The ranges of bond lengths and angles observed are therefore likely to be *ca.* 6 times larger than these values. *i.e.* $\mathrm{M–L} = \mu \pm 0.03$ Å; $\mathrm{L–M–L} = \mu \pm 3°$ (where μ is the mean value of the bond parameter). We have previously discussed the potential difficulties this may impose on structural studies which are based on differences in molecular geometry of the same order as σ. However it is worth noting that the conclusions of this paper apply to collections of X-ray data as present in the CSD and as such may not represent the limits of precision and accuracy currently achievable, especially given the greatly increased availability of low temperature and area detector data collection and the improved data quality that results.

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References

1 Part 7. J. J. Barker and A. G. Orpen, *Acta Crystallogr., Sect. B*, 1999, **55**, 203.
2 A. Martín and A. G. Orpen, *J. Am. Chem. Soc.*, 1996, **118**, 1464.
3 (*a*) A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1; (*b*) A. G. Orpen, *Acta Crystallogr., Sect. D*, 1998, **54**, 1194; (*c*) M. M. Harding, *Acta Crystallogr., Sect. D*, 2000, **56**, 857.
4 W. C. Hamilton and S. C. Abrahams, *Acta Crystallogr., Sect. A*, 1970, **26**, 18.
5 R. Taylor and O. Kennard, *Acta Crystallogr., Sect. B*, 1986, **42**, 112.
6 (*a*) D. Schwarzenbach, S. C. Abrahams, H. D. Flack, E. Prince and A. J. C. Wilson, *Acta Crystallogr., Sect. A*, 1995, **51**, 565; (*b*) *Guide to the Expression of Uncertainty in Measurement*, International Organisation for Standardisation (ISO), Geneva, 1993.
7 F. H. Herbstein, *Acta Crystallogr., Sect. B*, 2000, **56**, 547.
8 F. H. Allen, J. C. Cole and J. A. K. Howard, *Acta Crystallogr., Sect. A*, 1995, **51**, 95; F. H. Allen, J. C. Cole and J. A. K. Howard, *Acta Crystallogr., Sect. A*, 1995, **51**, 112.
9 F. H. Allen, S. E. Harris and R. Taylor, *J. Comput.-Aided Mol. Des.*, 1996, **10**, 247.
10 A. Almenningen, O. Bastiansen, L. Fernholt, B. N. Cyvin, S. J. Cyvin and S. Samdok, *J. Mol. Struct.*, 1985, **128**, 59 and refs. therein.
11 C. P. Brock and R. P. Minton, *J. Am. Chem. Soc.*, 1989, **111**, 4586.
12 A. I. Kitaigorodskii, *Adv. Struct. Res. Diffr. Methods*, 1970, **3**, 173.
13 F. A. Cotton and A. Yokochi, *Inorg. Chem.*, 1997, **36**, 2461.
14 (*a*) T. Wagner and U. Englert, *Struct. Chem.*, 1997, **8**, 357; (*b*) U. Englert, G. E. Herberich and J. Rosenplanter, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1098; (*c*) T. Wagner and U. Englert, IUCr Congress and General Assembly, 1999, Abstract P07.FF.008.
15 M. H. Johansson, S. Otto, A. Roodt and A. Oskarsson, *Acta Crystallogr., Sect. B*, 2000, **56**, 226.
16 (*a*) E. R. T. Tiekink, V. J. Hall and M. A. Buntine, *Z. Kristallogr.*, 1999, **214**, 124; (*b*) M. A. Buntine, V. J. Hall and E. R. T. Tiekink, *Z. Krist.*, 1998, **213**, 669; (*c*) M. A. Buntine, V. J. Hall, F. J. Kosovel and E. R. T. Tiekink, *J. Phys. Chem.*, 1998, **2**, 2472; (*d*) E. R. T. Tiekink, V. J. Hall and M. A. Buntine, *Z. Kristallogr.*, 2000, **215**, 215, E. R. T. Tiekink, V. J. Hall and M. A. Buntine, *Z. Kristallogr.*, 2000, **215**, 23.
17 S. J. Grabowski, *J. Chem. Res.*, 1988, (*S*) 252.
18 R. M. Ibberson, C. Morrison and M. Prager, *Chem. Commun.*, 2000, 539.
19 R. Taylor and O. Kennard, *Acta Crystallogr., Sect. B*, 1983, **39**, 517.
20 F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 1; F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 31.
21 Y. Le Page, *J. Appl. Crystallogr.*, 1987, **20**, 264.
22 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.
23 SYSTAT Inc., version 5.2, Evanston, IL, 1992.
24 G. Aullón, D. Bellamy, L. Brammer, E. A. Bruton and A. G. Orpen, *Chem. Commun.*, 1998, 653.
25 G. R. Lewis and A. G. Orpen, *Chem. Commun.*, 1998, 1873.
26 A. L. Gillon, A. G. Orpen, J. Starbuck, X.-M. Wang, Y. Rodríguez-Martín and C. Ruiz-Pérez, *Chem. Commun.*, 1999, 2287.
27 A. L. Gillon, A. G. Orpen, J. Starbuck, S. Rotter, X.-M. Wang, Y. Rodríguez-Martín and C. Ruiz-Pérez, *J. Chem. Soc., Dalton Trans.*, 2000, 3897.
28 D. W. Smith, *Coord. Chem. Rev.*, 1976, **21**, 93.
29 S. Keinan and D. Avnir, *Inorg. Chem.*, 2001, **40**, 318.
30 J. A. McGinnety, *J. Am. Chem. Soc.*, 1976, **94**, 8406.
31 G. A. Fisher and N. C. Norman, *Adv. Inorg. Chem.*, 1994, **41**, 223.
32 (*a*) R. J. Gillespie and R. S. Nyholm, *Q. Rev. Chem. Soc.*, 1957, **10**, 339; (*b*) R. J. Gillespie, *J. Chem. Educ.*, 1970, **47**, 18.
33 C. J. Carmalt, N. C. Norman and L. J. Farrugia, *Polyhedron*, 1995, **14**, 1355.
34 (*a*) F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms*, Clarendon Press, Oxford, 1993, pp. 601 and 604; (*b*) J. E. McGrady, R. Stranger and T. Lovell, *J. Phys. Chem. A*, 1997, **101**, 6265.
35 P. Baird, J. A. Bandy, M. L. H. Green, A. Hamnett, E. Marseglia, D. S. Obertelli, K. Prout and J. Qin, *J. Chem. Soc., Dalton Trans.*, 1991, 2377.
36 D. Bellamy, A. Christofides, N. G. Connelly, G. R. Lewis, A. G. Orpen and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 2000, 4038.
37 H.-B. Bürgi and J. D. Dunitz, *Structure Correlation*, ed. H.-B. Bürgi and J. D. Dunitz, Verlag Chemie, Weinheim, 1994, ch. 5, and references cited therein.
38 G. A. Landrum, N. Goldberg and R. Hoffmann, *J. Chem. Soc., Dalton Trans.*, 1997, 3605.
39 P. K. Bakshi, M. A. James, T. S. Cameron and O. Knopp, *Can. J. Chem.*, 1996, **74**, 559.
40 C. W. Snedecor and W. G. Cochrane, *Statistical Methods*, Iowa State University Press, Ames, IA, 7th edn., 1980, pp. 215–219.