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Bond-valence parameters for ammonium–anion interactions

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Bond-valence parameters r_0 and b, relating bond valence and bond length, are calculated for interactions between the ammonium ion and anions X = O, F, Cl. Searches in the Cambridge Structural Database (CSD) and in the Inorganic Crystal Structural Database (ICSD) were performed to obtain the lengths of $NH_4^+ \cdots X$ contacts for ammonium ion environments in different structures. The procedure, which represents an extension of previous methods, allows certain environments to be rejected and enables the calculation of r_0 and b from a reasonable range of interaction distances. Results are in very good agreement with the expected values on the basis of the assumed bond-valence model and their overall applicability to ammonium ion interactions is discussed.

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1. Introduction

Any attempt to use a crystal structure database to retrieve chemical information must address the problem of converting the information from crystallographic concepts (unit cell, atomic coordinates *etc.*) to chemical language (bond length, coordination number *etc.*; O' Keeffe, 1989). The bond valence s and its correlation with the bond length r provides a useful and quantitative description of inorganic bonding (Brown, 1978). Two parameters, b and r_0, are empirically determined such that the bond-valence sum (BVS) for a given ion is normally quite close to its oxidation state. The parameter b is commonly taken to be a constant equal to 0.37 (Brown & Altermatt, 1985) and r_0 has been calculated for a large number of cation–anion (Brese & O'Keeffe, 1991) and anion–anion (O'Keeffe & Brese, 1992) pairs.

Although the bond-valence method has a long history (since Pauling, 1929), it has only recently begun to supplement the use of ionic-radii sums to predict bond lengths in inorganic crystals. Calculated BVS are a better indication of the accuracy of the structure determination than the usual sums of radii, in most instances. A systematic study (Brown & Altermatt, 1985) has shown a relationship between r_0 values and the sum of the ionic radii, nevertheless, it had to be adapted to changes in coordination numbers and valences.

To our knowledge, bond-valence parameters of ammonium–anion interactions have not already been determined. Our main interest in determining such parameters is to study the similarity in ionic behaviour of the ammonium ion and the alkali metals ions. Several authors replace potassium or rubidium by ammonium in order to obtain more information about the structural transition mechanisms in alkali salts. We note that 84 compounds from 2480 entries in a database of structural phase transitions in crystals are ammonium salts (Tomaszewski, 1992). In addition, a knowledge of the hydrogen-bonding modes of the ammonium ion is essential to a theoretical description of the specific role of hydrogen bonding in driving the phase changes (González-Silgo *et al.*, 2000).

The bond-valence model established in inorganic chemistry also proves to be effective for several types of hydrogen bonds and a correlation between bond valences and $H\cdots X$ distances for a variety of anions X has been given by Brown & Altermatt (1985). Further, the NH_4^+ ion has been treated as an isotropic or spherical cation analogous to K^+ or Rb^+ in terms of the ionic radii model (Shanon, 1976). Thus, we might expect that ammonium–ligand interactions may also be interpreted using the bond–valence model. Moreover, the coordination number could determine the influence of distortions due to electronic effects, as in the Tl^+ ion (Brown, 1992). In this paper, we present an extension of BV parameter calculation procedures for $NH_4^+\cdots X$ interactions (X = O, F and Cl) from organic and inorganic structural data, where both parameters b and r_0 are adjusted by minimizing the standard deviation (σ) of the BVS's from known oxidation states.

2. Data retrieval

Crystallographic data for 533 NH_4^+ environments from 338 structures were studied, in which the X (= O, F, Cl) atoms around each ammonium ion are chemically identical, and (i) there is no disorder, (ii) the crystallographic R factor is < 0.1 and (iii) the structure was determined at room temperature. In order to start the analysis of $N\cdots X$ hydrogen bonds, these distances $d(N-X)$ were defined by a window based on the sum of van der Waals radii: $r_N + r_X - 1$ Å $< d(N-X) < r_N + r_X + 1$ Å.

We also performed a search for contact distances between the ammonium ion and other atom types (B, C, Si, Ge, P, As, Sb, S, Se, Te, Br, I), to ensure that there were no ligands involving elements other than those selected. An environment was rejected if any ligand different from the selected X (= O, F, Cl) atom was included in the coordination sphere. The possibility of the presence of other cations too close to ammonium was not taken into account, because the method of treating metal–metal bonding is not obvious in the bond-valence model (Brown, 1992).

Structure selection was restricted to room-temperature studies to avoid the effects of thermal expansion on the parameter r_0 (Brown *et al.*, 1997). Inorganic and organic structures were treated separately since r_0 is well defined in anion–cation interactions for inorganic compounds, but different values have been proposed for organic compounds (Wood & Palenik, 1999).

The CD-ROM version (1999, 50 000 entries) of the Inorganic Crystal Structural Database (ICSD; Bergerhoff *et al.*, 1983) was used for inorganic structure selection. Searches were performed using the program *RETRIEVE* (Berndt, 1997). A total of 290 inorganic structures were retrieved, 208 structures with 327 ammonium environments of O atoms, 53 structures with 77 ammonium environments of F atoms and 29 structures with 65 ammonium environments of Cl atoms. Version 5.11 (April 1998, 180 000 entries) of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) was used in organic structure studies. Searches were performed using the program *QUEST*. Only 47 structures with 63 ammonium environments of O atoms were found and a structure with one environment of Cl atoms.

3. Bond-valence parameters

The bond-valence model (BVM; Brown, 1992) states that the oxidation state V_j can be calculated from the sum of the individual bond valences s_{ij}

$$V_j = \Sigma_i s_{ij} \tag{1}$$

and that the bond valence s_{ij} can be calculated from the observed bond length r_{ij} using

$$s_{ij} = \exp[(r_0 - r_{ij})/b]. \tag{2}$$

The parameter b is commonly taken to be a universal constant and r_0 is refined from an initial given value. However, in this paper the most suitable values of b and r_0 are determined from a reasonable range of values. Parameter b is considered to be > 0.35 Å (close to the softness parameter for halide crystals; Urusov, 1995) and < 0.39 (close to the value for hydrogen bonds obtained by Steiner & Saenger, 1994). The lower limit of r_0 corresponds to the $K\cdots X$ ion pairs and the higher limit corresponds to $Cs\cdots X$, where X = O, F, Cl: 2.13 and 2.42 Å for $NH_4^+\cdots O$ contacts, 1.99 and 2.33 Å for $NH_4^+\cdots F$ contacts, and 2.52 and 2.79 Å for $NH_4^+\cdots Cl$.

Bond files produced from the CSD and ICSD databases (see §2) provided the basis for calculating the BV parameters. Four groups were separately treated in order to check the environments found: one for each type of $NH_4^+\cdots X$ pair in inorganic structures and an additional group of $NH_4^+\cdots O$ pairs in organic structures. Firstly, a suitable coordination number was selected for every environment by inspection of r_{ij}. Secondly, environments of the same group were compared with each other using the criteria described in §3.1 and, as a result, several environments were discarded. Finally, b and r_0 were calculated: the fitting values of r_0 from each group were determined for different values of b using the formula

$$\sigma = \left[\frac{\sum_{j=1}^{N}(1 - V_j)^2}{N(N-1)}\right]^{1/2}. \tag{3}$$

The value of b which minimizes σ was calculated using the number of environments, N, from all groups. The results are presented in §3.2 and discussed in §4.

3.1. Rejected environments

An overall assessment of the quality of each structure determination was guaranteed by the search criteria. However, it was appropriate to develop additional criteria which might indicate the need for further rejections of struc-

Table 1
Bond-valence parameters (BVP) of $NH_4^+ \cdots X$ (X = Cl, F, O) bonds compared with other alkaline ones.

	0.372 (20) Å		
b	$K \cdots X$ (Å)	$NH_4^+ \cdots X$ (Å)	$Rb \cdots X$ (Å)
X = Cl	r_0 = 2.52†	r_0 = 2.619 (10)	r_0 = 2.65†
X = F	r_0 = 1.99†	r_0 = 2.129 (10)	r_0 = 2.16†
X = O (inorganic structures)	r_0 = 2.13†	r_0 = 2.219 (10)	r_0 = 2.26†
X = O (organic structures)	r_0 = 2.113 (57)‡	r_0 = 2.233 (10)	–

† Brese & O'Keeffe (1991); b = 0.37. ‡ Wood & Palenik (1999); b = 0.37.

tures from the analysis. These criteria should be independent of the BV fitting parameters. Hence, every NH_4^+ environment was compared within its group to ensure the following:

(i) The function $V_j = V_j(r_0,b)$ for most environments corresponds to Fig. 1. Note that many pairs of (r_0,b) lead to V_j = oxidation state.

(ii) Most of the BV sums for possible pairs (b, r_0) fall into the range 0.4 v.u. wide. Furthermore, the standard deviation of BVS, σ [see (3)], has a minimum at a particular value of r_0 for every value of b (Fig. 2). This permits the selection of an r_0 value for each b in every group analysed.

(iii) The coordination number 'n' of most environments fell into a particular range of values.

Structures with an environment which did not satisfy these criteria were investigated individually and, as a result, 21 structures were rejected:

Entries 61433, 16210 and 23274 (ICSD) have obviously incorrect coordinates.

Entries 24501, 24503 and 26635 (ISCD) have no recorded R values and were published in 1932 and 1942.

Five structures (1265, 38266, 60752, 39126 from ISCD and LIATRH from CSD) are duplicates: they have the same chemical formula and cell parameters as other structures solved in the same or related space groups.

Two structures (ISCD 32572 and 100375) have anomalous calculated densities.

Four structures (ICSD 71011, 71012, 60626, 39525) have isomorphous alkaline salts which have: (i) a different number of atoms in the unit cell or (ii) a coordination polyhedron which is less distorted than the ammonium salt.

One structure is derived from a twinned crystal (ICSD 36044).

Three very distorted structures (ICSD 29238, 100400, 200811) having $R > 0.09$.

Additionally, 22 further environments (4% of the total) were rejected due to a high deviation in the BVS (criterion condition 2), since the BVS of most fell into the range 0.4 v.u. wide. The existence of spheres with a single distance r_i or very symmetrical environment, where steric effects are more likely, may explain the deviation observed in 10 of them (belonging to LIATRH01, SATART01, SATART06 from the CSD and 403058, 16148, 35112, 80063, 402540, 26311, 71308 from the ISCD).

3.2. Results

The standard deviation (σ) of the BVS from the known oxidation state was calculated from the total number of ammonium environments which were not rejected (N = 453), see Fig. 2. Table 1 shows the bond-valence parameters obtained from the analysis. The uncertainty of r_i, $u(r_i)$, is assumed to be 0.01 Å, although it is normally lower. The propagation of $u(r_i)$ in our calculation procedure is the main contribution to $u(r_0)$, then $u(r_0) \simeq u(r_i)$. Hence, the error propagation leads to an upper limit of $u(b) = 2u(r_i)$.

Table 2 shows the coordination number 'n' and the corresponding number of complexes 'N_X' used for each $NH_4^+ \cdots X$ interaction. Note that most frequent coordination numbers are 8 and 12.

4. Discussion

4.1. Applicability of the BV model to the ammonium ion

Our procedure for checking entries (§3.1) enabled us to generate a reliable set of NH_4^+ environments without previously setting a particular (r_0, b) pair. In practice, only 4% of the selected environments have a $|1 - \text{BVS}|$ value greater than 0.2 (see §3.1). Further, the standard deviation of the BVS obtained from final values of r_0 and b is equal to 0.004, *i.e.* it is lower than the uncertainty of BVS.

The r_0 values obtained here agree with the expected values, as discussed in §4.2, and the value of b = 0.372 (20) is in good agreement with the 'universal constant'. A value of b different from 0.37 for a reliable r_0 would indicate that an unsuitable model had been used. For instance, a relationship between s_{ij} and other structural parameters such as bond angles has been observed by Wang & Liebau (1996). The presence of directional hydrogen bonds in the ammonium–anion interaction could have caused similar behaviour, but such an anomaly has not been detected.

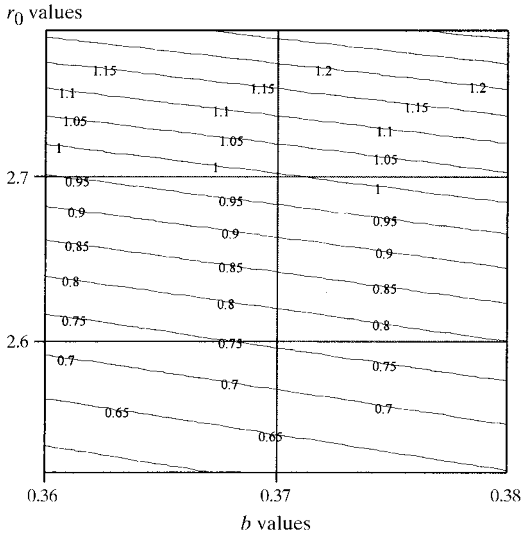

Figure 1
Curves with $\sum_i s_{ij}$ = constant in a particular environment showing the typical behaviour when the coordination sphere is 'well defined'.

Table 2
Coordination number '*n*' of ammonium environments.

n	N_X [$NH_4^+\cdots Cl$]	N_X [$NH_4^+\cdots F$]	N_X [$NH_4^+\cdots O$(inorganic)]	N_X [$NH_4^+\cdots O$(organic)]
4	1	1	1	0
5	1	0	2	1
6	4	2	21	8
7	7	2	25	11
8	8	19	50	11
9	4	11	34	8
10	5	10	64	9
11	0	7	35	8
12	9	16	34	1
Other	0	0	9	0

Assuming the uncertainty of r_i equal to 0.01, $u(r_0)$ is normal and $u(b)$ is lower than others given in the literature (Brown & Altermatt, 1985). Indeed, more accurate r_i would be necessary in order to reduce the $u(b)$ and $u(r_0)$ values. The availability of more quality structures would improve our knowledge of the relationship between bond valence and bond length. This would further improve our ability to understand and predict crystalline structures, and to carry out other theoretical studies.

4.2. Linear relationships between r_0 parameters

It has been shown (Brese & O'Keeffe, 1991) that a strong linear correlation exists between the r_0 parameters for bonds between a given cation and two different anions. The characteristic equations of bond parameters between any cation and fluoride or chloride with respect to the bond parameter between the corresponding cation and oxygen are

$$r_{0(\mathrm{N}\cdots\mathrm{F})} = 0.016 + 0.942 r_{0(\mathrm{N}\cdots\mathrm{O})} \tag{4}$$

$$r_{0(\mathrm{N}\cdots\mathrm{Cl})} = 0.341 + 1.020 r_{0(\mathrm{N}\cdots\mathrm{O})}. \tag{5}$$

The values of r_0 calculated in this way agree with the values obtained here. Substituting $r_{0(\mathrm{N}\cdots\mathrm{O})}$ = 2.22 Å (inorganic structures) or 2.23 Å (organic structures) gives a result which is in accordance with the estimated uncertainty: $r_{0(\mathrm{N}\cdots\mathrm{F})}$ = 2.11 or 2.12 Å and $r_{0(\mathrm{N}\cdots\mathrm{Cl})}$ = 2.60 or 2.62 Å, respectively. Moreover, we note that in all cases the r_0 parameter for $\mathrm{N}\cdots X$ interactions lies between the r_0 parameters for $\mathrm{K}\cdots X$ and $\mathrm{Rb}\cdots X$ interactions (Table 1).

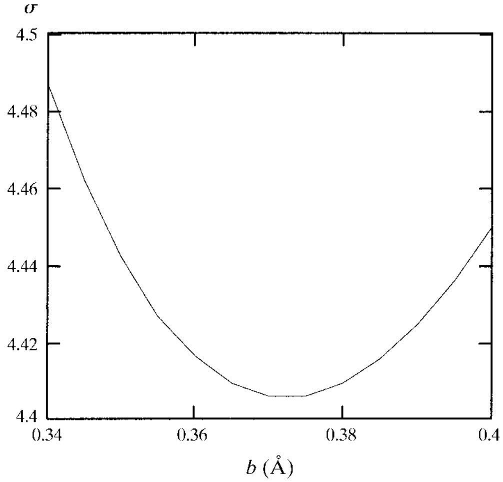

Figure 2
Standard deviation (σ) of the bond-valence sum (BVS) from the known oxidation state. b = 0.372 Å minimizes the value of $\sigma = 4.4 \times 10^{-3}$.

4.3. BVS deviation

The maximum difference between the BVS and the known oxidation state using the calculated BV parameters was found to be lower than 0.2 v.u. Accordingly, we can check the suitability of the database search restriction to ensure that there were no ligands involving elements other than those selected (see §2). When the number of structures is insufficient, BV parameters can be calculated from (4) and (5). Then, the r_0 values for the most typical $\mathrm{N}\cdots X$ contacts (X = B, C, Si, Ge, P, As, Sb, S, Se, Te, I, Br) were calculated from these equations. Results showed a significant BVS contribution (~ 0.07 for r_i = 4 Å).

A deeper analysis of those environments where the BVS values were close to the limit 1 ± 0.2 shows the following:

When well defined coordination spheres (n = 12) exist, the bond-valence sum around the X atoms showed that these environments were often overbonded. Note that half of the environments discarded using the criteria of §3.1 exhibit this characteristic. Steric effects may be responsible for this behaviour.

When there are m ($m > 1$) ammonium environments in the same structure, although one of them has a low BVS, $|m - \Sigma_{j\,=\,1-m}\,(\mathrm{BVS})_j|$ is often close to 0.1 v.u.

With regard to possible electronic distortion (see §1), the most frequent coordination numbers (n = 8, 12) are large, which results in a symmetric environment around the cation. In environments with low coordination number, the possible electronic effects would help to stabilize the distortion, owing to steric factors. Note that the slightly underbonded ammonium ions were found when n = 4, 5.

5. Conclusions

We consider that the arguments given in §4.1 show that the BVM is applicable to the ammonium ion. The r_0 value obtained lies between those of K and Rb atoms. In particular, knowledge of the BV parameters facilitates a number of studies concerning the ammonium ion, for instance, its role in the structural mechanisms of phase transitions.

The procedure for calculating BV parameters given in this paper allows us to confirm the suitability of fitting the parameter b = 0.37 as an universal constant. Similar procedures could be performed for different organic cations in order to verify this statement and justify a more theoretical study concerning the universal applicability of the b parameter.

The careful procedure for rejecting environments (§3.1) and checking the searches (§4.3) have determined some guidelines which will allow us to create new routines for VALMAP (González-Platas *et al.*, 1999), which checks known BV parameters and obtains new BV parameters directly from the crystallographic databases for any ionic interaction.

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