

Structural Systematics. 6.¹ Apparent Flexibility of Metal Complexes in Crystals

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Abstract: Data retrieved from the Cambridge Structural Database for crystal structures containing metal complexes have been analyzed to evaluate the effects of crystal environment on molecular geometry. Parameters for the same bonds in different crystal sites were compared and variances estimated for these parameters. The primary method used was to compare geometric data for crystal structures for which more than one molecule of complex is present per crystallographic asymmetric unit. Other methods used were comparison of geometry for molecules whose symmetry or pseudosymmetry is higher than the crystal site symmetry, combination of these two methods, and study of compounds for which more than one polymorph has been structurally characterized. These studies allow quantification of the oft-cited “crystal packing” effects on molecular structure. Typically the metal–metal and metal–ligand bond lengths show standard deviations (σ) on the order of 0.01–0.02 Å apparently due to the effects of crystal environment. The corresponding values for valence angles at the metal atoms typically lie in the range 1–2° although some are over 3°, and for torsion angles the values are still higher (typically 5–10° for cyclic bonds and $\gg 40^\circ$ for P–Ph bonds in MPPh₃ complexes). The variances of molecular parameters are *much larger* than the variances estimated from standard crystallographic least-squares procedures and appear to result in large part from crystal packing effects. The implications of these results for the interpretation of crystallographic data are considered. Among consequences discussed are the nature of the structure determined by crystallographic methods, the validity of modeling procedures which mimic crystallographically determined structures, and the relationship between parameters determined by crystallographic and other structural methods.

Introduction

The face of chemistry has been marked beyond recognition by crystal structure determination. The power of the technique first developed by the Braggs² has changed forever our ideas about the shapes of molecules. Today we take almost for granted the unambiguous veracity of crystal structure analysis as the ultimate arbiter, with a few notable exceptions, in the determination of the dimensions and stereochemistry of molecules in crystals. Indeed, there's the rub. From crystal structure determinations we can learn only the shape of the molecule in the crystal in which its structure has been determined. The molecular shape as determined in this way is the product both of the “inherent molecular structure” whatever that might be³ and the effect of the crystalline field in which it is located. For many years chemical crystallographers have invoked “crystal packing effects” as the cause of variations in molecular geometry that appear to have no chemical (*i.e.* intramolecular) cause. This paper seeks to measure the magnitude of these effects in a class of molecules which are rather prone to them: metal complexes. In this paper our purpose is to establish the variability of molecular geometry parameters in crystal structures, and to estimate how much of the variation is due to crystal packing effects rather than to experimental uncertainties.

Crystallographers are in general exceedingly punctilious about calculating and publishing estimated standard deviations (esds), or “standard uncertainties” as is the preferred terminology of

the ISO and IUCr⁴ for cell dimensions, atomic coordinates, bond lengths, angles *etc.*, usually based on least-squares refinement procedures. Careful studies by Taylor and Kennard⁵ and organized by the International Union of Crystallography⁶ of independently determined crystal structures have shown that the crystallographic esds published for atomic positional coordinates, and hence also the esds published for bond lengths and angles, usually underestimate the true standard deviations by a factor of *ca.* 1.5. Furthermore, Taylor and Kennard⁵ and Allen and co-authors⁷ have suggested that an even larger factor may be implied in the case of structures containing heavier atoms such as transition metals. For such atoms significant anharmonic motion may lead to small but important errors in the positional parameters of the heavy atoms derived from refinements in which the usual harmonic approximations are used.⁸ Finally Taylor and Kennard⁵ concluded that cell dimension esds are also underestimated by factors of between 2 and 5 implying an additional underestimate of the esds of bond lengths and angles.

In this paper and others^{9–11} analysis of sets of data from crystal structures reveals chemically important variation in

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parameters such as M–L (where M = d-block metal) bond distances or L–M–L angles. In these sets of data the total variance (σ_{tot}^2) observed for a parameter such as a bond length or angle can be decomposed into two terms as in eq 1.

$$\sigma_{\text{tot}}^2 = \sigma_{\text{env}}^2 + \sigma_e^2 \quad (1)$$

Here σ_{env}^2 denotes the variance in the parameter caused by the environment of the bond, and σ_e^2 is the variance due to uncertainties arising from the experimental determination of the crystal structure (see ref 5 for a discussion of the sources of σ_e^2). The σ_{env}^2 term may be further subdivided into terms arising from intra- and intermolecular factors. The first are the intramolecular steric and electronic factors which are usually considered to determine the 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. Therefore the overall expression (assuming no correlation between the components of σ_{tot}^2) becomes as given in eq 2.

$$\sigma_{\text{tot}}^2 = \sigma_c^2 + \sigma_p^2 + \sigma_e^2 \quad (2)$$

The value for σ_e^2 can be derived from the estimated standard deviation (esd) values obtained from the variance–covariance matrix produced by the crystallographic least-squares refinement from which the parameter is derived. Estimation of σ_p^2 is possible if we restrict ourselves to study of the parameter values in crystallographically different but chemically equivalent sites, for which $\sigma_c^2 = 0$ by definition since the intramolecular environment is identical. In this work we have done this in various ways: (i) study of polymorphs; (ii) study of multiple chemically identical molecules in the crystallographic asymmetric unit; (iii) study of molecules in which the molecular symmetry is higher than that of the crystal site in which they occur; and (iv) a combination of methods (ii) and (iii).

Kitaigorodskii suggested methods (i–iii) as ways of studying the effects of the crystalline field on the shapes of molecules in 1970¹² (see also an important discussion by Bernstein of these and related problems).¹³ At the time Kitaigorodskii felt confident that “the crystalline field does not change the bond lengths of organic molecules”. He further said that the principal effects of the crystal environment are on the conformations of organic molecules. Given the limited amount of highly precise structural data available at that time he was clearly justified. In this paper we show that whatever the truth of that statement for purely organic molecules (see below), metal complexes are apparently subject to observable distortions in bond lengths and angles as well as torsion angles.

Using the crystallographic information contained in the Cambridge Structural Database (CSD),¹⁴ we have studied the variance in the bond lengths, bond angles, and torsion angles of the fragments M–M, M–Cl, M(acac), M–N, M–CO, M(CO)₂, M–Ar, M–Ph, L_nMPPPh₃, Cp₂ML₂ (Cp = η -C₅H₅), Cp₂ML₃, M(dppe), and M₂(dppm). These are a representative

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set of ligand environments in which transition metals may be found in organometallic and coordination complexes and bioinorganic chemistry. As such they reflect the areas of direct concern to a wide range of synthetic, structural, and biological chemists. These species are also of current interest to molecular modellers and other computational chemists, as well as those concerned with other methods of molecular geometry determination such as EXAFS spectroscopy. More generally, use of geometric models based on crystallographic data is exceedingly widespread and their reliability is of great concern.

Other methods for study of the effects of the crystalline field on molecular geometry we have not employed in this paper include the study of crystal structures of complexes in which variation in solvate (see Braunstein *et al.*¹⁵ for a spectacular example) or counterion allows the same molecule or ion to be observed in more than one crystal environment.¹⁶ These approaches are not currently automated within the CSD system and hence we have not used them. Kitaigorodskii¹² also suggested comparison of gas-phase molecular structures with those in the crystalline phase (see ref 17 for an elegant example). Some aspects of the work in this paper have been reported in preliminary form.¹⁸

Experimental Section

Data Retrieval. Crystal structures containing the molecular fragments studied were located in the Cambridge Structural Database (CSD) using the QUEST program.¹⁴ Data for these crystal structures were retrieved from the April 1994, October 1994, and April 1995 versions of the CSD in which the master data file contained 120 481, 126 353, and 140 268 entries, respectively.

Crystallographic data retrieved were screened manually and automatically and only structures which fulfilled all of the following criteria were retained for further analysis: (a) a crystallographic *R* factor ≤ 0.07 had been reported; (b) the reported mean standard deviation of the C–C bond lengths was ≤ 0.03 Å; (c) there was no disorder in the fragment under study; (d) the compound contains a d-block metal (M = Sc–Zn, Y–Cd, La–Hg); and (e) the reported unit cell and non-hydrogen atomic coordinates do not apparently conform to a higher symmetry space group according to the MISSYM¹⁹ procedure implemented in the PLATON package.²⁰ The systems studied and the number of structures fulfilling all these conditions are listed in Table 1. Four methods were used to select crystal structures from which pairs of chemically identical, but crystallographically different parameters were obtained (see below). Methods (i), (ii), and (iii) rely on the selection of suitable crystal structures from the CSD, while method (iv) is a combination of methods (ii) and (iii) and was applied to appropriate structures of type (ii): (i) polymorphs for which crystal structure determinations have been reported and the CSD “polymorph” or “form” flag is set; (ii) structures with more than one molecule in the asymmetric part of the unit cell (*i.e.* $Z' > 1$ in the terminology of the CSD); (iii) structures in which molecular symmetry $>$ crystallographic site symmetry; and (iv) combinations of (ii) and (iii); for cases where the local symmetry is $> C_1$ (*e.g.* C_{3v} in P–C distances and C–P–C and M–P–C angles of MPPH₃ complexes; C_{2v} in Cp₂ML_n species).

Method (i) was used only for fragments M–M and M–Cl because of the small numbers of available data for other fragments. For the same reason method (iii) was not widely applied and was used only for the M–PPh₃ and M–Cl fragments in *trans*-M(PPh₃) and *trans*-Cl–M–Cl species, respectively. Method (ii) (or as its variant, iv) was used for all systems.

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Table 1. Bond Parameters Studied and Their Standard Deviations

fragment	parameter	method	CSD refcodes	observations (<i>n</i>)	sets (<i>m</i>)	σ (Å or deg)	σ_e (Å or deg)	σ_p (Å or deg)
M–M	M–M	(i) polymorph	17	17	8	0.016(2) ^a	0.006	0.015
		(iv)	293	1501	410	0.0340(1)	0.006	0.033
M–Cl	M–Cl	(i) polymorph	58	141	34	0.0113(7)	0.009	0.007
		(iv)	95	298	107	0.0112(5)	0.009	0.007
Cl–M–Cl	Cl–M–Cl	(iv)	83	277	85	1.43(6)	0.3	1.40
		(iii) symmetry	781	2002	1001	0.0193(3)	0.009	0.017
<i>trans</i> -Cl–M–Cl	M–Cl	(iii) symmetry	781	2002	1001	0.0193(3)	0.009	0.017
M–pyridine	M–N	(iv)	124	489	144	0.0250(8)	0.011	0.022
M–phenyl	M–C	(iv)	11	28	11	0.017(7)	0.015	0.008
M–aryl	M–C	(iv)	35	101	36	0.0152(11)	0.015	0.002
M–acac	M–O	(iv)	8	50	11	0.025(3)	0.015	0.020
M–CO (monocarbonyls)	M–C	(ii) $Z' > 1$	35	76	35	0.0121(10)	0.014	
M(CO) ₂ (dicarbonyls)	M–C	(iv)	94	556	170	0.0199(6)	0.014	0.014
		C–M–C		278	105	1.66(7)	0.4	1.60
[Cp ₂ ML ₂]	M–cent	(iv)	26	114	26	0.0087(6)		
		Cp–M–Cp		57		0.67(6)		
		Cp–M–L		228		2.02(19)		
		L–M–L		57		0.79(7)	0.15	0.78
		cent–M–cent–C		114		7.1(5)		
[Cp ₂ ML ₃]	M–cent	(iv)	7	32	7	0.0090(11)		
		Cp–M–Cp		16		0.96(17)		
		L–M–L		48		0.65(7)	0.15	0.63
		cent–M–cent–C		32		7.4(9)		
MPPH ₃	M–P	(iv)	73	154	73	0.0099(6)	0.005	0.009
		P–C _{ipso}	(iv)	462	462	0.0113(4)	0.009	0.007
		M–P–C _{ipso}		462	462	3.28(11)	0.45	3.25
		C _{ipso} –P–C _{ipso}		462	462	2.04(7)	1.35	1.20
		M–P–cent(C _{ipso}) ₃		154	154	1.16(7)		
		M–P–C _{ipso} –C _{ortho}		462	462	47.4(16)	1.95	47.40
		(iii) symmetry	269	540	270	0.0084(3)	0.005	0.007
MPPH ₃ in <i>trans</i> -M(PPh ₃) ₂	M–P	(iii) symmetry	269	540	270	0.0084(3)	0.005	0.007
		P–C _{ipso}		1620		0.0111(2)	0.009	0.006
		M–P–C _{ipso}		1620	1620	3.60(6)	0.45	3.57
		C _{ipso} –P–C _{ipso}		1620	1620	2.14(4)	1.35	1.66
		M–P–cent(C _{ipso}) ₃		540	540	1.26(4)		
		M–P–C _{ipso} –C _{ortho}		1620	1620	47.8(8)	1.95	47.71
		(iv)	22	126	22	8.0(5)		
MP ₂ C ₂ rings	M–P–C–C	(iv)	22	126	22	8.0(5)		
		P–M–P–C		126		6.1(4)		
		P–C–C–P		63		6.5(6)		
M ₂ P ₂ C rings	M–M–P–C	(iv)	12	72	12	9.7(8)		
		M–P–C–P		72		5.9(5)		
		P–M–M–P		36		2.7(3)		

^a Figures in parentheses are standard errors in the least significant digit, here and throughout this paper.

Data Analysis. A locally modified version of the program GEO-STAT²¹ was used to calculate the values of the bond lengths, bond angles, and torsion angles listed in Table 1 for each fragment. For complexes [Cp₂ML₂] and [Cp₂ML₃] the rotation of the Cp rings was studied in terms of the torsion angles cent–M–cent–C (cent = centroid of the Cp ring). A single dihedral angle, τ_M , was defined as the mean value of the torsion angles for a given Cp group. This torsion angle is indicative of staggered ($\tau_M = 36^\circ$) or eclipsed ($\tau_M = 0^\circ$) conformations. For the MPPH₃ fragment the torsion angle M–P–C_{ipso}–C_{ortho} (ω) was averaged over the values for the two ortho carbons [$\omega = \omega_1 + \omega_2 + 180$]/2.²² For the MPPH₃ fragment the angle formed by the metal, the phosphorus atom, and the centroid of the three C_{ipso} atoms was calculated.²³ For the two five-membered-ring systems studied [M(dppe) and M₂(dppm)] the intra-annular torsion angles were calculated for the ring conformation type in which the P–C–C–P [for M(dppe)] or P–M–M–P [for M₂(dppm)] torsion angle is positive (see ref 24 for a detailed discussion of the symmetry of the conformation space of these systems).

The datasets thus retrieved have sets (*m* in number) of at least two chemically identical fragments which are crystallographically distinct and therefore subject to different crystalline fields. From the *j*th set of these fragments for a given parameter, *p*, the unweighted mean parameter value $\langle p_j \rangle$ was obtained ($\langle p_j \rangle = \sum p_{ij}/n_j$ for $i = 1, n_j$, where

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there are n_j equivalent values in the *j*th set and p_{ij} is the parameter value for the *i*th member of the *j*th set). Differences $\Delta_{ij} = p_{ij} - \langle p_j \rangle$ were calculated. Figure 1 shows a histogram of the distribution of $\pm|\Delta_{ij}|$ values (i.e. both positive and negative values of a given Δ_{ij} are shown) for the M–Cl dataset derived by method (iii). The number of observations n ($=\sum n_j$) and sets *m* for each fragment as used in the calculation are listed in Table 1. The standard deviation (σ) of the total sample of Δ_{ij} values for each parameter was calculated as $\sigma^2 = \sum \Delta_{ij}^2 / (n - m)$. Bonds which showed $|\Delta_{ij}| > 4\sigma$ for any bond parameter were discarded and not used for calculation, and all relevant σ values recalculated. The standard error of σ was calculated using eq 3 below.²⁵ This equation assumes a normal distribution of σ and holds more closely as *n* becomes large as it is for almost all the cases here.

$$\text{standard error of } \sigma = \frac{\sigma}{\sqrt{2n}} \quad (3)$$

σ_e Estimation. The esd values for the parameters studied are not stored in the CSD, and therefore these values were obtained from the original literature for a wide selection of the structures used. For each parameter, a value representative of the highest esds observed for a range of structures in the dataset was selected and multiplied by a correction factor of 1.5.⁵ These values, which serve as very conservative (i.e. high) estimates of σ_e , are listed in Table 1. For some parameters studied in this work the value of the esd is not reported in the primary literature and the estimation of σ_e has not been possible.

R Factor Dependence. A study of the influence of the quality of the structure determination on the parameter standard deviation was

(25) Stuart, A.; Ord, J. K. *Kendall's Advanced Theory of Statistics*, 6th ed.; Edward Arnold: London, 1994; Vol. 1, p 364.

Table 2. Variation of σ with the Crystallographic R Factor Reported

Rfactor <		0.03	0.04	0.05	0.06	0.07
M–M ($Z' > 1$)	σ	0.0375(5)	0.0338(2)	0.0342(1)	0.0342(1)	0.0340(1)
	n/m	214/51	580/158	1113/297	1391/381	1501/410
M–Cl ($Z' > 1$)	σ	0.0066(9)	0.0105(7)	0.0114(6)	0.0111(5)	0.0112(5)
	n/m	27/11	129/50	209/79	276/100	298/107
M–Cl (symmetry)	σ	0.0161(6)	0.0183(4)	0.0187(3)	0.0187(3)	0.0193(3)
	n/m	356/178	956/478	1554/777	1866/933	2002/1001
Cl–M–Cl ($Z' > 1$)	σ	1.16(16)	1.34(9)	1.39(7)	1.35(6)	1.43(6)
	n/m	27/10	121/45	210/68	265/82	277/85
M–N ($Z' > 1$)	σ	0.0171(19)	0.0155(9)	0.0263(11)	0.0259(9)	0.0250(8)
	n/m	42/15	140/42	298/87	441/129	489/144
fragment M(CO) ₂ M–CO	σ	0.0115(3)	0.0170(5)	0.0179(5)	0.0195(6)	0.0199(6)
	n/m	72/13	264/87	390/126	504/161	556/170
OC–M–CO	σ	1.60(19)	1.73(11)	1.59(8)	1.54(7)	1.66(7)
	n/m	36/12	130/48	193/75	252/98	278/105
fragment MPPh ₃ M–P ($Z' > 1$)	σ	0.0065(12)	0.0086(9)	0.0098(7)	0.0099(6)	0.0099(6)
	n/m	15/7	51/23	98/46	134/63	154/73
M–P (symmetry)	σ	0.0062(6)	0.0081(4)	0.0076(3)	0.0077(2)	0.0084(3)
	n/m	56/28	196/98	352/176	486/243	540/270
P–C ($Z' > 1$)	σ	0.0090(9)	0.0106(6)	0.0110(5)	0.0114(4)	0.0113(4)
	n/m	45/7	153/23	294/46	402/63	462/73
P–C (symmetry)	σ	0.0094(5)	0.0100(3)	0.0100(2)	0.0107(2)	0.0111(2)
	n/m	168/28	588/98	1056/76	1458/243	1620/270
M–P–C ($Z' > 1$)	σ	3.6(4)	3.30(19)	3.17(13)	3.21(11)	3.28(11)
	n/m	45/7	153/23	294/46	402/63	462/73
M–P–C (symmetry)	σ	3.70(2)	3.59(11)	3.50(8)	3.55(7)	3.60(6)
	n/m	168/28	588/98	1056/76	1458/243	1620/270
C–P–C ($Z' > 1$)	σ	1.9(2)	1.91(11)	2.01(8)	1.99(7)	2.04(7)
	n/m	45/7	153/23	294/46	402/63	462/73
C–P–C (symmetry)	σ	2.28(13)	2.14(6)	2.14(5)	2.13(4)	2.14(4)
	n/m	168/28	588/98	1056/76	1458/243	1620/270

carried out. For a given parameter, structures were classified in groups according to the magnitude of their crystallographic R factor and then σ for each group was calculated [see Table 2 and Figures 2a and 2b]. This method is only possible when the number of structures is large enough to calculate a reliable value for σ . For that reason σ values for the groups of structures with lower R factors are less reliable and as a consequence in some cases σ was not calculated.

Values of σ_e were estimated as indicated above and used to estimate the nonexperimental contribution (σ_p^2) to the total parameter variance (σ^2) according to eq 4 which is based on eq 2 with $\sigma_e^2 = 0$ as is the case here.

$$\sigma_p = \sqrt{\sigma^2 - \sigma_e^2} \quad (4)$$

Results and Discussion

The values of σ obtained by the various methods described above are listed in Tables 1 and 2. The method used here makes some important assumptions which should be clarified. The calculation of σ assumes that the various sets (pairs or triples or more numerous sets) of values for a given bond parameter (M–Cl say) each provide estimates of the variance of that parameter which may be derived from the Δ_{ij} values. These estimates of variance were pooled to provide a more reliable estimate of the variance (σ^2) for the given parameter using standard procedures²⁶ in which the pooled estimate of variance (here σ^2) is given by the sum of squares ($\sum \Delta_{ij}^2$) divided by the number of degrees of freedom, ndf [$\text{ndf} = \sum (n_j - 1) = (n - m)$]. The key assumption here is that the various different sets of Δ_{ij} are drawn from the same parent distribution, *e.g.* that the

(26) Snedecor, G. W.; Cochran, W. G. *Statistical Methods*, 7th ed.; Iowa State University Press: Ames, 1980; pp 215–219.

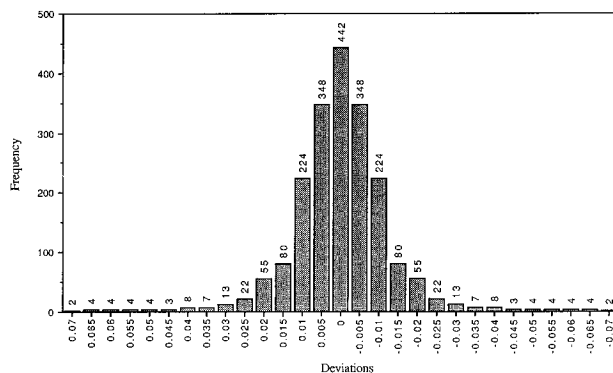


Figure 1. Histogram of $\pm\Delta_{ij}$ values for the M–Cl symmetry dataset.

variation of the deviations of all the M–Cl distances from their mean values may be described by a single value of σ . This is clearly not exactly true since we might expect slightly different behavior for M–Cl bonds in different molecules, especially as a consequence of varying M (and/or its oxidation state for example). Nevertheless, this is the only practical assumption open to us at present and hence it was used. In an attempt to judge the veracity of this assumption some distributions (*e.g.* M–Cl) were studied manually in detail. Figure 1 shows the distribution of $\pm|\Delta_{ij}|$ values in this case. It should be noted that at no stage in this work is it assumed that the distribution of Δ_{ij} values is normal.

As may be seen in Table 1, values of σ for bond lengths range from 0.0084(3) to 0.0340(1) Å, from 0.65(7) to 3.60(6)° for bond angles, and from 2.7(3) to 47.8(8)° for torsion angles. In some cases, *e.g.* M–Cl bond lengths, several estimates of σ

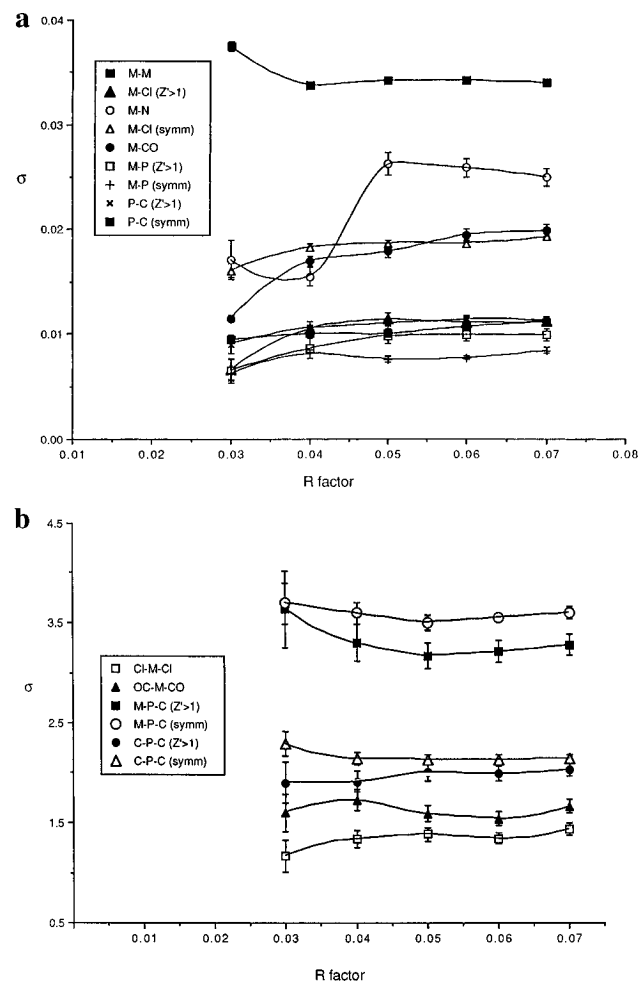


Figure 2. (a) Variation of σ values for bond lengths (with standard errors, see Table 2) with crystallographic R factor. The solid lines indicate polynomial interpolations between the points. (b) Variation of σ values for bond angles (with standard errors, see Table 2) with crystallographic R factor. The solid lines indicate polynomial interpolations between the points.

were obtained using various of the methods [0.0113(7), 0.0112(5), and 0.0193(3) Å for M–Cl by methods (i, iv, iii), respectively]. In general the agreement between σ values from different methods is reasonable. Thus a Kruskal–Wallis analysis of variance²⁷ for these three sets of Δ_{ij} values indicates that the null hypothesis, that the samples are drawn from the same population (*i.e.* have the same σ values), cannot be rejected at the 99% confidence level. This is as to be expected if the values of σ are robust descriptors of the variability of the parameters studied. There is some indication that estimates of σ based wholly on molecular symmetry (*i.e.* method (iii)) are higher than those from other methods (see *e.g.* M–CO and M–Cl). This might be a consequence of these datasets being depleted of very small values of Δ_{ij} since in many structures containing otherwise appropriate ML_n (*e.g.* MCl_2) fragments the Δ_{ij} values are constrained to be exactly zero by imposed crystallographic symmetry and are therefore discarded.

In all cases bar one the σ values are larger than the estimates of σ_e hence allowing calculation of values for σ_p (see Table 1). Since the σ_e values are conservative (high) estimates we may therefore assume that the σ_p values in Table 1 are lower limit estimates. In all cases the metal–ligand bond distance σ values are >0.01 Å. This is in contrast to similar data for organic

structures²⁸ in which σ values of ≤ 0.01 Å were observed for a substantial number of bond length distributions where a variety of both molecular *and* crystal environments were included. This latter observation is consistent with Kitaigorodskii's dictum that the crystalline field does not affect bond lengths in organic molecules. The implication of the data in Tables 1 and 2 is that this does not hold for metal complexes.

As an alternative method of estimating the experimental contribution (σ_e) to σ , values of σ were calculated for successively more restricted crystallographic R values (in those cases for which there are sufficient data). In this way we attempted to provide values for σ which may be extrapolated to $R = 0$ for which σ_e would be at a minimum. Table 2 lists the σ values and Figures 2a and 2b illustrate their variations. In general the values of σ for the highest precision (*i.e.* lowest R value) structure determinations are consistent with the values of σ_p calculated using eq 4 (see Table 1). Equation 4 of course provides only a crude estimate of σ_p since it is based on a conservative and approximate value for σ_e . It should be noted that simply restricting the crystallographic R factor is a crude and potentially unreliable way of increasing the experimental precision of the parameters studied.⁷ Notably in cases where heavy elements are present low crystallographic R factors may be obtained even though metal–ligand and even more so intraligand dimensions are rather poorly determined.

In this paper we have estimated the variance of a number of molecular parameters (σ^2) due to factors other than intramolecular effects and random experimental errors of the sort estimated by crystallographic least squares (σ_e^2). What then is the source, or are the sources, of the variances, σ_p^2 , that remain, which are often much larger than σ_e^2 ? One important source is undoubtedly the variation in crystallographic environments to which the molecules are exposed. This is precisely the crystalline field or crystal packing effects that have been held responsible on many occasions for variation of molecular parameters from their ideal or expected values for reasons that were otherwise inexplicable. However, we should consider other possible sources of these variances.

Compositional Disorder. Parkin *et al.*²⁹ have demonstrated that compositional disorder can lead to anomalous variations in crystallographically determined bond lengths. This is certainly possible for some of the parameters studied here, most obviously for M–Cl bond lengths and Cl–M–Cl angles in which replacement of chloride by other halide, pseudo-halide, or near-isomorphous groups such as methyl is conceivable. However, for many examples it is harder to conceive of a mechanism by which this effect could play a large role. Furthermore, since it is *variation* in compositional disorder between different sites *in the same crystal* that is required for this effect to make a contribution to σ_p^2 as calculated by methods (ii), (iii), and (iv), we can reasonably expect this source of variance to be a minor one.

Librational Effects. Distances and other parameters derived from crystallographic data are based on atomic positions averaged over disorder whether dynamic or static. The dimensions discussed here are not corrected for libration and similar effects and therefore are liable to be affected differently by these systematic errors in the different crystal environments in which they are located. This seems unlikely to be a major contributor here. Although the vast majority of the structures used in this study were determined at room temperature the dimensions under study involve the metal atoms of rather large complexes. These parts of the molecule are almost always near the center of mass of the complex and hence subject to rather small

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librational motions and hence corrections. Since it is the differences in the corrections for identical molecules that would contribute to the σ_p^2 , we can be confident that this source of variance is a minor one.

The polymorph approach is likely to be more severely affected than the other methods by the nonpacking effect sources of variance described above. The fact that this method does not yield substantially different estimates of variance than the other methods may therefore be taken as an indication that they do not make a major contribution to the observed variances.

Systematic Errors. As noted above there is some anecdotal evidence in the literature^{3,4} that the crystallographic least-squares estimates of σ_e are more drastic underestimates for the heavier elements. Why this should be so is not transparent although anharmonic motion of the heavy atoms (and its not being accurately treated in the crystal structure analysis) has been suggested as one cause.⁸ However, it is conceivable that unresolved crystallographic problems such as unrecognized twinning,^{5,30} incorrect space group assignment,³¹ absolute structure assignment,³² imperfectly corrected absorption effects, or inadequacies in the cell dimension esds (see above, and ref 5) could also contribute to the observed σ . In any event the underestimate of σ_e would have to be truly spectacular for this to explain all the variance observed here. It may be however that the values of σ reported here conceal different values for different elements (of the 5d elements compared with those of the 3d elements, for example). It should be noted that our procedures should have eliminated almost all incorrect space groups within the dataset by application of the MISSYM¹⁹ procedure as implemented in PLATON²⁰ and discarding all doubtful cases from the datasets. The proportion of structures discarded in this way (27 from a total of 1802 unique CSD refcodes, ca. 1.5%) is striking.

Mechanisms of Crystalline Field Effects. It is worth considering what the mechanisms of any packing effects might be. In at least the case of the M–Cl bonds we might anticipate that hydrogen bonding, usually reckoned the strongest of intermolecular interactions, would play a role in distortions leading to different parameter values in differing crystal environments. In fact in at least one case in the *trans*-Cl–M–Cl dataset this appears to be the case. Thus $\Delta_{ij} = \pm 0.0395$ Å is associated with a CH \cdots Cl contact having an H \cdots Cl distance of 2.80 Å.³³ In other cases it might be that dipole–dipole interactions play a significant role (*e.g.* for metal carbonyls). These types of packing effects might be termed first-order effects in which there is a direct perturbation of a bond parameter by an interaction with the local environment. It is clear, however, that many of the parameters in Table 1 cannot be affected by first-order effects since they are insulated from the crystalline field by ligands (as for M–M) or substituents (*e.g.* M–P, P–C in M–PPh₃). In these cases second-order effects appear to operate in which, for example, changes in conformation cause

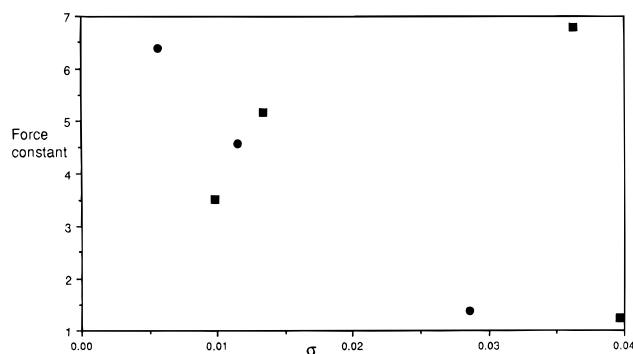


Figure 3. Force constants (N m^{-1}) for platinum- (●) and ruthenium- (■) containing bonds³⁴ vs corresponding values of σ (see Table 3).

Table 3. Force Constants³⁴ and σ Values for Platinum and Ruthenium Bonds

bond	σ (Å)	pairs/sets	freq (cm^{-1})	force constant (N/m)
Pt–Cl	0.0115(20)	16/7	320	4.58
Pt–P	0.0057(14)	8/4	400	6.38
Pt–N	0.0286(46)	19/6	265	1.37
Ru–Cl	0.0098(34)	22/7	300	3.53
Ru–Ru	0.0362(2)	584/96	300	6.79
Ru–N	0.0396(34)	68/21	260	1.24
Ru–O	0.0134(13)	12/1	500	5.15

distortions in bond angles which in turn affect bond lengths. Presumably the relative softness of metal–ligand bond lengths, and of valence angles at both metals and ligand contact atoms, facilitate these distortions and render them observable as here.

Clearly the bond parameters for some metals might be expected to be more easily distorted than those of others. As an extreme example Cu–Cl distances in Cu(II) complexes vary widely as a result of Jahn–Teller effects.⁹ In practice, as noted above, inspection of the larger Δ_{ij} values shows no significant contribution from metals for which such effects would be expected. Nevertheless, it is likely that the σ values in Table 1 reflect some average of a variety of different variances for different metals.

In light of the previous discussion we considered the possibility that there would be a simple relationship between parameter softness as measured by σ and the force constants for the deformation in question. Clearly one would expect some relationship. However, there is no simple link as shown by graphs of force constants³⁴ versus standard deviation for selected bonds that do not in any way resemble linear plots (see Figure 3, Table 3, and footnote 35). This is understandable since the variations observed here (σ_p), insofar as they arise from crystalline field effects, do so as a result of both the softness of *and* the forces placed on the bond in question. We have no way (here anyway) of measuring these forces³⁶ and so must leave this point unresolved.

Conclusions

Perhaps the most important result of this work is that the molecular structure of individual metal complexes as revealed

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(34) Values taken from: (a) *Spectroscopic Properties of Inorganic and Organometallic compounds*; Davidson, G., Senior Reporter, Royal Society of Chemistry: London, 1994, and other earlier members of the series. (b) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1994.

(35) A referee has pointed out that the appearance of Figure 3 would be better in line with expectation if the point for Ru–Ru bonds were removed (or if one or both of the σ or force constant values for this point were greatly reduced).

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by crystal structure analyses is of limited reliability. These limitations appear to be reflected in what might be termed inherent standard deviations in metal–ligand (or metal–metal) bond lengths of which most lie between 0.01 and 0.02 Å. There appears to be relatively little variation between values for different bond types although it seems that metal–metal bonds ($\sigma = 0.0340(1)$ Å) are exceptionally prone to deformation (as has been noted anecdotally on a number of occasions, *e.g.* ref 37) although they will also be especially prone to the effects of systematic errors as discussed above. Similarly, bond angles have an inherent standard deviation of between 1 and 2° in most cases, although on occasion (notably for tilting of PPh₃ ligands as reflected in the larger σ for M–P–C as compared with C–P–C angles) larger values of up to 3.6° are observed. Torsion angles, as noted by Kitaigorodskii,¹² are especially prone to the effects of the crystalline field, showing σ values of up to 47°. Acyclic bonds appear a pathological case, if torsions about P–C_{ipso} in MPPH₃ are representative, and are particularly affected. In contrast intracyclic torsions (*e.g.* about P–C bonds in M(dppe) complexes) have smaller σ values.

It seems likely that the major contributions to these inherent uncertainties arise from the crystalline field. However, it may be that other sources (as described above) play some part and therefore we have used the term apparent in the title and elsewhere to qualify our assignment of the source of these uncertainties. It may be as important that consumers of crystallographic data on molecular structures of metal complexes appreciate the limitations on the reliability of this type of structural data, whatever their source.

If we assume that the arguments above hold and that σ_p values are larger than σ_e , especially for reasonably precise structures, then some interesting corollaries arise. First we might consider that these data provide some estimate of the amount by which molecular structures vary in the solution phase as the local solvent field varies with time (if we assume as a first approximation that the forces on the molecule in solution are of the same order as those in the solid). While it has been widely supposed that solid state structures are not an infallible guide to solution state geometries the present study provides some insight into how much molecular geometries might vary. In any event these results remind us that the structures of metal complexes are not fixed and are apparently variable even in terms of bond lengths and angles as well as the more expected torsion angles.

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Crystallographic results are very widely used to gauge the quality of other methods of determining molecular geometry, whether experimental (such as EXAFS spectroscopy) or computational (*e.g.* molecular mechanics or quantum methods). In the computational field both molecular mechanics force field (see, *e.g.* refs 38 and 39) and quantum chemistry (see, *e.g.* ref 40) methods have been calibrated by comparison with crystallographically determined parameters. In these cases discrepancies between experimental and calculated values for M–L bond lengths and bond angles of *ca.* 0.02 Å and 1 or 2°, respectively, have been regarded^{38–40} as signifying “good agreement”. In light of the study reported here, these discrepancy criteria do indeed look appropriate. However, we note that while root-mean-square deviations of these magnitudes are to be expected, mean deviations should not be so large, and substantial values might indicate systematic inadequacies in the modeling procedure. In the light of the results above it is clear that discrepancies between crystallographic and other values on the order of the σ in Table 1 are likely to be insignificant.

Finally, we should consider where these results leave studies which are based on variations in molecular dimensions that may be on the order of the σ values in Table 1. Into this category might come structure–property relationship studies or attempts to test theoretical predictions such as our own studies of metal–phosphine bonding.^{1,41} It is clear that trouble may result unless considerable care is taken to choose situations where the geometrical effects are large compared with σ or to use statistical methods to check hypotheses that are not dependent on σ_e values derived from crystallographic least squares. In some important instances variations in bond lengths are very much on the order of the σ values here. For example, the Re–Re bond lengths measured in [Re₂Cl₄(PMe₂Ph)₄]ⁿ⁺ ($n = 0, 1, 2$) and related species⁴² vary by only small amounts (*e.g.* in the three complexes listed 0.045 Å) in crystal structures containing these complexes. It is clear that such small variations may be due to intermolecular aspects of the crystal structure rather than being an inherent property of the molecule. Careful analysis (by experimental and computational means in this case)⁴² was required to extract the chemical principles at work. More generally it is usually assumed that shorter bonds are stronger, although this truism has recently been called into question by a stimulating article reporting bond lengths and thermochemical data for open titanocene complexes (see ref 43 and references therein). In any such discussion the question arises as to when a bond length is “longer”. Conventionally the answer has been based on comparison of the bond lengths in light of their crystallographic esds. As argued above perhaps σ values of the sort presented here may in fact be more appropriate measures of the uncertainties in the bond lengths and other parameters.

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