

## 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  $m - q_l \simeq q_u - m$ , 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 ( $\mu_2$ ) 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  $\eta^n$  implies  $n$  atoms of the ligand are bonded to metal atoms, and  $\mu_m$  that  $m$  metal atoms are bonded to the ligand. Thus, acetates are represented by entries headed 5.5.2.1 ( $\eta^1$ ), 5.5.2.2 (chelating,  $\eta^2$ ) and 5.5.2.3 (bridging,  $\mu_2$ ). 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 <sub>4</sub> )  | 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 <sub>2</sub> )                                  | 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 <sub>2</sub> )  | 3.9                     |
|  | vinyl/alkenyl (CRCR <sub>2</sub> )   | 3.10                    |
|  | aryl (C <sub>6</sub> R <sub>5</sub> )  | 3.11                    |
|  | acyl [C(O)R]   | 3.12                    |
|  | alkyl (CR <sub>3</sub> )   | 3.13                    |
|  | $\eta$ -alkenes (C <sub>2</sub> R <sub>4</sub> , allenes, <i>etc.</i> )      | 3.14                    |
|  | alkynes (RCCR)   | 3.15                    |
|  | $\eta^3$ ligands (allyls, <i>etc.</i> )                                      | 3.16                    |
|  | $\eta^4$ ligands (conjugated dienes, <i>etc.</i> )                           | 3.17                    |
|  | $\eta^5$ ligands (dienyls, <i>etc.</i> )                                     | 3.18                    |
|  | $\eta^6$ ligands (arenes, <i>etc.</i> )                                      | 3.19                    |
|  | $\eta^7, \eta^8$ ligands   | 3.20                    |
| carboranes, boroles  | 3.21   |                         |
| miscellaneous (CO <sub>2</sub> , CS <sub>2</sub> , <i>etc.</i> ) | 3.22   |                         |
| Nitrogen   | nitride (N)  | 4.1                     |
|  | nitrene/imide (NR)   | 4.2                     |
|  | methyleneamido (N=CR <sub>2</sub> )  | 4.3                     |
|  | nitriles (NCR)   | 4.4                     |
|  | isocyanate, isothiocyanate (NCO, NCS)  | 4.5                     |
|  | dinitrogen (N <sub>2</sub> )   | 4.6                     |
|  | diazonium (N <sub>2</sub> R), diazoalkanes (N <sub>2</sub> CR <sub>2</sub> ) | 4.7                     |
|  | azide (N <sub>3</sub> )  | 4.8                     |
|  | nitrosyl, thionitrosyl (NO, NS)  | 4.9                     |
|  | amide (NR <sub>2</sub> )   | 4.10                    |

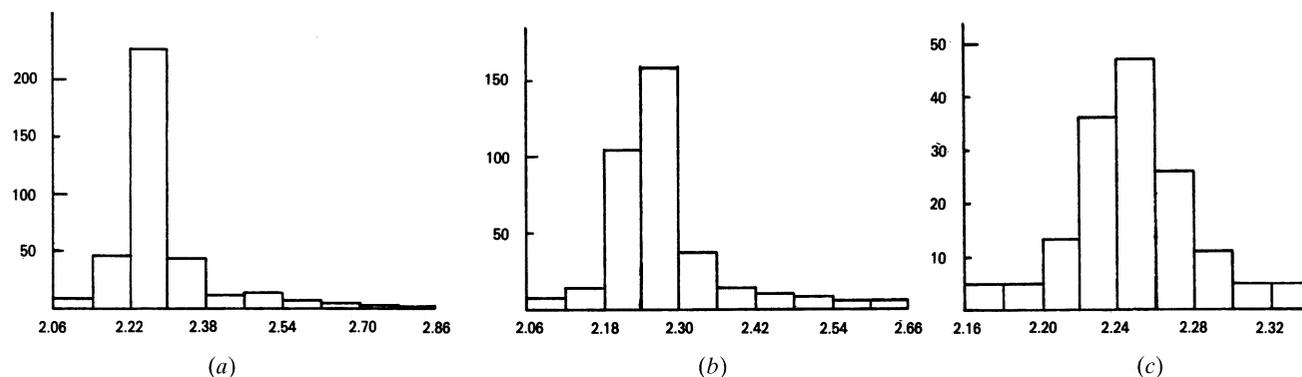


Fig. 9.6.2.1. Effects of outlier removal and subdivision based on coordination number and oxidation state. Cu—Cl: (a) all data; (b) all data without outliers [ $> 4\sigma$  (sample) from mean]; (c) all data for which Cu is 4-coordinate, Cu<sup>II</sup>.

|     | $d$   | $m$   | $\sigma$ | $q_l$ | $q_u$ | $N$ |
|-----|-------|-------|----------|-------|-------|-----|
| (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 |