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Calculation of the crystal densities of molecular salts and hydrates using additive volumes for charged groups

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Standard group volumes which can be used to estimate the crystal densities of molecular salts and hydrates are reported, as a complement to values derived recently for the functional groups of neutral organic compounds. These new parameters were derived from a least-squares fit of cell volumes for a set of 1132 ionic molecular crystals from the Cambridge Structural Database. Their values point to the unusual overlap between monovalent O atoms and neighbouring H atoms. Using the new group volumes presently obtained, the crystal densities of the salts are predicted with an average error of <2.5%, while previous atom-based schemes yield average errors of >3%. To illustrate the possible application of the present database, the problem of designing environmentally friendly propellants is addressed.

1. Introduction

Methods to estimate the properties of new materials prior to their actual synthesis are very useful for design purposes. With regard to crystal densities, besides the empirical approaches based on van der Waals volumes (Piacenza *et al.*, 1989) or other molecular descriptors (Cho *et al.*, 2001), most schemes rely on additive contributions for the molar volume (Tarver, 1979; Stine, 1981; Mighell *et al.*, 1987; Ritchie & Bachrach, 1987; Horvath, 1992; Ammon & Mitchell, 1998; Hofmann, 2002). Volume additivity has the advantage of speed and simplicity as no estimate for the molecular conformation or crystal packing is needed. Using average atomic volumes which are independent of bonding patterns, a very general scheme that can handle most elements in the periodic table has been reported (Mighell *et al.*, 1987). This approach was recently extended to include thermal expansion (Hofmann, 2002). However, the volume occupied by a given atom clearly depends on its environment. Therefore, using group volumes rather than simple atom volumes should allow more accurate density predictions. This is of special interest in the field of energetic materials, where density is the key parameter for reliable performance prediction (Mader, 1996; Ammon & Mitchell, 1998). In fact, the group contribution approach is very accurate, using extensive crystal databases to derive the group volumes (Stine, 1981; Ammon & Mitchell, 1998). For instance, recent parameters derived from a set of 11 557 compounds reproduce the observed densities with an average error close to 2% (Ammon & Mitchell, 1998). However, these parameters are restricted to the organic crystals of neutral molecules containing only C, H, N, O and F atoms. In addition, the group contribution methods currently available focus on neutral organic compounds and cannot handle molecular salts or hydrates.

Examples of the crystals addressed in this study are shown in Fig. 1. In practice, salts exhibit specific properties which might be of practical interest. For instance, ammonium perchlorate is used as a high-density energetic oxidizer which enters the composition of propellants. However, environmental considerations make it more desirable to replace perchlorate with more friendly, *i.e.* chlorine-free, systems. More generally, the design of the energetic materials depends on the use of stable oxidizing moieties, since the energy provided by such systems stems from the oxidization of C and H atoms. In most cases, oxygen is provided by $-NO_2$ groups. However, too many nitro groups are likely to affect the stability of the molecule since $X-NO_2$ bonds are rather unstable. In this context, ammonium nitrate salts $X-NH_3^+\cdot NO_3^-$ might provide a valuable alternative.

The first step in designing such salts involves identifying the target compounds of interest. As the methods used to estimate the performances of propellants become more accurate, the search for new compounds can be made more efficient because the number of candidate structures that may safely be ruled out because of poor performances increases. To date, the density of crystal salts may only be estimated using atomic volumes (Mighell *et al.*, 1987; Hofmann, 2002). Indeed, notwithstanding preliminary work restricted to ammonium crystals (Ritchie & Bachrach, 1987), no systematic set of group

volumes has been reported for charged moieties. This is the goal of the present study.

## 2. Parameterization

2.1. Database

Salt crystals from the Cambridge Structural Database (Allen, 2002) are used to derive the standard volumes of charged groups, in order to extend the scope of a recent group-contribution method (Ammon & Mitchell, 1998) to salts. Of course, beyond the groups whose volumes are to be derived in the present study, all other group volumes needed to estimate the densities of the crystals selected must be available from the original method. Moreover, only fully ordered salt structures with R factors < 0.05 and for which no errors were reported have been considered. Entries for which the chemical formula (stored in the CIF) was not consistent with the file containing the molecular geometry (in .mol2 format, as taken from the Cambridge Structural Database) were discarded. Such inconsistencies occur mostly because some atoms (typically H atoms) are missing in the geometry file, or because some atoms are invariant under some symmetry operations of the crystal space group.

Although the crystal densities may vary by a few percent owing to temperature effects, the performances of propellants are usually evaluated assuming standard conditions (298 K, 1 atm). Furthermore, thermal expansion can hardly be included within the group contribution approach as it depends on the anharmonicity of the intermolecular potential (Ashcroft & Mermin, 1976). This difficulty is illustrated by a recent attempt at introducing an average thermal expansion coefficient α for molecular crystals. The author reported that the value obtained for this coefficient was ill-defined, with a standard deviation comparable to its absolute value (Hofmann, 2002). Therefore, the scope of the present work is only to extend the original method (Ammon & Mitchell, 1998) to salts, without introducing temperature effects. The structures considered were measured at room temperature (283–303 K).

Finally, only compounds with commonly charged groups which are of practical relevance (listed in Table 1) were retained. The automatic identification of charged groups relies on atom connectivities, as provided in the . mol2 files. The final set contains 1132 crystals. In what follows, they will be referred to according to their identifier in the database (six uppercase letters).

2.2. Fitting procedure

As the cell volume is simply evaluated as the sum of the volumes of all the groups in the crystal, a linear least-squares fitting procedure may be applied. In contrast with some previous authors (Stine, 1981; Ammon & Mitchell, 1998), no attempt was made to derive so-called 'non-linear volumes' which were aimed at minimizing the least-squares errors on the densities. Such a non-linear fit would be equivalent to fitting against inverse volumes, weighting the entries according
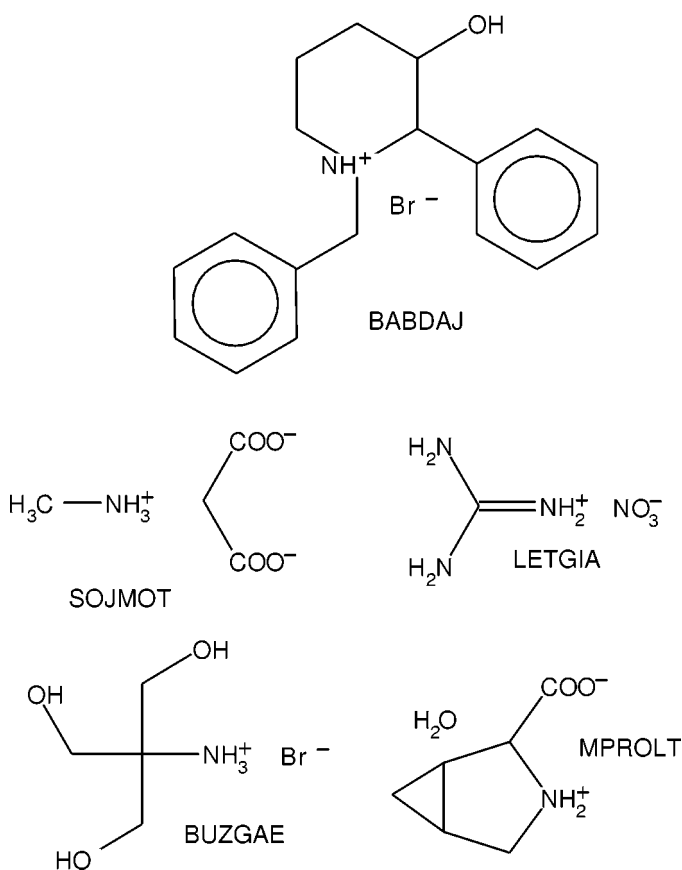
Figure 1
Compounds showing the most significant differences between calculated and observed densities, identified with their reference codes from the Cambridge Structural Database.

Table 1
Group volumes v_i and associated standard deviations σ_i derived from the present work (in Å).

Group densities d_i (in g cm^{-3}) are also reported to help in the design of high-density compounds. N_{obs} is the number of crystals which contain the group considered, *i.e.* the number of observations used in the determination of the group volume. For each group, the volumes obtained from the atomic increments of Mighell *et al.* (1987) (v_M) and Hoffman (2002) (v_H) are also reported.

Group	v_i	σ_i	d_i	N_{obs}	v_M	v_H
H_2O	22.951	0.045	1.30	218	20.80	21.55
$=NH_2^+$	25.742	0.127	1.03	46	21.80	21.96
$>NH^+$	16.272	0.067	1.53	210	16.40	16.88
$>N<^+$	8.975	0.085	2.59	93	11.00	11.80
$>NH^+$	16.522	0.063	1.51	240	16.40	16.88
$>NH_2^+$	21.453	0.062	1.24	199	21.80	21.96
$-NH_3^+$	25.128	0.049	1.12	381	27.20	27.04
NH_4^+	36.868	0.180	0.81	18	32.60	32.12
$-O^-$	6.445	0.113	4.12	49	10.00	11.39
$-COO^-$	30.395	0.045	2.40	479	33.94	36.65
NO_3^-	46.888	0.117	2.20	36	41.00	45.97
Cl^-	27.834	0.046	2.12	437	25.00	25.80
Br^-	39.396	0.070	3.37	148	30.50	32.70

to the mass of the atoms in the unit formula. On the other hand, as charged groups occur in pairs, the set of equations is highly redundant. For instance, since the ammonium group $-NH_3^+$ is often associated with nitrate NO_3^- as the counter-ion, many equations simply specify the value of the total volume of the ammonium nitrate pair. Therefore, to estimate the volume V_k^{calc} occupied by the n_{ki} newly introduced groups i in crystal k, according to

$$V_k^{calc} = \sum_i n_{ki} v_i, \qquad (1)$$

the average group volumes v_i are obtained using the singular value decomposition procedure (Press *et al.*, 1992). The latter involves a minimization of the squared residual

$$\sum_k \left(V_k^{obs} - \sum_i n_{ki} v_i \right)^2, \qquad (2)$$

where V_k^{obs} is the target value for V_k^{calc}. V_k^{obs} is obtained as the difference between the experimental cell volume and the contribution to this volume that may be derived from the volume parameters already available (Ammon & Mitchell, 1998). The **n** matrix with components n_{ki} is expressed as $n = \mathbf{A}\mathbf{w}\mathbf{B}^T$, where $\mathbf{B}^T$ denotes the transposition of a square orthogonal matrix **B**, **w** a square diagonal matrix with singular values $w_j \geq 0$ on the diagonal, and **A** a column-orthogonal matrix. The volumes v_i of charged groups i are the components of the vector **v** defined as

$$\mathbf{v} = \sum_j (\mathbf{A}_j \cdot \mathbf{V}^{obs}/w_j)\mathbf{B}_j. \qquad (3)$$

Associated standard deviations σ_j may be obtained from

$$\sigma_i^2 = \sum_j \left(\frac{B_{ij}}{w_j} \right)^2. \qquad (4)$$

Details of the algorithm are given by Press *et al.* (1992) and references therein.

2.3. Cross validation

For further assessment of the significance of the group volumes derived from the fit, the data set was split into two subsets of 566 crystals. The cell volume and density of every crystal in a given subset were predicted, rather than fitted, using parameters derived from the other subset. To assess the predictive value of the present parameterization, we focus on the average absolute deviation (a.a.d.) between calculated and observed cell volumes, where the calculated data are *predicted* (during the cross-validation step) rather than *fitted* on the whole dataset. This allows the a.a.d.s thus obtained to be compared with the average errors previously reported for crystals beyond the training set (Ammon & Mitchell, 1998).

2.4. Volume increments

Commonly charged groups in organic salts mostly involve tetravalent N atoms (formal charge +1) and monovalent O atoms (formal charge −1). For sp^2 tetravalent N atoms, only the $=NH_2^+$ group is considered. For sp^3 tetravalent N atoms, five volumes are introduced, according to the number of bonded H atoms (Table 1). A special volume denoted as $>NH^+$ is used for pyridine N with a proton attached. In addition to the generic volume for monovalent oxygen $-O^-$, special volumes are used for the very common $-COO^-$ anionic group and for the nitrate ion NO_3^-. In addition, the halogen anions Cl^- and Br^- are considered as they are present in many salts of interest. Finally, since many of the crystals retained contain water molecules, a specific volume for water in ionic organic crystals has to be fitted also. It will be useful to estimate the volume of the hydrate crystals.

3. Results

3.1. Average group volumes

The average volumes obtained are listed in Table 1. They yield the average and standard relative errors of 2.4 and 3.1%, respectively, for the volumes of the 1132 crystals considered. On the other hand, the cross-validation yields average and standard relative errors on *predicted* crystal volumes of 2.4 and 3.2%. Thus, the present model is quite reliable at predicting crystal volumes and hence densities. The mean difference between the group volumes obtained from both subsets is < 2 Å^3, except for $-O^-$, whose volume may vary by as much as 5 Å^3 according to the set used for calibration. Therefore, the volume of this moiety is ill-defined. In fact, $-O^-$ is very often involved in hydrogen bonds and the distance between this atom and neighbouring protons is very variable. For instance, the $O\cdots H$ distance is close to 2 Å ($\pm$ 0.1 Å) in many compounds (such as picrates, like BEBPIH) and only 1.562 Å for salicylic acid in ZAJHEX (57% of the van der Waals' distance). From calculations of isolated ion pairs, we can estimate the decrease in the van der Waals' volume associated with this overlap as 1.6 Å^3. Taking a standard value of 0.7 for the packing coefficient, this suggests a decrease of 2.3 Å^3 for the crystal volume. Considering the fluctuations (up to 2 Å^3) of the other volume increments, the problem with defining a

single volume for $-O^-$ is understandable. In addition, the $-O^-$ volume is all the more difficult to estimate accurately as it represents a minor fraction of the total crystal volume. Notwithstanding $-O^-$, variations of the volume parameters with the calibration set are $< 5\%$.

With regard to the volumes of the five groups containing sp^3 tetravalent N atoms, it may be noted that they increase almost linearly with the number of H atoms. This indicates that the five group volumes introduced may be approximated with a combination of only two values for the tetravalent nitrogen and associated hydrogen. The data suggest a volume of 6.973 Å^3 for ammonium H, consistent with the values reported previously for H bonded to C or N atoms (Ammon & Mitchell, 1998).

The comparison (Table 1) between the present group volumes v_i with the values obtained from the sets of atomic volumes reported previously (Mighell *et al.*, 1987; Hofmann, 2002) is of special interest. The volumes derived from these two earlier atom-based schemes are fairly similar, despite some differences for oxygen-rich groups owing to the relatively large difference (13%) between atomic volumes of this element in the two parameters sets. More significant differences are observed on comparing the group volumes derived from atomic contributions to the present values. The latter should be more reliable as they partly incorporate the dependence of atomic volumes on neighbouring atoms. For instance, the water volume obtained here is larger than the sum of the corresponding atomic volumes. Indeed, most O atoms in crystals are bonded to atoms larger than hydrogen. Their volume is thus decreased owing to the overlap associated with such bonding. This is not the case for O in water. Accordingly, the larger volume derived for water in the present work is reasonable.

A comparison of the volumes for groups containing the same atoms further illustrates the fact that a group-contribution approach may account for the role of coordination, in contrast to previous schemes based on atomic volumes. The smaller volume of $>NH_2^+$ (21.453 Å) compared with that of $=NH_2^+$ (25.742 Å) probably stems from the higher coordination of nitrogen in the former group. Since the N atom is more crowded, its volume is naturally smaller.

3.2. Group densities

In addition to the volume data, the group densities are reported in Table 1. As they allow the immediate identification of the effect of a given group on the density, they should be helpful when density is a design criterion. Notwithstanding their obvious dependence on the chemical elements of the group, these densities reveal the effect of bonding patterns. For instance, the carbonate group $-COO^-$ is found to be more effective than the nitro group $-NO_2$ in increasing the crystal densities, while their respective masses suggest the opposite. Not surprisingly, $-O^-$ exhibits the highest density owing to its small volume, although the value of 4.12 g cm^{-3} obtained is subject to large uncertainties. It reflects the significant overlap between $-O^-$

and neighbouring protons for the crystals considered. A closer examination of the results obtained previously for non-ionic crystals reveals similar findings, as the highest densities (up to 2.94 g cm^{-3}) were obtained for some N—O groups in *N*-oxides, *i.e.* for groups containing monovalent O atoms. Finally, also considering the value of 2.40 g cm^{-3} obtained for $-COO^-$, the especially small volume occupied in crystals by monovalent O atoms (owing to significant overlaps with neighbouring protons) appears to be systematic. A last point worth noting regarding the group densities concerns water. The density of ice (1.0 g cm^{-3} at 273 K) is abnormally low owing to the dense hydrogen-bond network which opposes the close-packing principle (Gavezzotti, 2002). The group density of 1.3 g cm^{-3} obtained for H_2O molecules in the present work reflects the fact that they can pack more efficiently in organic crystals compared with ice, since they are involved in fewer hydrogen bonds.

3.3. Calculated crystal densities

The distribution of the relative deviations (in %) between calculated and experimental densities is shown in Fig. 2 to enable a straightforward comparison with similar histograms from previous papers (Ammon & Mitchell, 1998; Cho *et al.*, 2001). The most significant deviations ($>10\%$) are all positive, reflecting low-density packing modes. The latter occur when the shape of the molecule does not lend itself to a compact structure, as for BABDAJ. In a few cases, measurements carried out on high-temperature polymorphs (metastable at
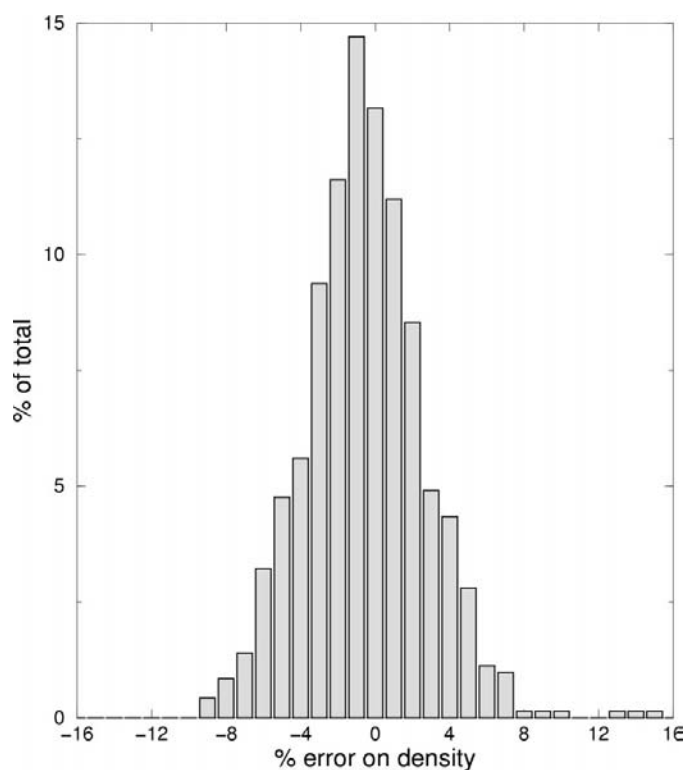
Figure 2
Distribution of the relative differences between calculated and observed densities.

ambient conditions) or the unrecognized inclusion of solvent molecules during crystallization (Hofmann, 2002) cannot be excluded either.

For the 1132 salts considered, the a.a.d. from experimental values is 2.38%. The densities estimated using the previous atom-based approaches of Mighell *et al.* (1987) and Hofmann (2002) are somewhat less accurate, with respective values of 3.14 and 3.37% for the a.a.d. The lower accuracy obtained using Hofmann parameters might be associated with the fact that they were designed in order to reproduce densities at all temperatures, through the inclusion of only a single additional adjustable parameter (the average thermal expansion coefficient α). On the other hand, and although the comparison is awkward as it involves calculations on different sets of molecules, it is worth noting that the present densities are not as accurate as those reported by Ammon & Mitchell (1998) for non-ionic molecular crystals, who obtained a value of 2.04% for the a.a.d. For ionic crystals in the calibration set, a lower value of the a.a.d. might be obtained through the definition of more specific volumes. For instance, the groups listed in Table 1 could be allowed to depend on their involvement or not in a ring, which is common when defining group volumes (Stine, 1981; Ammon & Mitchell, 1998). However, whether such additional groups would improve the accuracy of the predicted densities is questionable. In fact, there are a number of reasons why salt densities might be more difficult to estimate from group volumes than the densities of non-ionic crystals.

Firstly, salts often contain small ionic species. In such a case, the intermolecular volume (outside the Van der Waals' atomic spheres) makes a relatively large contribution to the molar volume. As this contribution is most dependent on the molecular conformation and packing, larger errors in densities may be expected.

Moreover, while hydrogen bonds do not significantly affect the crystal densities of neutral compounds (Dunitz *et al.*, 2000), the charged species considered here show particularly strong hydrogen bonds which may enhance the densities in a non-additive way. In fact, hydrogen bonds involving mono-valent O atoms explain the small volume obtained for $-(O^-)$.

Finally, labile H atoms in the ionic groups listed in Table 1 may be subject to tautomerizations (especially *via* tunneling), thus leading to further uncertainties in the structure determination. For instance, an erroneous formula unit is reported in the database for BOYDUO (Fig. 3). Indeed, the amine group expected on the six-membered ring is unlikely as it would exhibit a C—NH$_2$ bond length of 1.34 Å. This value reflects the double-bond character. Thus, the X-ray data clearly indicate that the assumed amino group is in fact a $=$NH$_2^+$ structure and this rules out the presence of an ammonium moiety. On the other hand, the hygroscopic character of many salts further increases the chance of carrying out crystallographic measurements on defective crystals.

By far the most significant (+21%) deviation between calculated and observed densities is observed for BABDAJ. Other errors > 10% relate to LETGIA, BUZGAE and

Table 2
Ionic crystals for which the densities calculated with the present model are especially poor.

Densities obtained in the present work and using the atom-based schemes of Mighell *et al.* (1987) and Hofmann (2002) are compared with experimental values. All densities are given in g cm^{-3}

Crystal code	Present work	Mighell	Hofmann	Exp
BABDAJ	1.388	1.373	1.386	1.145
LETGIA	1.602	1.685	1.613	1.410
BUZGAE	1.768	1.747	1.720	1.540
SOJMOT	1.376	1.331	1.316	1.224
MAMHOX	1.568	1.539	1.495	1.422
MPROLT	1.394	1.310	1.302	1.275
DEKDAY	1.539	1.516	1.480	1.641
RAWBAS	1.709	1.736	1.659	1.619

SOJMOT (+13% to +15%), MAMHOX and MPROLT (+10%). These compounds are shown in Fig. 1, except MAMHOX whose formula is H$_3$C—NH$_3^+\cdot{}^-$OOC—COOH. In Table 2, the poor densities calculated using the present method are compared with the values derived from atom-based approaches. All three estimation procedures yield very similar results, except for MPROLT for which the densities calculated with earlier methods (Mighell *et al.*, 1987; Hofmann, 2002) are in much better agreement with this experiment. Therefore, the most severe errors on calculated densities are common to other additive schemes. They point to deviations from the close-packing principle. For BABDAJ, the low compactness of the experimental unit cell may be explained by the overall shape of the cation which prevents efficient packing. Indeed, there appears to be no way to fill the empty volume between the rings. However, in most cases there is no such trivial explanation for the abnormally low densities of those compounds.

3.4. Further extension of the database

In the present work, average volumes have been derived for commonly charged groups. Indeed, to ensure significant averaging of individual parameters, most volumes have been derived using at least 36 observations (Table 1). The only exception concerns the ammonium ion NH$_4^+$, whose volume is averaged from 18 crystals. This cation is of special interest in the field of energetic materials as it is present in compounds
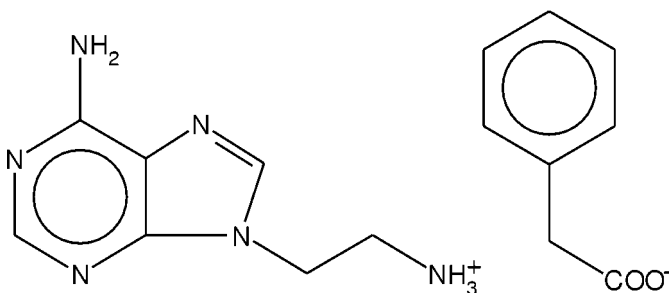
Figure 3
Formula unit reported for BOYDUO. In fact, this formula is not consistent with the C—NH$_2$ bond length derived from the X-ray data (see text).

such as ammonium perchlorate (AP) and ammonium dinitramide (ADN).

In fact, the extension of the present scheme to less common groups is straightforward, although the volumes thus obtained might be less transferable when derived from small datasets. For instance, divalent N atoms with the formal charge -1 are of interest in energetic crystals. However, few crystals containing this moiety have been characterized so far. To enable density predictions for salts containing dinitramide $(O_2N-N^-NO_2)$, an average volume of 83.37 $\text{\AA}^3$ has been derived for this anion using 11 crystals from the Cambridge Structural Database. Then, this volume has been used to calculate densities for these compounds. A value of 2.82% is obtained for the a.a.d. from experiment, with densities underestimated by 6.2% for DEKDAY and overestimated by 5.5% for RAWBAS. These results are consistent with the average accuracy obtained for salts, somewhat lower than the accuracy obtained for covalent crystals. Nonetheless, those values are significantly better than the densities derived from available atomic volumes, also reported in Table 2.

When extending the method to handle additional structures, unrealistic volumes may arise if the linear equations used to derive volume increments are underestimated. A closer examination of the volumes obtained from a preliminary study of nitrates and perchlorates salts (Ritchie & Bachrach, 1987) is interesting in this respect. Indeed, starting from the Stine (1981) parameterization, a volume as small as 0.232 $\text{\AA}^3$ was reported for ammonium nitrogen N^+. In contrast, a value of 8.976 $\text{\AA}^3$ is obtained using the data from Table 1 combined with the above-mentioned value of 6.973 $\text{\AA}^3$ for the volume occupied by ammonium N atoms. On the other hand, the work based on Stine parameters reported a volume of 57 $\text{\AA}^3$ for nitrate anions, significantly larger than the 47 $\text{\AA}^3$ value reported in Table 1. Thus, the very small volume reported previously for N^+ makes up for the overestimated volume of the nitrate anion. As a consequence, this former parameterization is restricted to ammonium nitrate ions. In contrast, the present scheme may be applied to any crystal containing either ammonium or nitrate, whatever the counterion may be. This example illustrates the interest of the singular value decomposition procedure, which makes it easy to identify ill-defined linear systems that may occur for small datasets.

4. Application

To illustrate the use of the data in Table 1, the design of $R-$ $NH_3^+\cdot NO_3^-$ salts as environmentally friendly substitutes for ammonium perchlorate in propellant compositions is considered. First, it may be noted from the data obtained in this work that the $-NH_3^+\cdot NO_3^-$ ion pairs contribute a relatively high value of 1.82 g cm^{-3} to the density of the salt, despite the presence of three H atoms. The potential interest of such salts in the field of energetic materials is thus confirmed. In this context, suitable R substituents should contribute to the high values of the density and energy content of the material. Aromatic rings are interesting in this respect. Moreover, the

number of C and H atoms should be restricted to optimize the oxygen balance. Thus, nitrogenated heterocycles are natural candidates as R substituents. On the other hand, owing to the magnitude of the attractive electrostatic interactions between ions, salts often exhibit a very negative heat of formation. While highly energetic substituents may partially make up for the negative electrostatic contribution to the heat of formation, the latter can be minimized using large substituents. Indeed, an R substituent of sufficient size increases the average distance between charged groups, thus reducing the magnitude of the electrostatic energy.

As a preliminary assessment of this approach, (1a) and (2a) have been considered as leading compounds in developing high-energy salts with NO_3^- anions. The group volumes reported here allow the estimation of the corresponding densities, which are 1.49 and 1.67 g cm^{-3}, respectively, for nitrate salts with (1a) and (2a) as cations (Fig. 4). Considering the fact that these model structures exhibit no high-density groups (such as nitro groups, N-oxides, ternary N atoms etc.), these values are encouraging. Indeed, calculations indicate that enhanced values of 1.8–1.9 g cm^{-3} should be obtained after twofold nitration. However, Density Functional Theory (DFT) calculations, carried out with the Jaguar program (Wright, 2002), indicate that structures (1a) and (2a) are unstable with respect to tautomerizations, yielding compounds (1b) and (2b), shown in Fig. 4. Indeed, at the B3LYP/6-31G* level, significant energy differences are found, (1b) being more stable than (1a) by 78 kJ mol^{-1} and (2b) more stable than (2a) by 103 kJ mol^{-1}. According to the volumes given in Table 1, nitrate salts with (1b) and (2b) as cations exhibit slightly lower densities: 1.45 and 1.62 g cm^{-3}, respectively. Actually, these nitrate salts have been synthesized and characterized through
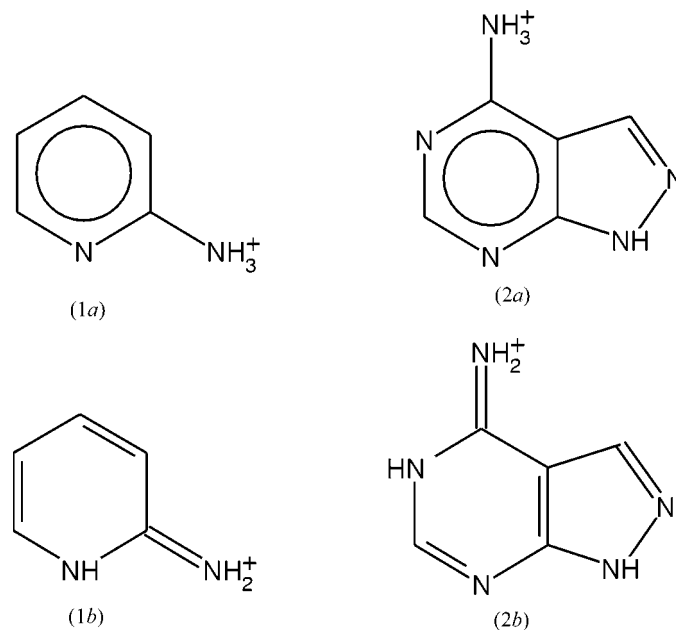
Figure 4
Model compounds used to investigate the interest of ammonium nitrate salts as energetic materials.

X-ray diffraction (details of the experiments to be reported elsewhere). The compounds obtained turned out to be (1b) and (2b), thus confirming the tautomerization expected on the basis of the DFT calculations. A value of 1.45 g cm^{-3} was derived from the X-ray measurements for the nitrate salt of (1b). The crystal obtained from (2b) contains one H_2O molecule for each cation, in addition to the counterion NO_3^-. The calculated and X-ray densities for this crystal are then 1.59 and 1.66 g cm^{-3}, respectively. Thus, the present group parameters yield a density which is in excellent agreement with experiment for (1b) with NO_3^-, while the 4.2% under-estimation for the water-containing nitrate salt of (2b) remains consistent with the usual limitations of group contribution approaches.

5. Conclusions

The present extension of the group contribution method of Ammon & Mitchell (1998) may be used to estimate the density of hydrate and salt crystals such as the energetic compounds based on amonium nitrate and nitrogenated heterocycles. It may also be used to evaluate the consistency of experimental unit-cell parameters with the expected chemical composition of a crystal. This latter application of density estimation methods is especially useful for salts, for which the retention of water molecules or tautomerizations are relatively frequent. The average error with respect to experimental densities is 2.38%.

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