

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 Print compilations have been effectively superseded by computerized databases.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

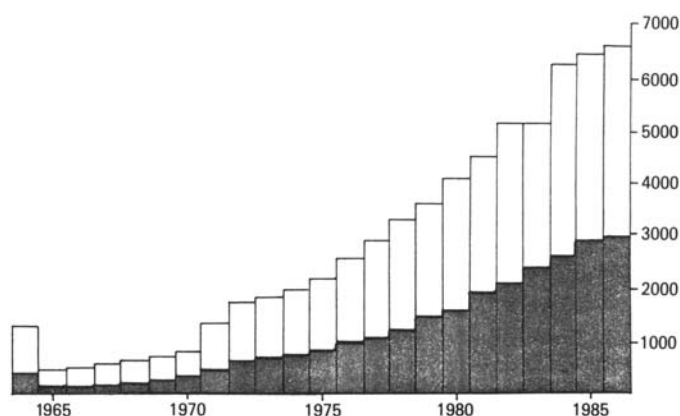


Fig. 9.6.1.1. Growth of the Cambridge Structural Database as number of entries (N_{ent}) added annually. The structures containing *d*- or *f*-block metals are indicated by shading.

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 $[\text{Cr}(\text{CO})_6]$.