

9.6. Typical interatomic distances: organometallic compounds and coordination complexes of the *d*- and *f*-block metals

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9.6.1. Introduction

The determination of molecular geometry is of vital importance to our understanding of chemical structure and bonding. The majority of experimental data have come from X-ray and neutron diffraction, microwave spectroscopy, and electron diffraction. Over the years, compilations of results from these techniques have appeared sporadically. The first major compilation was Chemical Society Special Publication No. 11: *Tables of Interatomic Distances and Configuration in Molecules and Ions* (Sutton, 1958). This volume summarized results obtained by diffraction and spectroscopic methods prior to 1956; a supplementary volume (Sutton, 1965) extended this coverage to 1959. Summary tables of bond lengths between carbon and other elements were also published in Volume III of *International Tables for X-ray Crystallography* (Kennard, 1962). Some years later, the Cambridge Crystallographic Data Centre (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979) produced an atlas-style compendium of all organic, organometallic and metal-complex crystal structures published in the period 1960–1965 (Kennard, Watson, Allen, Isaacs, Motherwell, Pettersen & Town, 1972). More recently, a survey of geometries determined by spectroscopic methods (Harmony, Laurie, Kuczkowski, Schwendemann, Ramsay, Lovas, Lafferty & Maki, 1979) has extended coverage in this area to mid-1977. A notable compendium of structural data, without geometric information, was given in *Comprehensive Organometallic Chemistry* (Bruce, 1981), covering all complexes with metal–carbon bonds. The BIDICS (Brown, Brown & Hawthorne, 1982) series, which finished in 1981, provided for some years a full coverage of metal complexes giving both bibliographic and geometric information. There have also been valuable annual summaries, without geometric information, on the structures of organometallic compounds determined by diffraction methods (Russell, 1988).

The production of further comprehensive compendia of X-ray and neutron diffraction results has been precluded by the steep rise in the number of published crystal structures, as illustrated by Fig. 9.6.1.1. Print compilations have been effectively superseded by computerized databases. In particular, the

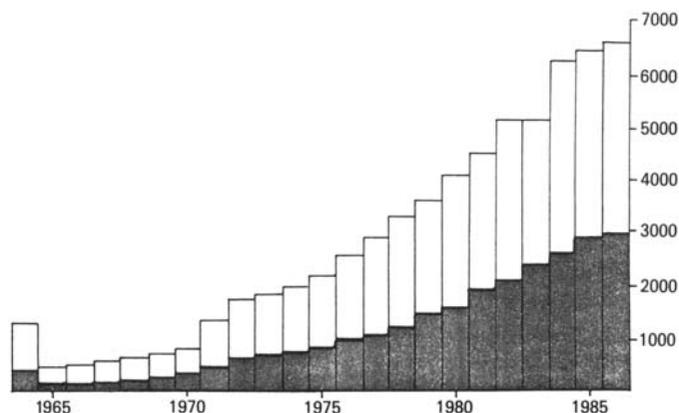


Fig. 9.6.1.1. Growth of the Cambridge Structural Database as number of entries (N_{ent}) added annually. The structures containing *d*- or *f*-block metals are indicated by shading.

Cambridge Structural Database now contains bibliographic, chemical, and numerical results for some 86 000 organo-carbon crystal structures. This machine-readable file fulfils the function of a comprehensive structure-by-structure compendium of molecular geometries. However, the amount of data now held in the CSD is so large that there is also a need for concise, printed tabulations of average molecular dimensions.

The only tables of average geometry in general use are those contained in the Chemical Society Special Publications of 1958 and 1965 (Sutton, 1958, 1965), which list mean bond lengths for a variety of atom pairs and functional groups. Since these early tables were based on data obtained before 1960, we have used the CSD to prepare a new table of average bond lengths in organic compounds (see Chapter 9.5) and in metal complexes. The table given here (Table 9.6.3.3) specifically lists average lengths for metal–ligand distances, together with intra-ligand distances, involving bonds between the *d*- and *f*-block metals (Sc–Zn, Y–Cd, La–Hg, Ce–Lu, Th–U) and atoms H, B, C, N, O, F, Si, P, S, Cl, As, Se, Br, Te, and I of ligands. Mean values are presented for 324 different bond types involving such metal–ligand bonds.

9.6.2. Methodology

9.6.2.1. Selection of crystallographic data

All results given in Table 9.6.3.3 are based on X-ray and neutron diffraction results retrieved from the September 1985 version of the CSD. Neutron diffraction data only were used to derive mean bond lengths involving hydrogen atoms. This version of the CSD contained results for 49 854 single-crystal diffraction studies of organo-carbon compounds; 9802 of these satisfied the acceptance criteria listed below and were used in the averaging procedures:

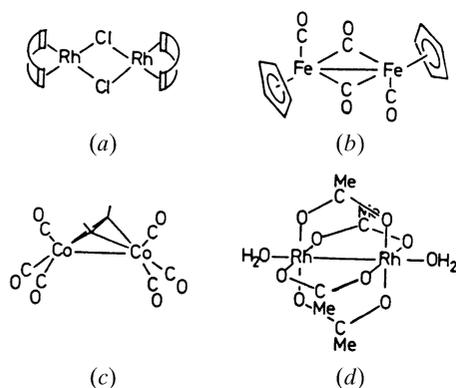
- (i) Structure contains a *d*- or *f*-block metal.
- (ii) Atomic coordinates for the structure have been published and are available in the CSD.
- (iii) Structure was determined from diffractometer data.
- (iv) Structure does not contain unresolved numeric data errors from the original publication (such errors are usually typographical and are normally resolved by consultation with the authors).
- (v) Only structures of higher precision were included on the basis that *either* (a) the crystallographic *R* factor was ≤ 0.07 and the reported mean estimated standard deviation (e.s.d.) of the C—C bond lengths was $\leq 0.030 \text{ \AA}$ (corresponds to AS flag = 1, 2 or 3 in the CSD), *or* (b) the crystallographic *R* factor ≤ 0.05 and the mean e.s.d. for C—C bonds was not available in the database (AS = 0 in the CSD).
- (vi) Where the structure of a given compound had been determined more than once within the limits of (i)–(v), then only the most precise determination was used.

The structures used in Table 9.6.3.3 do not include compounds whose structure precludes them from the CSD (*i.e.* not containing ‘organic’ carbon). In practice, structures including at least one C—H bond are taken to contain ‘organic’ carbon. Thus, the entry for Cr—CO distances has a contribution from $[\text{NEt}_4][\text{Cr}(\mu\text{-H})(\text{CO})_{10}]$ but *not* from $\text{K}[\text{Cr}(\mu\text{-H})(\text{CO})_{10}]$ or $[\text{Cr}(\text{CO})_6]$.

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9.6.2.2. Program system

All calculations were performed on a University of Bristol VAX 11/750 computer. Programs *BIBSER*, *CONNSEER*, *RETRIEVE* (Allen *et al.*, 1979) and *GEOSTAT* (Murray-Rust & Raftery, 1985*a,b*), as locally modified, were used. A stand-alone program was written to implement the selection criteria, whilst a new program (*STATS*) was used for statistical calculations described below. It was also necessary to modify *CONNSEER* to improve the precision with which it locates chemical substructures. In particular, the program was altered to permit the location of atoms with specified coordination numbers. This was essential in the case of carbon so that atoms with coordination numbers 2, 3, and 4 (equivalent to formal hybridization state sp^1 , sp^2 , sp^3) could be distinguished easily and reliably. Considerable care was taken to ensure that the correct molecular fragment was located by *GEOSTAT* in the generation of geometrical tabulations. Searches were conducted for all metals together and statistics for individual metal elements and subdivision of the entry for a given metal carried out subsequently. An important modification to *GEOSTAT* allowed for calculation of metal-atom coordination number with due allowance for multihapto ligands and μ_2 ligands. Thus, η^5 -C₅H₅, η^6 -C₆H₆, and other η^5 and η^6 ligands were assigned to occupy 3 coordination sites, η^3 and η^4 ligands such as allyls and dienes to occupy 2 coordination sites, and η^2 ligands such as alkenes 1 site, and so on. The approach taken in dealing with (μ_2) bridging ligands was that when a metal-metal bond is bridged by one atom of a ligand [*e.g.* as in Cl, CO, OMe *etc.* as in (a), (b) below] then only the non-metal atom is counted as occupying a coordination site. For the relatively rare case of bridging polyhapto ligands (in which the bridging atoms are linked by direct bonds), the assignment follows logically, thus, μ_2 - η^2 , η^2 -alkyne, see (c) below, occupies one site on each metal. Bridging ligands that do not have one atom bonded to both metals [*e.g.* acetate in (d) below] contribute to metal coordination numbers as do terminal ligands. In examples (a)–(d) below, the metal atoms therefore have coordination numbers as follows: (a), Rh 4; (b), Fe 6; (c), Co 4; (d), Rh 6. For cases where coordination number is very difficult to assign, notably where a metal atom is bonded to more than one other metal atom as in metal cluster complexes, no assignment was attempted.



The non-location of hydrogen atoms presents major difficulties, both in the determination of coordination numbers for metal atoms, and for correct identification of ligands (*e.g.* to distinguish methoxide from methanol). Care was therefore taken to exclude cases where any ambiguity existed [*e.g.* no data taken for M —(OCH₃) and M —O(H)CH₃ distances when both are present in a structure in which hydrogen-atom positions were not reported].

9.6.2.3. Classification of bonds

The classification of metal–ligand bonds in Table 9.6.3.3 is based on the ligating contacting atom. Thus, all metal–boron distances appear in sections 2.1–2.3 of Table 9.6.3.3, all metal–carbon distances in sections 3.1–3.22, and so on. Where intra-ligand interatomic distances (*e.g.* P–C distances in tertiary phosphines) are given in Table 9.6.3.3, they are averaged over all metals and precede the individual metal–ligand interatomic distances for that ligand.

Table 9.6.3.3 is designated: (i) to appear logical, useful, and reasonably self-explanatory to chemists, crystallographers, and others who may use it; (ii) to permit a meaningful average value to be cited for each bond length. With reference to (ii), it was considered that a sample of bond lengths could be averaged meaningfully if: (a) the sample was unimodally distributed; (b) the sample standard deviation (σ) was reasonably small, ideally less than *ca* 0.04 Å; (c) there were no conspicuous outlying observations – those that occurred at $> 4\sigma$ from the mean were automatically eliminated from the sample by *STATS*, other outliers were inspected carefully; (d) there were no compelling chemical reasons for further subdivision of the sample. It should be noted that Table 9.6.3.3 is not intended to be complete in covering all possible ligands. The purpose of the table is to provide information on the interatomic distances for ligands of the greatest *chemical* importance, notably for those that are simple and/or common.

9.6.2.4. Statistics

Where there are less than four independent observations of a given bond length, then each individual observation is given explicitly in Table 9.6.3.3. In all other cases, the following statistics were generated by the program *STATS*.

(i) The unweighted sample mean, d , where

$$d = \sum_{i=1}^n d_i/n$$

and d_i is the i th observation of the bond length in a total sample of n observations. Recent work (Taylor & Kennard, 1983, 1985, 1986) has shown that the unweighted mean is an acceptable (even preferable) alternative to the weighted mean, where the i th observation is assigned a weight equal to $1/\text{var}(d_i)$. This is especially true where structures have been pre-screened on the basis of precision.

(ii) The sample median, m . This has the property that half of the observations in the sample exceed m , and half fall short of it.

(iii) The sample standard deviation, σ , where

$$\sigma = \left[\sum_{i=1}^n (d_i - d)^2 / (n - 1) \right]^{1/2}$$

(iv) The lower quartile for the sample, q_l . This has the property that 25% of the observations are less than q_l and 75% exceed it.

(v) The upper quartile for the sample, q_u . This has the property that 25% of the observations exceed q_u and 75% fall short of it.

(vi) The number (n) of observations in the sample.

The statistics given in Table 9.6.3.3 correspond to distributions for which the automatic 4σ cut-off (see above) had been applied, and any manual removal of additional outliers (an infrequent operation) had been performed. In practice, a very small percentage of observations were excluded by these methods. The major effect of removing outliers is to improve

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the sample standard deviation, as shown in Fig. 9.6.2.1(b) in which four (out of 366) observations are deleted.

The statistics chosen for tabulation effectively describe the distribution of bond lengths in each case. For a symmetrical, normal distribution, the mean (d) will be approximately equal to the median (m), the lower and upper quartiles (q_1, q_u) will be approximately symmetric about the median $m - q_1 \approx q_u - m$, and 95% of the observations may be expected to lie within $\pm 2\sigma$ of the mean value. For a skewed distribution, d and m may differ appreciably and q_1 and q_u will be asymmetric with respect to m . When a bond-length distribution is negatively skewed, *i.e.* very short values are more common than very long values, then it may be due to thermal-motion effects; the distances used to prepare the table were not corrected for thermal libration.

In a number of cases, the initial bond-length distribution was clearly not unimodal as in Fig. 9.6.2.1(a). Where possible, such distributions were resolved into their unimodal components (as in Fig. 9.6.2.1c) on chemical or structural criteria. The case illustrated in Fig. 9.6.2.1, for Cu—Cl bonds, is one of the most spectacular examples, owing to the dramatic consequences of oxidation state and coordination number (and Jahn–Teller effects) on the structures of copper complexes.

9.6.3. Content and arrangement of table of interatomic distances

Table 9.6.3.1 indicates how the interatomic distances covered in Table 9.6.3.3 are subdivided. Metal–ligand distances are grouped according to the ligand contact atom, which leads to ordering by atomic number of that contact atom. For a given contact atom (H, B, C, *etc.*), the ligands are grouped by type as listed in Table 9.6.3.1. The class of ligand is identified numerically (*e.g.* alkoxides are class 5.3, alcohols class 5.23, ethers 5.24, *etc.*). Particular ligands are identified by a third number (*e.g.* methoxide is ligand 5.3.1). Finally, alternative bonding modes for a particular ligand are denoted by a fourth number [*e.g.* terminal alkoxides 5.3.1.1, bridging (μ_2) alkoxides 5.3.1.2]. In general, the bonding modes are arranged in the sequence $\eta^1, \eta^2, \dots, \eta^n, \mu_2, \mu_3, \dots$, where η^n implies n atoms of the ligand are bonded to metal atoms, and μ_m that m metal atoms are bonded to the ligand. Thus, acetates are represented by entries headed 5.5.2.1 (η^1), 5.5.2.2 (chelating, η^2) and 5.5.2.3 (bridging, μ_2). For each ligand, the metal–ligand bonds then follow a sequence of ascending atomic

Table 9.6.3.1. *Ligand index*

Contact atom	Ligand class	Ligand class identifier
Hydrogen	hydride	1.1
	tetrahydroborate (BH ₄)	1.2
Boron	borohydrides	2.1
	boranes/carboranes	2.2
	boroles, borylenes, other heteroboracycles	2.3
Carbon	carbide (C)	3.1
	carbyne/alkylidyne (CR)	3.2
	vinylidene/alkenylidene (CCR ₂)	3.3
	acetylde/alkynyl (CCR)	3.4
	cyano (CN)	3.5
	isocyanides (CNR)	3.6
	carbon monoxide (CO)	3.7
	thiocarbonyl (CS)	3.8
	carbene/alkylidene (CR ₂)	3.9
	vinyl/alkenyl (CRCR ₂)	3.10
	aryl (C ₆ R ₅)	3.11
	acyl [C(O)R]	3.12
	alkyl (CR ₃)	3.13
	η -alkenes (C ₂ R ₄ , allenes, <i>etc.</i>)	3.14
	alkynes (RCCR)	3.15
	η^3 ligands (allyls, <i>etc.</i>)	3.16
	η^4 ligands (conjugated dienes, <i>etc.</i>)	3.17
	η^5 ligands (dienyls, <i>etc.</i>)	3.18
	η^6 ligands (arenes, <i>etc.</i>)	3.19
	η^7, η^8 ligands	3.20
carbaboranes, boroles	3.21	
miscellaneous (CO ₂ , CS ₂ , <i>etc.</i>)	3.22	
Nitrogen	nitride (N)	4.1
	nitrene/imide (NR)	4.2
	methyleneamido (N=CR ₂)	4.3
	nitriles (NCR)	4.4
	isocyanate, isothiocyanate (NCO, NCS)	4.5
	dinitrogen (N ₂)	4.6
	diazonium (N ₂ R), diazoalkanes (N ₂ CR ₂)	4.7
	azide (N ₃)	4.8
	nitrosyl, thionitrosyl (NO, NS)	4.9
	amide (NR ₂)	4.10

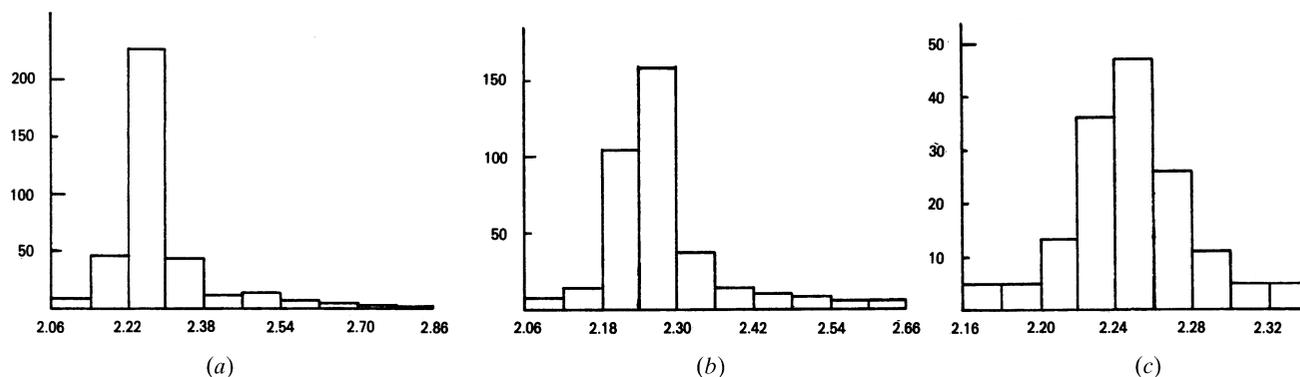


Fig. 9.6.2.1. Effects of outlier removal and subdivision based on coordination number and oxidation state. Cu—Cl: (a) all data; (b) all data without outliers [$> 4\sigma$ (sample) from mean]; (c) all data for which Cu is 4-coordinate, Cu^{II}.

	d	m	σ	q_1	q_u	N
(a)	2.282	2.255	0.105	2.233	2.296	366
(b)	2.276	2.254	0.092	2.232	2.292	362
(c)	2.248	2.246	0.032	2.233	2.263	153