Predicting Bond Lengths in Inorganic Crystals

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Bond lengths in inorganic crystals can be predicted by solving a model based on a network of chemical bonds. The results agree with observed bond lengths to within a few hundredths of an ångström for most bonds except for those to alkali metals. An earlier method of predicting bond lengths [Baur (1970), *Trans. Amer. Cryst. Assoc.* **6**, 129–155] gives predictions of comparable overall accuracy but the difference in the approaches leads to significant differences in the predictions for individual bonds. The two methods each have their own strengths and should be considered as complementary. The model has possible extensions to amorphous materials and suggests, for example, that the lone pair of valence electrons is not responsible for the distorted environments found in $TeCl_4$ and TeI_4 in the solid state.

One of the basic assumptions made in most chemical (as opposed to physical) theories of matter is that atoms are only involved in two-body interactions, either bonding or non-bonding. Neglecting in a first approximation the non-bonding interactions, any chemically bonded group of atoms, whether a small molecule such as H_2O or a crystal such as diamond, can be thought of as a network of bonds with atoms occupying the nodes. The mathematical properties of such a network can be useful in predicting the properties of the bonds and hence of the material. A concept that is helpful for network analysis is bond valence or bond strength, as originally defined by Pauling (1929) and recently refined by a number of workers (Allmann, 1975). Although the bond valence is numerically similar to the widely used bond order it has a greater practical use since it is defined in an empirical manner and can be determined from measured bond lengths. Bond order, on the other hand, is defined in terms of electronic structure and cannot be readily and precisely determined.

The concept of bond valence, *i.e.* the amount of valence associated with a particular bond, derives from the nineteenth century theory of valence. Valence was introduced as a property of atoms to account for the law of multiple proportions. It follows from this definition that it is always possible to distribute the total valence of each atom between the bonds that it forms in such a way that each bond receives an equal contribution of valence from the atom at either end. A corollary is that the total bond valence received by each atom in the network is equal to its atomic valence. This can be called the 'valence sum rule' and is an extension of the electroneutrality principle of Pauling (1929). Recent accurate determinations of crystal structures have

shown that in most inorganic materials there is a good correlation between the length of a bond and its valence so that it is now possible to determine the valence of a bond within a few per cent from experimentally determined bond lengths (Brown & Wu, 1976, and references therein). Such valences obey the valence sum rule and their failure to do so usually indicates an inadequately determined or interpreted structure.

In some cases it is possible to make an *a priori* prediction of the bond valences and hence the bond lengths. The network of chemical bonds is mathematically similar to an electrical network that can be solved from Kirchhoff's laws (Mackay & Finney, 1973). The valence sum rule is mathematically equivalent to Kirchhoff's current law and can be formulated as 'the sum of (bond) valences at a node is equal to the (atomic) valence of that node'. Unfortunately, Kirchhoff's voltage equation does not apply to chemical networks. Instead a rule that appears to apply in a less rigorous form is: 'consistent with the valence sum rule, the (bond) valences around each node tend to be as nearly equal as possible'. This I call the 'equal valence rule' and if it were rigorously true the network would be over-determined by a factor of two. Only in elemental and binary compounds (*e.g.* diamond, NaCl) can it normally be fully satisfied.

There are several ways in which the equal valence rule can be applied. One procedure that proves effective is described below. Initial values of the bond valences around each atom are obtained by dividing the atomic valence by its coordination number. Since this gives two valences for each bond (one derived from the atom at each end of the bond), the two values are averaged. These averaged values will in general no longer obey the valence sum rule and they are therefore adjusted by adding (or subtracting) equal increments to all bonds around each atom in turn in such a way that the valence sum rule is obeyed around that

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atom. After the environment of each atom has been adjusted once each bond will have been adjusted twice. Thus the rule will still no longer be obeyed by the first atoms adjusted and a second cycle of adjustments must be made. As the process is repeated the bond valences converge to values which satisfy the valence sum rule around all atoms. The number of cycles needed is approximately equal to the number of atoms in the repeating unit of the network. The refined values (S) are used to calculate bond lengths (R) from a correlation such as $S = (R/R_1)^{-N}$, where R_1 and N are tabulated parameters (Brown & Wu, 1976). All the calculations reported in this paper were made with the program *BONDS* on a CDC 6400 computer.

Attempts were made to improve the predictions by weighting the increments added to the bond valences during the refinement, either in proportion to the valence of the atom at the further end of the bond or by the deviation from the initial (symmetric) value, but none of these schemes gave better overall agreement than the unweighted refinement.

Discussion

The valence sum rule works well in crystals in which there are no delocalized bonds (*i.e.* in crystals where the two-body-interaction assumption is valid) and where, when formal + and − charges are assigned to each atom, bonds only occur between atoms of opposite charge.* It therefore works for urea and the ammonium ion, but not for the hydrazinium ion or, in general, for organic materials. The equal valence rule is more restricted since it cannot predict distortions arising from electronic effects (*e.g.* Jahn–Teller, stereoactive non-bonding electron-pair effects) or from steric effects arising from the influence of the neglected non-bonding interactions (*e.g.* the distortions found in

* This restriction can be avoided in certain cases, *e.g.* the bonding of NO₂ to Cu through N, by the use of directed valences; that is to say in certain cases the bond valence is subtracted rather than added according to the direction of the bond valence.

perovskites and the asymmetry of hydrogen bonds). For the remaining materials, comprising the bulk of non-hydrated inorganic compounds, the procedure described above usually predicts bond valences to within about 0·05 valence units (v.u.) and hence distances ranging in accuracy from 0·02 Å for high-valence bonds (*e.g.* S—O, N—O) to 0·2 or 0·3 Å for low-valence bonds (*e.g.* those to alkali metals) (Fig. 1).

The inability to predict valences to better than ±0·05 v.u. may arise from two causes: firstly, the neglect of non-bonding interactions and, secondly, the restriction that the predicted bonding network must correspond to a geometrically possible arrangement of atoms. A network of valences does not normally contain sufficient information to fix the coordinates of all atoms in the crystal. Some information about non-bonding interactions or bond angles is also needed but the fact that
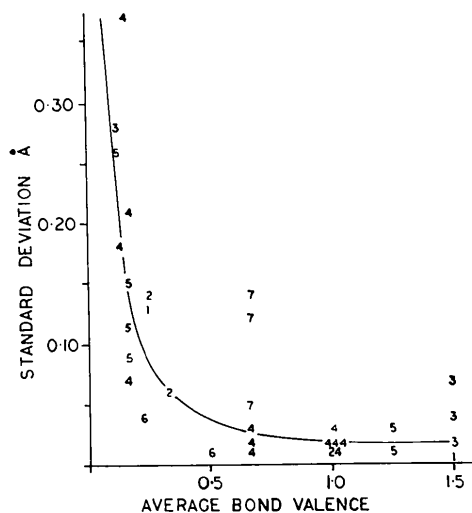

Fig. 1. Standard deviations between predicted and observed bond lengths around various cations as a function of average valence of bonds formed by the cation. The numbers refer to the tables from which data are taken. The solid line represents the deviation expected if all valences are correctly predicted with a standard error of 0·05 valence units.

Table 1. *Prediction of bond lengths in* (H₅O₂)₂SO₄ (*Kjällman & Olovsson,* 1972)

	Network		Baur (1970)	Observed
	valence (v.u.)[1]	length (Å)[2]	length (Å)	length (Å)
S—O(1) (×4)	1·50	1·476	1·473	1·479
σ(S—O)[4]		0·003	0·006	
O(2)—H(1)···O(2)	0·75, 0·25	2·63	2·73	2·66
O(2)—H(2)···O(2)	0·75, 0·25	2·63	2·73	2·66
O(2)—H(3)···O(2)	0·50, 0·50	2·41	—[3]	2·43
σ(O—H···O)[4]		0·03	0·13	

Notes: (1) The valences in (H₅O₂)₂SO₄ are uniquely determined by the valence sum rule. (2) Bond-length–bond-valence correlations are taken from Brown & Wu (1976) in all tables except where otherwise noted. Correlation for (O—H···O) bonds is taken from Brown (1976*b*). (3) Baur's method does not work for symmetrical hydrogen bonds. (4) Standard deviation of predicted from observed lengths.

the valence network transforms into a spatially possible arrangement of atoms places restrictions on the network which have not been included in the present model.

A related method of predicting bond lengths based directly on Pauling's original electroneutrality principle has been described by Baur (1970). His method, like that described here, is an attempt to ensure that the valence sum rule is obeyed, but his procedure is different, involving adjustments made to an ideal regular cation environment. In the examples given below the predictions of the network theory are compared with the prediction of Baur's method.

Table 2. *Prediction of bond lengths in diopside* $CaMgSi_2O_6$ *(Clark, Appleman & Papike,* 1969)

	Network valence (v.u.)	length (Å)	Baur (1970) length (Å)	Observed length (Å)
Si—O(1)	1·07	1·60	1·62	1·60
Si—O(2)	1·17	1·56	1·59	1·58
Si—O(3)	0·88	1·67	1·67	1·66
Si—O(3)	0·88	1·67	1·67	1·69
σ(Si—O)		0·01	0·01	
Ca—O(1) (×2)	0·32	2·35	2·43	2·36
Ca—O(2) (×2)	0·42	2·24	2·32	2·35
Ca—O(3) (×2)	0·12	2·80	2·62	2·56
Ca—O(3) (×2)	0·12	2·80	2·62	2·72
σ(Ca—O)		0·14	0·07	
Mg—O(1) (×2)	0·30	2·15	2·10	2·12
Mg—O(1) (×2)	0·30	2·15	2·10	2·06
Mg—O(2) (×2)	0·40	2·01	2·06	2·05
σ(Mg—O)		0·06	0·02	

Table 3. *Prediction of bond lengths in* $K_2S_5O_{16}$ *(De Vries & Mijlhoff,* 1969)

	Network valence (v.u.)	length (Å)	Baur (1970) length (Å)	Observed length (Å)
S(1)—O(1) (×2)	1·03	1·61	1·61	1·59
S(1)—O(8) (×2)	1·97	1·38	1·44	1·40
σ[S(1)—O]		0·02	0·03	
S(2)—O(1)	0·97	1·63	1·61	1·67
S(2)—O(2)	1·16	1·57	1·61	1·51
S(2)—O(6)	1·94	1·39	1·44	1·43
S(2)—O(7)	1·94	1·39	1·44	1·42
σ[S(2)—O]		0·04	0·06	
S(3)—O(2)	0·84	1·69	1·61	1·83
S(3)—O(3)	1·70	1·43	1·45	1·42
S(3)—O(4)	1·70	1·43	1·45	1·42
S(3)—O(5)	1·77	1·42	1·44	1·42
σ[S(3)—O]		0·07	0·11	
K—O(3)	0·15	2·80	2·82	2·95
K—O(3)	0·15	2·80	2·82	2·80
K—O(4)	0·15	2·80	2·82	2·77
K—O(4)	0·15	2·80	2·82	3·10
K—O(5)	0·23	2·68	2·81	2·71
K—O(6)	0·07	3·07	2·81	2·78
K—O(7)	0·07	3·07	2·81	2·71
K—O(8)	0·03	3·30	2·81	2·73
σ(K—O)		0·28	0·13	

Table 4. *Prediction of bond lengths in* $Na_2B_4O_7$ *(Krogh-Moe,* 1974)

	Network valence (v.u.)	length (Å)	Baur (1970) length (Å)	Observed length (Å)
B(1)—O(1)	0·71	1·50	1·49	1·49
B(1)—O(2)	0·77	1·48	1·47	1·49
B(1)—O(3)	0·73	1·49	1·49	1·49
B(1)—O(4)	0·79	1·46	1·46	1·45
σ[B(1)—O]		0·01	0·01	
B(2)—O(4)	0·77	1·48	1·46	1·44
B(2)—O(5)	0·76	1·48	1·47	1·49
B(2)—O(6)	0·77	1·48	1·47	1·47
B(2)—O(7)	0·70	1·51	1·49	1·49
σ[B(2)—O]		0·02	0·01	
B(3)—O(8)	0·80	1·46	1·47	1·48
B(3)—O(9)	0·73	1·49	1·49	1·47
B(3)—O(10)	0·72	1·50	1·50	1·49
B(3)—O(11)	0·75	1·48	1·49	1·43
σ[B(3)—O]		0·03	0·03	
B(4)—O(10)	0·96	1·39	1·39	1·41
B(4)—O(13)	0·90	1·42	1·40	1·45
B(4)—O(14)	1·14	1·33	1·31	1·30
σ[B(4)—O]		0·03	0·03	
B(5)—O(1)	1·03	1·37	1·37	1·34
B(5)—O(3)	1·02	1·37	1·37	1·36
B(5)—O(13)	0·95	1·40	1·40	1·40
σ[B(5)—O]		0·02	0·02	
B(6)—O(3)	0·99	1·38	1·37	1·37
B(6)—O(6)	1·04	1·36	1·36	1·36
B(6)—O(11)	0·97	1·39	1·37	1·36
σ[B(6)—O]		0·02	0·01	
B(7)—O(2)	1·04	1·36	1·36	1·34
B(7)—O(7)	1·00	1·38	1·37	1·35
B(7)—O(12)	0·96	1·39	1·38	1·40
σ[B(7)—O]		0·02	0·02	
B(8)—O(5)	1·04	1·37	1·36	1·35
B(8)—O(8)	1·03	1·37	1·36	1·36
B(8)—O(12)	0·94	1·40	1·38	1·40
σ[B(8)—O]		0·01	0·01	
Na(1)—O(2)	0·19	2·38	2·43	2·44
Na(1)—O(4)	0·22	2·32	2·41	2·59
Na(1)—O(5)	0·21	2·34	2·43	2·37
Na(1)—O(9)	0·13	2·61	2·46	2·37
Na(1)—O(11)	0·15	2·54	2·46	2·77
Na(1)—O(12)	0·11	2·73	2·49	2·44
σ[Na(1)—O]		0·21	0·15	
Na(2)—O(1)	0·12	2·67	2·51	2·60
Na(2)—O(3)	0·14	2·55	2·51	2·52
Na(2)—O(9)	0·12	2·69	2·51	2·84
Na(2)—O(10)	0·11	2·73	2·55	2·51
Na(2)—O(10)	0·11	2·73	2·55	2·50
Na(2)—O(11)	0·13	2·60	2·51	2·87
Na(2)—O(14)	0·28	2·18	2·34	2·30
σ[Na(2)—O]		0·18	0·19	
Na(3)—O(3)	0·14	2·58	2·46	2·70
Na(3)—O(6)	0·19	2·39	2·43	2·33
Na(3)—O(7)	0·13	2·62	2·47	2·57
Na(3)—O(8)	0·18	2·43	2·43	2·36
Na(3)—O(10)	0·10	2·78	2·50	2·81
Na(3)—O(14)	0·27	2·20	2·32	2·27
σ[Na(3)—O]		0·07	0·17	

Table 4 (cont.)

Na(4)–O(1)	0.15	2.53	2.46	2.72
Na(4)–O(4)	0.23	2.29	2.41	2.40
Na(4)–O(7)	0.17	2.46	2.47	2.26
Na(4)–O(13)	0.07	2.98	2.53	2.42
Na(4)–O(13)	0.07	2.98	2.53	2.37
Na(4)–O(14)	0.31	2.13	2.32	2.38
σ[Na(4)–O]		0.37		0.16

Table 5. *Prediction of bond lengths in* Na_2PO_3F *(Durand, Cot & Galigné, 1974)*

	Network valence (v.u.)	length (Å)[1]	Baur (1970) length (Å)	Observed length (Å)
P(1)–O(1)	1.40	1.50	1.54	1.49
P(1)–O(2)	1.42	1.50	1.53	1.50
P(1)–O(3)	1.40	1.50	1.54	1.51
P(1)–F(1)	0.78	1.62	–[2]	1.62
σ[P(1)–O,F]		0.01		0.04
P(2)–O(4)	1.27	1.53	1.58	1.50
P(2)–O(5)	1.48	1.48	1.52	1.47
P(2)–O(6)	1.33	1.52	1.56	1.49
P(2)–F(2)	0.91	1.56	–[2]	1.59
σ[P(1)–O,F]		0.03		0.07
Na(1)–O(2)	0.17	2.44	2.48	2.39
Na(1)–O(4)	0.09	2.82	2.63	2.85
Na(1)–O(4)	0.09	2.82	2.63	2.60
Na(1)–O(5)	0.16	2.47	2.47	2.84
Na(1)–O(5)	0.16	2.47	2.47	2.70
Na(1)–O(6)	0.11	2.70	2.58	3.02
Na(1)–O(6)	0.11	2.70	2.58	2.51
Na(1)–F(2)	0.09	2.70	–[2]	2.30
σ[Na(1)–O,F]		0.26		0.25
Na(2)–O(1)	0.20	2.36	2.44	2.44
Na(2)–O(2)	0.21	2.32	2.43	2.30
Na(2)–O(3)	0.20	2.36	2.44	2.33
Na(2)–O(4)	0.13	2.60	2.55	2.72
Na(2)–O(6)	0.15	2.52	2.50	2.64
Na(2)–F(1)	0.10	2.60	–[2]	2.30
σ[Na(2)–O,F]		0.15		0.12
Na(3)–O(1)	0.18	2.41	2.44	2.36
Na(3)–O(2)	0.20	2.37	2.43	2.49
Na(3)–O(3)	0.18	2.41	2.44	2.51
Na(3)–O(4)	0.12	2.68	2.55	2.47
Na(3)–O(5)	0.19	2.39	2.42	2.30
Na(3)–O(6)	0.13	2.59	2.50	2.52
σ[Na(3)–O]		0.12		0.07
Na(4)–O(1)	0.21	2.32	2.44	2.38
Na(4)–O(3)	0.21	2.32	2.44	2.40
Na(4)–O(4)	0.15	2.54	2.55	2.62
Na(4)–O(4)	0.15	2.54	2.55	2.42
Na(4)–O(6)	0.16	2.47	2.50	2.48
Na(4)–F(1)	0.12	2.53	–[2]	2.66
σ[Na(4)–O,F]		0.09		0.07

Notes: (1) Parameters used for calculating bond lengths to F were P–F: $R_1 = 1.532$, $N = 4.29$; Na–F: $R_1 = 1.532$, $N = 4.29$. (2) Baur (1970) does not give parameters for bonds to F.

Examples

$(H_5O_2)_2SO_4$ *(Table* 1)

There is only one possible solution for this structure that satisfies the valence sum rule and it gives a good prediction even for the hydrogen bonds, indicating that the requirements of the valence sum rule are more stringent than the tendency of O–O repulsion to produce asymmetric hydrogen bonds (Brown, 1976a). Baur's method gives predictions that are less good though still qualitatively correct.

Diopside *(Table* 2), $K_2S_5O_{16}$ *(Table* 3) *and* $Na_2B_4O_7$ *(Table* 4)

These examples show the ability of the method to predict large and small distortions in straightforward cases. Except for the bonds around S(3) in $K_2S_5O_{16}$, the predicted bond valences agree with the observed ones within 0.05 v.u. (Fig. 1). Both Baur's and the network method give comparable overall agreement but for individual bonds the two predictions are significantly different as is to be expected from the different ways in which the bond lengths are calculated. The network method tends to predict distortions larger than observed while Baur's method tends to predict them smaller (see for example the predictions of Na–O and K–O bonds). In particular, for bonds with a valence of less than half the average for a particular cation, the network method gives valences that are too small, leading in the case of very weak bonds to predicted distances that are more than 0.5 Å too long. This effect can be seen in the bonds Na(4)–O(13) in $Na_2B_4O_7$ and K–O(8) in $K_2S_5O_{16}$ and is responsible for the large standard deviations around these cations. Otherwise the deviations are comparable with those obtained by Baur's method which conservatively predicts very small distortions.

The $S_5O_{16}^{2-}$ ion provides a particularly interesting test of the theories. Both methods fail to predict the very weak terminal bridge S(3)–O(2). Because it neglects distortions on neighbouring ions, Baur's method necessarily makes all the bridging bonds equally long and the terminal bonds almost the same length. The network method correctly predicts asymmetric bridges but underestimates the degree of asymmetry.

Table 6. *Prediction of bond lengths in* $CaCrF_5$ *(Wu & Brown,* 1973)

	Network valence (v.u.)	length (Å)[1]	Observed length (Å)
Cr–F(1) (×2)	0.41	1.95	1.94
Cr–F(2) (×2)	0.48	1.90	1.92
Cr–F(3) (×2)	0.61	1.83	1.85
σ(Cr–F)		0.01	
Ca–F(1)	0.18	2.50	2.50
Ca–F(2) (×2)	0.26	2.37	2.29
Ca–F(2) (×2)	0.26	2.37	2.39
Ca–F(3) (×2)	0.39	2.21	2.21
σ(Ca–F)		0.04	

Note: (1) Parameters used for calculating bond lengths were Cr–F: $R_1 = 1.700$, $N = 6.5$; Ca–F: $R_1 = 1.732$, $N = 4.48$.

Table 7. *Prediction of bond lengths in* TeI_4 *(Krebs & Paulat, 1976)*

	Network valence (v.u.)	length (Å)[1]	Observed length (Å)
Te(1)–I(1)	1·00	2·77	2·77
Te(1)–I(2) (×2)	1·00	2·77	2·75
Te(1)–I(7) (×2)	0·40	3·16	3·28
Te(1)–I(9)	0·20	3·50	3·20
σ[Te(1)–I]			0·14
Te(2)–I(1)	1·00	2·77	2·77
Te(2)–I(3)	1·00	2·77	2·77
Te(2)–I(7)	0·60	2·98	2·93
Te(2)–I(8)	0·60	2·98	2·99
Te(2)–I(9)	0·40	3·17	3·24
Te(2)–I(10)	0·40	3·17	3·25
σ[Te(2)–I]			0·05
Te(3)–I(5) (×2)	1·00	2·77	2·79
Te(3)–I(6)	1·00	2·77	2·76
Te(3)–I(7) (×2)	0·40	3·16	3·23
Te(3)–I(10)	0·20	3·50	3·21
σ[Te(3)–I]			0·12

Note: (1) Parameters used for calculating Te—I bond lengths were taken from Krebs & Paulat (1976).

Na_2PO_3F *(Table 5) and* $CaCrF_5$ *(Table 6)*

These examples show that the method is not restricted to oxides. Baur does not give correlations for bonds to F but his method is expected to work equally well for fluorides and oxides.

TeI_4 *(Table 7)*

The bond lengths in TeI_4 are correctly predicted by the network method except around the triple-bridging I(9) and I(10). The calculated valences (0·40 and 0·20) differ appreciably from the observed (0·33) leading to the prediction of one exceptionally long bond. If Baur's method had been applied here, it would have correctly predicted the equivalence of the bonds to I(9) and I(10) but would have failed to predict the asymmetries around the double-bridging I(7) and I(8) which the network method predicts well.

The distortions in molecules like TeI_4 are generally attributed to the steric influence of the lone pair of electrons on the Te^{IV} atoms (Gillespie & Nyholm, 1957). This calculation shows that the bonding network itself is sufficient to produce the observed distortion without invoking any electronic effects. It is possible that TeI_4 adopts this particular structure rather than a more symmetric one because of the influence of the lone pair, but there are few structures, if any, in which an AB_4 compound can crystallize with A in regular-octahedral coordination. $TeCl_4$ (Buss & Krebs, 1971) has a related structure in which the bond lengths can be correctly predicted ($\sigma = 0·02$ Å) using only the valence sum rule. When one considers that the $TeCl_6^{2-}$ (Webster & Collins, 1973), $TeBr_6^{2-}$ (Brown, 1964) and TeI_6^{2-}

(Syoyama, Osaki & Kusanagi, 1972) ions are all regular octahedra it appears that only in the fluorides does the lone pair have any influence upon the stereochemistry of solid complexes in which Te^{IV} is bonded only to halogen atoms (Alcock, 1972; Brown, 1974).

Conclusion

Examples are given of the predictions of bond lengths in oxides and halides indicating that the observed distortions frequently arise from the nature of the bonding network. Such a network has to obey the valence sum rule around each atom and follows less rigorously a rule which states that the valence is as far as possible uniformly distributed among the bonds (equal valence rule). Two methods of prediction based on these principles have been compared and both account equally well for many of the observed deviations from highly symmetric coordination. Baur's (1970) method is simpler to apply but requires parameters to be evaluated for each bonding pair of atoms and for each cation coordination. Since it is based on making linear adjustments only around the anions, Baur's method does not take into account the influence of the distortions that occur at the cations and neighbouring anions. The network method allows for these effects and can be applied to any system for which bond-valence–bond-length correlations are known or can be derived, but it tends to overestimate the distortions, particularly when one or more of the bonds is very weak.

While the above examples have been taken from crystals there is no reason why these techniques should not work as well for the random networks found in amorphous solids. They might also apply in liquids where the network is continually changing. If so, it should prove useful for testing proposed models of amorphous and liquid materials since the bond lengths can be predicted for networks of any size and the results compared with the observed radial distribution functions.

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Structures Cristallines et Moléculaires du Complexe de l'Iodure de Zinc et du Complexe de l'Iodure de Cadmium avec le Bis(méthylamino)-1,3 Diméthyl-2,2 Propane

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The crystal structures of 1,3-bis(methylamino)-2,2-dimethylpropanezinc iodide, $(CH_3)_2C[CH_2N(H)CH_3]_2ZnI_2$ (BSNZnI$_2$), and 1,3-bis(methylamino)-2,2-dimethylpropanecadmium iodide, $(CH_3)_2C[CH_2N(H)CH_3]_2CdI_2$ (BSNCdI$_2$), are isomorphous, and were solved by the symbolic addition method with data collected on a single-crystal diffractometer (Mo $K\alpha$ radiation). They crystallize in the monoclinic system, space group $P2_1/c$, with eight molecules in a unit cell (two molecules per asymmetric unit). The lattice constants are $a = 16\cdot935$ (6), $b = 12\cdot831$ (5), $c = 13\cdot372$ (5) Å, $\beta = 102\cdot86$ (3)° for BSNZnI$_2$, and $a = 17\cdot055$ (5), $b = 13\cdot016$ (4), $c = 13\cdot563$ (4) Å, $\beta = 102\cdot54$ (2)° for BSNCdI$_2$. The refinement was carried out by least-squares calculations with anisotropic temperature factors included for all atoms except H. A correction was made for absorption but not for extinction, and the final R was 0·042 for BSNZnI$_2$ and 0·039 for BSNCdI$_2$. The structure consists of BSNXI$_2$ molecules, which group themselves, *via* hydrogen bonds, in two series of alternate planes parallel to the *bc* plane; each series consists of symmetrically related molecules. The six-membered chelate ring system of each molecule in the 'dimeric' unit adopts a pseudocyclohexane conformation in which the *N*-methyl substituents occupy the equatorial positions. However, the N–Cd–N bond angle is significantly smaller than the corresponding N–Zn–N bond angle, *i.e.* 90·7 *versus* 98°.

Introduction

La détermination des structures cristallines et moléculaires du complexe de l'iodure de zinc et du complexe de l'iodure de cadmium avec le bis(méthylamino)-1,3 diméthyl-2,2 propane, fut entreprise dans le but de vérifier la nature pseudocyclohexane de ces hétérocycles à six chaînons chélatés. De façon plus spécifique, nous avons cherché à expliquer pourquoi en solution à la température ambiante, le système BSNZnI$_2$ est 'rigide', c'est-à-dire que l'inversion chaise–chaise se fait à une fréquence assez faible pour nous permettre d'observer deux raies d'absorption en RMN, alors que le système BSNCdI$_2$, dans les mêmes conditions, demande un abaissement de température avant de présenter un comportement semblable. Nous