

9. BASIC STRUCTURAL FEATURES

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_l, q_u) will be approximately symmetric about the median $m - q_l \approx q_u - m$, 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_l 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
	acetylide/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
carboranes, 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

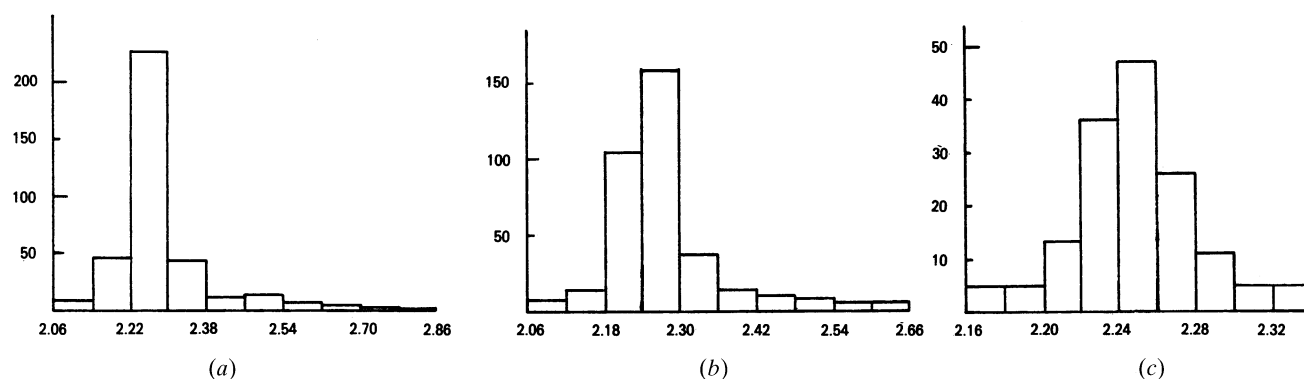


Fig. 9.6.2.1. Effects of outlier removal and subdivision based on coordination number and oxidation state. Cu—Cl: (a) all data; (b) all data without outliers [$> 4\sigma$ (sample) from mean]; (c) all data for which Cu is 4-coordinate, Cu^{II}.

	d	m	σ	q_l	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

9.6. TYPICAL INTERATOMIC DISTANCES: ORGANOMETALLIC COMPOUNDS AND COMPLEXES

Table 9.6.3.1. *Ligand index (cont.)*

Contact atom	Ligand class	Ligand class identifier
Nitrogen (<i>cont.</i>)	amidinate [RNC(R)NR]	4.11
	Schiff bases	4.12
	phthalocyanines, porphyrins, pyrroles	4.13
	pyrazolate, imidazolate and derivatives	4.14
	pyridine, polypryidyls (bpy, <i>o</i> -phen)	4.15
	pyrazines, pyridazines, pyrimidines	4.16
	other N ₂ ligands (NRNR ₂ , NNR ₂ , NRNR)	4.17
	triazenido (RNNNR)	4.18
	hydrazones and related species (NR ₂ N=CR)	4.19
	oximes	4.20
	<i>N</i> -nitrite (NO ₂)	4.21
	amine (NR ₃)	4.22
	borazines	4.23
	Oxygen	oxo (O)
hydroxy (OH)		5.2
alkoxy, aryloxy, <i>etc.</i> (OR)		5.3
<i>O</i> -ketones (OCR ₂), urea		5.4
carboxylates (O ₂ CR)		5.5
oxalate (O ₂ CCO ₂)		5.6
acetylacetonates [RC(O)CRC(O)CR]		5.7
α , β -diones (<i>e.g.</i> <i>o</i> -quinones)		5.8
carbonate (CO ₃ ²⁻)		5.9
<i>N</i> -oxides (<i>e.g.</i> pyridine <i>N</i> -oxide)		5.10
nitrate (NO ₃ ⁻)		5.11
<i>O</i> -nitrite (NO ₂ ⁻)		5.12
dioxygen, peroxides		5.13
phosphine oxides (OPR ₃)		5.14
phosphate (PO ₄ ³⁻)		5.15
other P—O anions		5.16
<i>O</i> -dialkyl sulfoxides (OSR ₂)		5.17
sulfate (SO ₄ ²⁻)		5.18
other S—O anions (sulfonates, <i>etc.</i>)		5.19
<i>O</i> -SO ₂		5.20
other oxyanions (<i>e.g.</i> ClO ₄ ⁻)		5.21
aqua		5.22
alcohols (ROH)		5.23
ethers (ROR')		5.24
miscellaneous (η^2 -acyl, η^2 -CO ₂ , μ -NCO)	5.25	
Fluorine	fluoride (F)	6.1
	fluoroanions (BF ₄ ⁻ , PF ₆ ⁻)	6.2
Silicon	miscellaneous	7.1
Phosphorus	phosphorus (P)	8.1
	phosphinidenes (PR)	8.2
	phosphides (PR ₂)	8.3
	oligo-phosphorus ligands (P ₃ , PR ₂ PR ₂ , PRPR, <i>etc.</i>)	8.4
	phosphines (PR ₃)	8.5
	diphosphines (<i>e.g.</i> diphos)	8.6
	phosphites [P(OR) ₃]	8.7
	aminophosphines, cyclotriphosphazenylyl, misc. P—N ligands	8.8
Sulfur	sulfides (S)	9.1
	thiolates (SR)	9.2

Table 9.6.3.1. *Ligand index (cont.)*

Contact atom	Ligand class	Ligand class identifier
Sulfur (<i>cont.</i>)	<i>S</i> -thiocyanate (SCN)	9.3
	thioketones, thiourea (S=CR ₂)	9.4
	thiocarboxylates (S ₂ CR ⁻)	9.5
	thiocarbamates (S ₂ CNR ₂ ⁻)	9.6
	xanthates (S ₂ COR ⁻), dithio-carbonates	9.7
	trithiocarbonate (CS ₃ ²⁻), thioxanthates	9.8
	α , β -dithiones	9.9
	phosphine sulfides	9.10
	dithiophosphinates (S ₂ PR ₂ ⁻)	9.11
	polysulfur ligands (S ₂ , SSR, <i>etc.</i>)	9.12
	thioethers (SR ₂)	9.13
	<i>S</i> -SO ₂ , <i>S</i> -SO ₃ , <i>etc.</i>	9.14
	disulfides (RSSR)	9.15
<i>S</i> -dialkyl sulfoxides (R ₂ SO)	9.16	
miscellaneous (η^2 -CS ₂)	9.17	
Chlorine	chloride (Cl)	10.1
Arsenic	arsines (AsR ₃)	11.1
	miscellaneous	11.2
Selenium	miscellaneous	12.1
Bromine	bromide (Br)	13.1
Tellurium	miscellaneous	14.1
Iodine	iodide (I)	15.1

number of the metal. For a given metal, the first line of an entry in Table 9.6.3.3 gives statistics covering all appropriate occurrences of metal–ligand distances. Further lines give statistics for metal–ligand distances for subdivision based largely on chemical criteria (*e.g.* metal oxidation state or coordination number). Cases where one atom of a ligand bridges two or more metal atoms were included only when the metal atoms were all of the same type and, unless specified, only when the metal–ligand distances were symmetrical (range for distances ≤ 0.1 Å).

In many instances, the number of structures having interatomic distances involving a given metal for a particular ligand is too small (< 4) for statistics to be quoted. In these cases, individual structures, and the distances in them, are given. These structures are identified by their CSD reference code (*e.g.* BOZMIN); short-form literature references, ordered alphabetically by reference code, are in Appendix 2.

Each line of Table 9.6.3.3 contains nine columns of which six record the statistics of the bond-length distribution described above. The content of the remaining three columns: Bond, Substructure, and Note, are described below.

9.6.3.1. *The 'Bond' column*

This specifies the atom pair to which the line refers. Therefore, in the case of triethylphosphine complexes (section 8.5.2), there are 18 lines, in which the bond column contains P—C, followed by 17 entries for Ti—P through to Au—P, indicating statistics for both intraligand and metal–ligand atom pairs.

9.6.3.2. *Definition of 'Substructure'*

This column provides details of any subdivision of particular metal–ligand bonds that has been applied. Thus, for terminal