The Automatic Searching for Chemical Bonds in Inorganic Crystal Structures

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Abstract

The program *SINDBAD* is described; it provides a chemical description of an inorganic compound from its crystallographic data by selecting those interatomic distances that correspond to chemical bonds. It has been used to check all the entries in the Inorganic Crystal Structure Database, to create a bond file for systematic studies of crystal chemistry and to construct a bond index to the database.

1. Introduction

Information about crystal structures is usually stored in the form of crystallographic concepts (unit cell, atomic coordinates, *etc.*) but is normally required in terms of chemical concepts (bond length, coordination number, *etc.*). The problem of converting the information from a crystallographic to a chemical language depends on the definition of the chemical concepts. In the field of inorganic chemistry the definition of a chemical bond is a matter of debate but, if the definition is elusive, the concept itself is central to structural chemistry. Any attempt to use a crystal structure database to retrieve chemical information must address this problem of definition and this paper describes a solution for inorganic compounds.

A program, *SINDBAD* (§earch of the Inorganic Database for Bonds and Distances), has been written to determine which of the interatomic distances calculated between the atoms in an inorganic crystal correspond to chemical bonds. The immediate purpose of the program is to check for possible errors in the data in the Inorganic Crystal Structure Database (ICSD) (Bergerhoff, Hundt, Sievers & Brown, 1983) but it also produces a file (BONDFILE) which lists all bonds present in each compound. The BONDFILE can be used to produce indices to the database or to explore systematic aspects of crystal chemistry. The algorithms of *SINDBAD* could be incorporated into standard crystallographic computing packages to provide a chemical interpretation and check of newly determined inorganic crystal structures.

2. The chemical model

In order to select the chemical bonds from among the interatomic distances calculated by a molecular-geometry program, it is first necessary to have a definition of a chemical bond that can be applied automatically by computer.

Although there exists a widely accepted definition of a chemical bond in organic chemistry, in inorganic chemistry there is less concensus. The bond-valence model (Brown, 1978), however, provides a useful and quantitative description of inorganic bonding. In this model all atoms are considered to be cations or anions according to the sign of the oxidation state.* All neighbouring cation–anion distances are considered to be bonds although not all of equal strength. Each bond between atoms i and j is associated with a number, s_{ij} (the bond valence or bond strength), which varies inversely with the length (r_{ij}) according to the relation

$$s_{ij} = \exp\left[(r_0 - r_{ij})/B\right], \qquad (1)$$

where r_0 and B are empirical constants whose determination for a given pair of atoms is described in the following paper (Brown & Altermatt, 1985). In most inorganic compounds bond valences have been found to obey the relation

$$\sum_j s_{ij} \simeq V_i \qquad (2)$$

for all i, where V_i is the oxidation state of atom i.

An important feature of this model is that the bonds are not all considered equal. The bond valence provides a scale in which bonds with valences greater than about 0·6 are those often described as covalent, whereas weaker bonds correspond to those generally referred to as ionic or electrostatic.

There are a number of features that make this model useful for the present purpose. Firstly, variations in the sizes of atoms are all contained in the parameter r_0 of equation (1), so that the definition of a bond in terms of bond valence is independent of atomic size. Secondly, the model allows the bond assignments to be checked to see whether they are chemically reasonable. Valences are first calculated from the bond distances using equation (1), then the bond-valence sums are checked to see that they correspond to the assigned oxidation states using equation (2). Thirdly,

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* This extended definition of the terms 'anion' and 'cation' will be used throughout this paper. The terms are not intended to imply that the bonding is necessarily ionic.

in cases where the valence sum and oxidation state do not agree, their difference can often be used to identify errors in the crystallographic data.

The model does have limitations. It works well only for those compounds which (i) obey the relation

$$\sum_i V_i = 0 \qquad (3)$$

(valence compounds) and (ii) contain only bonds between anions and cations (heteroionic bonds).* The majority of compounds in the ICSD are of this kind, but there are a few which do not meet these criteria and for which special treatment is needed.

3. Program *SINDBAD*

SINDBAD uses as input the lattice parameters, space-group symbol, atomic coordinates (and standard errors), occupation numbers (normally 1·0) and, when available, the oxidation states assigned to the atoms. The latter are used both to select the bond windows (the range of distances that correspond to chemical bonds) and to check the structure by comparison with the bond-valence sums [equation (2)]. When H-atom coordinates are not reported for a crystal structure *SINDBAD* also expects a flag indicating how many H atoms are bonded to each anion, for without these flags the check provided by equation (2) will fail.

SINDBAD is written in FORTRAN and is an integral part of a continually evolving multipurpose molecular-geometry package running at McMaster University on a CDC CYBER computer. The algorithms it uses are listed in the Appendix and a flow diagram is given in Fig. 1. The element name is first converted into its Periodic-Table coordinates (P = period, G = group) using the latest ACS standard group numbering ($1 \le G \le 18$, omitting the designator 'd') (Loening, 1984). In this way the oxidation number can be directly compared with its expected value (G, $G-10$ or $G-18$) and transition elements can be readily distinguished from main-group elements ($2 < G \le 12$).

In module (1) the program sets the bond windows, *i.e.* the range of distances between any two atoms that are to be considered as bonds. Wherever possible the range is defined in terms of the bond valence using the assigned oxidation states but in cases where oxidation states are zero or not available, a distance range is defined directly.

In module (2) all distances that lie within the bond windows are calculated around each atom in the asymmetric unit. The checking module, (3), computes

the bond valences [equation (1)] and the valence sums at each atom [equation (2)]. The difference found between the valence sum and the corresponding oxidation state is classified in one of three ways: Acceptable, Warning or Error. The presence of an Error flag or the existence of interatomic distances occurring below the bond-window minimum [flagged in module (2)] usually indicates an error in the input data, a poor crystal structure determination or the failure of the program as discussed below. Structures that produce only Warnings are usually satisfactory but need to be examined to find the few cases where there actually is a problem. If either a Warning or Error flag is set the error-analysis module, (4), of *SINDBAD* prints out diagnostic information that could be useful in pinpointing the problem.

If the structure is flagged as Acceptable, or if the user decides that a structure flagged with a Warning or Error is correct, the bond distances can be written to a BONDFILE. Since each bond is calculated twice, the bond originating at the anion is dropped. For each bond the BONDFILE contains the bond length, atom names, the symmetry operations needed to generate the position of the terminal atom (anion) from its position in the asymmetric unit, the components of the bond along the crystal axes, the standard error in the bond length and the bond valence. In addition it contains the formula, ICSD entry (collection) number (where appropriate), unit cell, space group [Hall (1981) computer-interpretable symbol] and the properties of each atom (element, identifier, oxidation number, occupation number, multiplicity, special-position flag and coordination number as calculated by *SINDBAD*). The intent is that the BONDFILE should contain sufficient information to reconstruct the complete bonding network of the crystal so that it can be used for further studies without reference to the original database.

4. Results

SINDBAD has been developed in order to analyse the crystal structures stored in the ICSD and it has been tested on the inorganic compounds it contains,

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* Note that molecules such as acetic acid (CH_3COOH) satisfy these conditions provided that the C atoms are assigned oxidation states of -4 and $+4$ respectively but that any bonding network which contains an odd-membered ring (*e.g.* S_2N_3) cannot, in principle, satisfy the second condition.
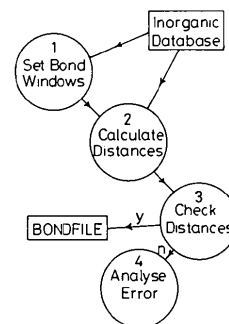

Fig. 1. Flow diagram for *SINDBAD*.

namely those that do not contain organic fragments (*i.e.* that contain no C–C or C–H bonds) and do not have metallic character (*i.e.* either they must contain at least one O, S or halogen atom or else they must not contain any element from left of the Zintl line). This definition excludes the majority of transition-metal complexes from the study. Metal and alloy structures (for which the bond-valence model is inappropriate) are automatically rejected by *SINDBAD*. Likewise rejected are structures in the ICSD that are incomplete (*e.g.* missing coordinates for non-H atoms). Neither of these types of structure is considered in the following discussion.

Over half of the remaining 14 000 entries passed through all stages of *SINDBAD* without a problem. A further 28% had correct bonds assigned although the checking module flagged a Warning or Error, 12% had errors in either the structure determination or the database and 7% were structures whose chemistry was such that *SINDBAD* was unable to make a reasonable bond assignment. An analysis of the problems encountered is given below.

(i) Errors in the database

These may arise from errors in the original paper or errors introduced when entering the data into the database. One of the uses of *SINDBAD* is to locate such errors so that they can be corrected in future releases.* Database errors are of several types. The largest number are minor ones which involve misassigned oxidation numbers or misassignments of the H attachment flags. Where the author provides no information about the H attachments, it is difficult for the abstractor to make a correct assignment. However, the error-analysis routine in *SINDBAD* can make the correct assignment by testing the shortfall in the anion valence sum (Donnay & Allmann, 1970)). Misassigned oxidation states (*e.g.* in compounds such as $CuFeO_2$) can also be spotted from the calculated bond-valence sums.

More serious for most database users are errors in the lattice parameters, space group or atomic coordinates. These may be transcription errors or the result of errors or ambiguities in the original publication. The output of *SINDBAD* often assists in the locations of these errors, which, when once recognized, are corrected by reference to the original paper or, if necessary, by consultation with the author.

(ii) Disordered structures

Many structures in the ICSD are disordered as indicated by the existence of atoms with partial

occupancies. A survey of disordered structures reveals that the types of disorder found in inorganic crystals are almost as numerous as the disordered structures themselves and that it would be extremely difficult (even if rewarding) to write a program that would provide a satisfactory description of even the majority of such structures. Consequently, in order that most disordered structures are passed to the BONDFILE, the tolerances on the check program are increased and the BONDFILE is flagged so that the strange bond lengths and coordination numbers can, when appropriate, be ignored by subsequent programs. Even with the relaxed tolerances, not all disordered structures pass the *CHECK* program and in a few cases the disordering is so severe that *SINDBAD* is unable to make any intelligible interpretation.

(iii) Compounds for which the chemical model is inappropriate

The bond-valence model requires that bonds occur only between atoms that are formally treated as cations and anions as described above. While this condition is satisfied for the majority of compounds in the ICSD there are a few that have bonds between two anions or two cations (homoionic bonds).

The bond-valence model usually works if the fragment containing the homoionic bond can be isolated and treated as a complex ion [*e.g.* O_2^{2-}, N_2^{4-} (in $N_2H_5^+$), Hg_2^{2+}]. The model makes no prediction about the homoionic bond itself, but the external heteroionic bonds formed by the complex do obey the valence-sum rule [equation (2)]. For such complexes the magnitude of the assigned oxidation number of each atom should be reduced by 1 for each homoionic bond it forms. The presence of a reduced oxidation state associated with an atom is used by the program as an indication that homoionic bonds are expected. This adaptation of the model works reasonably well provided that the oxidation state of any atom is not reduced too far. Consequently the more homoionic bonds there are in a structure the less useful is the bond-valence model and the more likely *SINDBAD* is to fail.

Among the structures where problems arise are metal hydrides, suboxides and subhalides as well as transition-metal cluster compounds. Homoionic molecules composed of pnictides, chalcogenides or halides may also give problems as may the carbonyl and cyanide complexes of transition metals. A formally correct description of these latter compounds can usually be given if the C atom is given oxidation number +4 and the transition metal a (large) negative oxidation number [*e.g.* Cr(−12) in $Cr(CO)_6$] but such a description does not correspond to usual practice which is to treat the C as having an oxidation number of +2 and the transition metal as having an oxidation number close to zero. A test for an oxidation state of

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* The initial development of *SINDBAD* used an early (1983) database release in which many of the entries had not been checked. The database error rate has been greatly reduced since the *SINDBAD* runs reported here.

+2 for C allows *SINDBAD* to recognize CO and CN groups but a consistent treatment of the metal–C bond is not possible. In cyanide complexes, where the cyanide group behaves as pseudohalogen, the metal–C bond behaves as a heteroionic bond and the valence should be added to the metal valence sum. Because the metal–C bond appears to the program to be homoionic, cyanide complexes fail the check even though the bonds may be correctly calculated.

Another situation in which the program necessarily fails is the case where no hydrogen coordinates are given in the database and the only bonds formed by an anion (typically Cl) are acceptor hydrogen bonds. In this case *SINDBAD* cannot find any bonds to the anion and flags an Error.

5. Applications of the BONDFILE

The BONDFILE has been designed to assist in the production of a bond index to the ICSD based on the format of the earlier bond index, BIDICS (1969-81). It lists in alphabetical order the different types of bond that exist in the structures included in the ICSD (Fig. 2). Unlike BIDICS, the new index includes neither metals nor most of the transition-metal complexes as these are not included in the ICSD. On the other hand the index does cover all the inorganic crystal structures determined since 1913. It is designed to be published as a book but it could also be adapted for on-line searching.

The index is produced by scanning the BONDFILE for each type of bond and sorting the resultant output. Because the bond index only includes ICSD entries that have successfully passed through *SINDBAD*, it currently only includes references to about 80% of the inorganic structures with coordinates in the

database. The remainder, as well as entries added to the database in the future, will be included in later updates.

The BONDFILE also has the potential for many types of systematic analysis of inorganic crystal structures. Examples are the refinement of the parameters used in calculating the bond valences (Brown & Altermatt, 1985), exploring the crystal environment of particular atoms or developing programs for structure modelling. Some of these studies are in progress in our laboratory.

APPENDIX
Algorithms for *SINDBAD*

Glossary

(i) *Atoms*

G	Group number $(0 < G \leq 18)$
P	Period $\quad (0 < P \leq 7)$
OX	Oxidation number
OC	Occupation number
Σ	Sum of bond valences

(ii) *Bonds*

r	Length
s	Valence

(iii) *Types of atom*

			Definition
A	Anion		$0 > OX$
A^*	Anion in lower oxidation state		$0 > OX > G - 18$
C	Cation		$0 < OX$
CT	Transition-metal cation		$0 < OX; 2 < G \leq 12$
CT^*	CT but in lower oxidation state		$0 < OX < G \leq 12$
CM	Main-group cation		$0 < OX; G - 10 > 2$ or $G \leq 2$
CM^*	CM but in lower oxidation state		$0 < OX < G - 10 > 2$ and $G > 2$
B	Non-ion		$0 = OX$

NB: OX(1) = oxidation number of first atom.
OX(CM) = oxidation number of main-group cation, *etc.*

Module (1). *Definition of the bond window*

Seven different algorithms are used for calculating the bond windows according to the nature of the terminal atoms as indicated in the table given below. Where bond-length–bond-valence parameters are available the window is set according to the valence ranges $(s_{max} - s_{min})$ given, otherwise the distances ranges $(r_{min} - r_{max})$ are used.

A	A^*	CT	CT^*	CM	CM^*	B	
0	0	1	1	1	1	6	A
	2	1	1	1	1	6	A^*
		0	0	0	4	6	CT
			3	0	4	6	CT^*
				0	0	6	CM
					5	6	CM^*
						6	B

Rules

(0) Do not calculate distances $\qquad (r_{min} = 1 \cdot 0 \text{ Å}, r_{max} = 0 \cdot 0 \text{ Å})$

(1) $s_{max} = [1 + 0 \cdot 1 \times G(A)] \times |OX(A)| \qquad r_{min} = 1 \cdot 0 \text{ Å}, r_{max} = 3 \cdot 4 \text{ Å}$
$\quad s_{min} = 0 \cdot 038 \times OX(C)$
$\quad$ Exceptions: if $G(C) = 5$ or 6 $\qquad s_{min} = 0 \cdot 1$ (Nb, Ta, Mo and W)
$\qquad\qquad$ if bond is C–O or C–N $\quad s_{max} = 3 \cdot 6$ to accommodate
$\qquad\qquad$ if C = hydrogen $\qquad s_{max} = 2 \cdot 0$ experimental error

974	77 ACBCA	33	1954	Br	(-1)	6 2.749	X	.079	$K_4(Bi_2Br_{10})(H_2O)_4$
602	76 ACBCA	32	2570	Cl	(-1)	7 3.16	X	.094	$Bi_{12}O_{15}Cl_6$
602	76 ACBCA	32	2570	Cl	(-1)	8 3.05	X	.094	$Bi_{12}O_{15}Cl_6$
484	76 MRBUA	11	183	Cl	(-1)	8 3.125	X	.04	$InBi_2S_4Cl$
602	76 ACBCA	32	2570	Cl	(-1)	9 3.17	X	.094	$Bi_{12}O_{15}Cl_6$
164	76 ACBCA	32	2319	N	(-3)	6 2.74	X	.076	$Rb(Bi(SCN)_4)$
602	76 ACBCA	32	2570	O	(-2)	6 2.36	X	.094	$Bi_{12}O_{15}Cl_6$
295	76 JSSCB	17	151	O	(-2)	7 2.11	X	.097	$(Bi_2O_3)_3(B_2O_3)_5$
602	76 ACBCA	32	2570	O	(-2)	7 2.14	X	.094	$Bi_{12}O_{15}Cl_6$
139	75 ACBCA	31	127	O	(-2)	7 2.19	X	.10	Bi_2UO_6
602	76 ACBCA	32	2570	O	(-2)	8 2.04	X	.094	$Bi_{12}O_{15}Cl_6$
45	76 ACBCA	32	1163	O	(-2)	8 2.201	X	.061	$Bi_3(FeO_4)(MoO_4)_2$
295	76 JSSCB	17	151	O	(-2)	9 2.12	X	.097	$(Bi_2O_3)_3(B_2O_3)_5$
602	76 ACBCA	32	2570	O	(-2)	9 2.30	X	.094	$Bi_{12}O_{15}Cl_6$
378	76 ACBCA	32	1947	S	(-2)	5 2.599	X	.086	$Bbi(Bi_2S_3)_9Br_3R$
167	76 ACBCA	32	2401	S	(-2)	5 2.61	X	.137	$PbCuBi_5S_9$
378	76 ACBCA	32	1947	S	(-2)	6 2.616	DX	.086	$Bbi(Bi_2S_3)_9Br_3R$
167	76 ACBCA	32	2401	S	(-2)	6 2.63	X	.137	$PbCuBi_5S_9$
164	76 ACBCA	32	2319	S	(-2)	6 2.705	X	.076	$Rb(Bi(SCN)_4)$
167	76 ACBCA	32	2401	S	(-2)	7 2.61	X	.137	$PbCuBi_5S_9$
484	76 MRBUA	11	183	S	(-2)	8 2.666	X	.04	$InBi_2S_4Cl$

Fig. 2. Sample of the bond index. The first column lists the ICSD entry number, columns 2-5 give the literature citation. Then follow the second-atom name and oxidation number, the first-atom coordination number, the average bond length, disorder flag (*D*), radiation used, crystallographic *R* factor and formula.

(2) $s_{max} = 3.0$, $s_{min} = 0.5$

$r_{min} = 1.0$ Å, $r_{max} = 2.5$ Å

(3) $s_{max} = 2 \times MIN\,[OX(1), OX(2)]$

$s_{min} = 0.15 \times MAX\,[OX(1), OX(2)]$

$r_{min} = 1.0$ Å

$r_{max} = 2.0 + 0.075$
$\times [P(1) + P(2)]$ Å

(4) $s_{max} = 1.5$

$s_{min} = 0.38 \times OX(CM^*)$

Exceptions: if CM^* is $C(+2)$

$s_{max} = 3.6$

$s_{min} = 0.038$
$\times OX(CT)$

$r_{min} = 1.0$ Å

$r_{max} = 1.4 + 0.1 \times P(CM) + 0.2$
$\times P(CT)$ Å

$r_{min} = 1.0$ Å

$r_{max} = 3.0$ Å

(5) $s_{max} = 2 \times MIN\,[OX(1), OX(2)]$

$s_{min} = 0.15 \times MAX\,[OX(1), OX(2)]$

$r_{min} = 1.0$ Å

$r_{max} = 0.9 + 0.2$
$\times [P(1) + P(2)]$ Å

(6)

$r_{min} = 1.0$ Å
$r_{max} = 3.4$ Å

Module (2). *Calculation of bonds*

If $|s_{max}| > 0$ and bond-valence parameters are available, set r_{max} and r_{min} from s_{min} and s_{max} respectively.

Calculate all distances lying between r_{min} and r_{max}.

If either atom is $C(+2)$, $N(-1)$ or $N(-2)$, any interatomic vector closer than $55°$ to a shorter vector is removed from the bond list. This is necessary to eliminate distances to second neighbours, e.g. metal$\cdots$O in M–C–O and $N(1)\cdots$H in $N(1)$–$N(2)$–H.

Module (3). *Bond calculation check*

(i) Calculate the bond valence from the bond lengths using $s = \exp[(r_0 - r)/B]$ based on tabulated values of r_0 and B or, if these are not available, values calculated using the algorithm of Brown & Altermatt (1985).

(ii) Modify the bond valence as follows:

(a) If either atom is H and $s > 0.8$ set $s = 0.8$ v.u. (allows for unrealistically short X–H bonds).

(b) If the terminal atom is a cation change sign of s.

(c) If $OC(\text{terminal}) < OC(\text{central})$ set $s = [OC(t)/OC(c)] \times s$ (allows for cases where the terminal atom is substitutionally disordered).

(iii) Sum the valences of heteroionic bonds around the central atom

$$\Sigma_i = \sum_j s_{ij}(C\text{–}A)$$

(homoionic bonds do not contribute to the assigned oxidation number).

Add -0.8 v.u. for each dummy H atom attached to the central atom.

(iv) Check the difference between the oxidation number of the central atom and its bond-valence sum. Let $\Delta = 0.25 + (1.1 - OC)|OX|$ be the permitted tolerance where OC and OX refer to the central atom. (This allows an increase in the tolerance for central atoms that have high oxidation states or low occupation numbers.)

Then agreement is satisfactory if

$$|OX - \Sigma| < \Delta$$

$|OX + \Sigma| < \Delta$ — (bond valences may have wrong sign, e.g. for CO and CN)

$|OX - \Sigma| < 0.5$ — if central atom is H

$-0.7 < OX - \Sigma < 0.3$ — if central atom is O, S, F or Cl and the structure contains undetermined H atoms (allows for acceptor hydrogen bonds whose lengths cannot be calculated)

$|3 - \Sigma| < \Delta$ — if central atom is $C(+2)$ (cyanide groups need special treatment).

Any atom whose bonding fails all the above tests is flagged as follows:
WARNING if $|OX - \Sigma| < 0.8$
ERROR if $|OX - \Sigma| > 0.8$.

In addition an ERROR flag is set

(i) if any atom is found to form no bonds, or

(ii) if distances are found with $r < r_{min}$ and $OC(1) + OC(2) > 1.0$. (In this case it is impossible for the two sites to be simultaneously occupied.)

Module (4). *Error analysis*

If a WARNING or an ERROR is flagged, check:

(i) Does the cell correspond to space-group setting:

(a) For hexagonal, trigonal and rhombohedral (hexagonal setting) is $\gamma = 120.°$?

(b) For monoclinic, are the correct two angles $90°$ for the setting used?

(ii) Does the number of assigned H atoms correspond to the number of dummy H atoms given? If not, how many H atoms would have to be attached to each anion to give the correct valence sums?

(iii) Is the coordination number of $P(+5)$, $S(+6)$ and $Cl(+7)$ equal to 4?

(iv) Does any bond exceed its maximum possible valence? i.e. is $s > MIN\,[OX(1), OX(2)]$.

(v) Does a halogen anion form no bonds in a structure where H-atom coordinates have not been determined? In this case the anion probably only forms hydrogen bonds.

All of the above tests will print an appropriate diagnostic statement if the error condition is found.

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Bond-Valence Parameters Obtained from a Systematic Analysis of the Inorganic Crystal Structure Database

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Abstract

The parameters needed to calculate bond valences from bond lengths have been determined for 750 atom pairs using the Inorganic Crystal Structure Database. The most accurate 141 are listed and an algorithm is given which allows the calculation of the remainder as well as the calculation of parameters for over a thousand other bond types. Graphical bond-valence-bond-length correlations are presented for hydrogen bonds.