A Cooperative Disorder Model for the Silver Ion Distribution and Flow in the One-Dimensional Ionic Conductor [(CH₃)₂N(CH₂CH₂)₂O]Ag₄I₅

John S. Rutherford[1]

Chemistry Department, Sultan Qaboos University, P.O. Box 36, Al-Khod 123, Sultanate Of Oman

A theoretical model shows that the silver ion distribution observed within the iodide tetrahedra of [(CH₃)₂N(CH₂CH₂)₂O]Ag₄I₅ is consistent with their disorder being a cooperative effect. The results indicate that the occurrence of silver ions in neighboring tetrahedra is thus eliminated, and the number of second and third neighbor Coulomb interactions is reduced as far as possible, consistent with a minimum Helmholtz energy for the system. The relative permittivity experienced by the silver ions is calculated to be about 50; the resulting low Coulomb interaction between cations in iodide matrices should facilitate their flow. However, in the title compound a bottleneck will occur in the flow of silver ions between adjacent iodide icosahedra unless some are allowed to temporarily occupy higher energy sites and arrangements, and this is the probable cause of the abnormally high activation energy for electrical conduction observed in this compound. © 1998 Academic Press

INTRODUCTION

This paper continues a previous study (1, 2) of the potential usefulness of graph theory, commonly applied in chemistry only to molecules, to problems in solid state chemistry involving extended systems. In particular, it applies graph matrix and related methods to treat the statistical mechanics of the disordered distribution of silver ions in the one-dimensional ionic conductor N,N-dimethylmorpholinium pentaiodotetraargentate (I), [(CH₃)₂N(CH₂CH₂)₂O]Ag₄I₅.

The crystal structure of the title compound was determined by Xie and Geller (3), and from the structure determination they were able to deduce that the observed electrical conductivity is due to the silver ions, which are restricted to moving in channels that lie within parallel columns formed by the iodide tetrahedra. These columns were shown to contain 23 such iodide tetrahedra per repeat unit, each of which was assumed to contain a potential silver

ion site. In fact, the sum of the various partial occupancies for these sites found in the crystal structure determination came close to the 8 silver ions per repeat unit required by the stoichiometry of the compound. However, Xie and Geller's study left two major questions open: the reasons behind the unusual disordered arrangement of silver ions within the tetrahedral sites and the cause the temperature dependence of the conductivity, interpreted by Xie and Geller as an abnormally high activation energy compared to other silver iodide derived ionic conductors.

GEOMETRIC DESCRIPTION OF THE STRUCTURE

Regular icosahedra, having 5-fold axes, cannot be tesselated to fill space. However, they may share faces to form arrangements of rods, nets, or even three-dimensional networks, provided the remaining space is taken up in other ways. In this particular compound, the iodide ions from rods or columns of face-sharing icosahedra and the remaining space is occupied by the organic cations.

If, as here, the icosahedron consists of a central atom and its 12 neighbors, it can be considered to be built up from 20 individual tetrahedra. For example, for each tetrahedron that makes up a regular icosahedron, the three edges that radiate from the central atom have relative length 1, while the three edges surrounding the corresponding icosahedron face have length 1.087. Similarly there are three interfacial angles which are constrained to be 72°, through the first set of edges being co-incident with the 5-fold axes, while the other three interfacial angles are 69.10°. (In a regular tetrahedron all interfacial angles are 70.53°.) In other words, compared to a regular tetrahedron, the tetrahedra contained in a regular icosahedron are compressed only slightly along one 3-fold axis. In this study we are concerned with the connectivity of the Ag⁺ sites, those being the centroids of these tetrahedra. These sites form a dodecahedron, the face dual of the icosahedron, just as the centroids of the icosahedron's faces do on a slightly larger scale. When we then link the icosahedra together, not only do we open
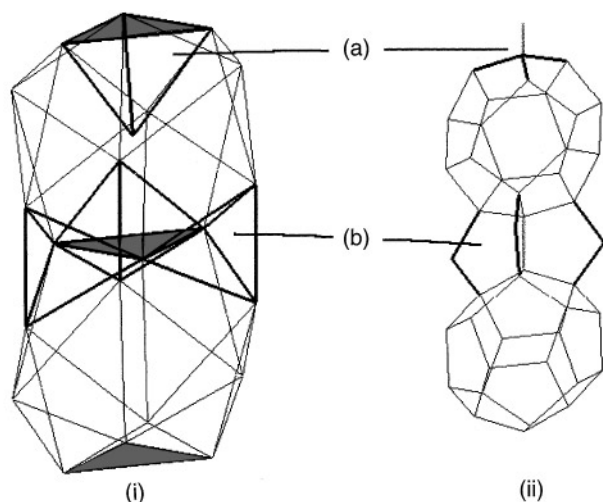
FIG. 1. Two of the face-sharing icosahedra (i), with the shared faces shaded, and the corresponding linked dodecahedra (ii). (a) (i) One of the tetrahedra forming the icosahedron (heavy lines), with the external face (shared by the next icosahedron) shaded. (ii) The corresponding tetrahedral arrangement of links to neighboring sites within the dodecahedron (heavy lines) and to the next icosahedron (grey line). (b) (i) The three tetrahedra of the collar (heavy lines), joined by the neck face (shaded). (ii) The corresponding collar (heavy lines) and neck (grey) links between the dodecahedra.

a direct link, the throat between the two tetrahedra now sharing the common face, but we also create a collar, consisting of three additional tetrahedra, around the link, which provides indirect paths from one icosahedron to the next. As a result the repeat unit has 23 possible silver ion sites in total. This relationship between the iodide icosahedron and the dodecahedron of silver ion sites is shown in Fig. 1.

ANALYSIS OF THE SILVER ION DISTRIBUTION

As indicated in the Introduction, it is convenient to introduce some elements of graph theory in modeling this system; the necessary concepts are discussed in the book by Trinajstic (4). In particular, graph properties will be expressed whenever possible in matrix notation, as this not only is compact, but also simplifies the computer programming involved.

The polyhedron of interest in this study is the dodecahedron; it has 12 pentagonal faces, 20 vertices, corresponding to the tetrahedral sites, and 30 edges, which correspond here to the links between nearest neighbor silver ion sites. When the connections between the neighboring icosahedra are added, this becomes 23 sites and 37 links between them. We wish to approximate the complete arrangement of silver ions in the crystal (or in the independent individual columns) by repetitions of the various arrangements of 8 silver ions among the 23 sites possible in this repeat unit. This approach in graph theory is analogous to using a periodic boundary condition where continuous functions are involved; it was used pre-

viously with success in bond resonance calculations (2). However, it relies on the assumption that no significant error in the relative probabilities arises from the fitting together at the joins of the individual pieces of the pattern, and consequently the distribution of these pieces (here the 8 ion arrangements over 23 sites) is adequately representative of the overall distribution. This requirement is addressed in the Appendix. The process indicated generates the finite graph shown in Fig. 2; it combines the 20 vertices and 30 edges of the symmetric planar graph of a pentagonal dodecahedron with 3 additional vertices and 7 additional edges, which arise from the face-sharing of adjacent icosahedra.

Associated with this graph are several graph properties significant to our discussion:

(1) It is not planar; this refers to the topology of the overall graph. The graph of any polyhedron is planar, since the polyhedron can be inscribed on the surface of a sphere and subsequently deformed to the planar Schlegel projection, but the linking of opposite faces of the icosahedron produces a graph which cannot be inscribed on a plane without crossovers.

(2) It has radius 3; no vertex is at a graph distance greater than 3 from any one of the vertices marked A or B in Fig. 2. However, the other vertex types have some other vertices at graph distance 4, suggesting that the A and B vertices are in this sense more "central" to the graph than the other types.

(3) It has diameter 4; the shortest path between any two vertices of the graph is never more than 4. This is despite the

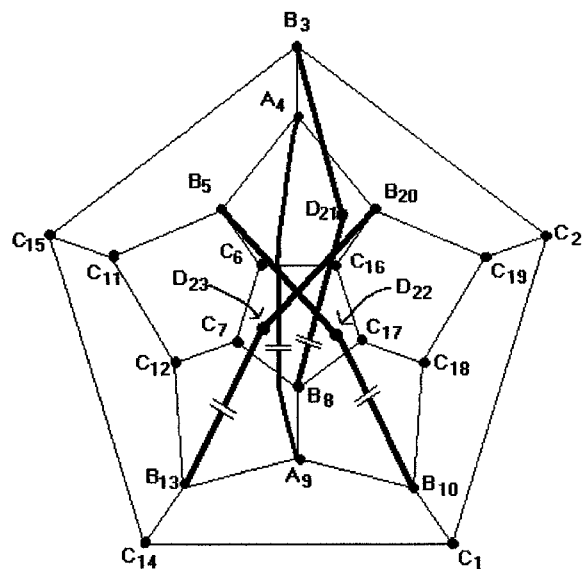
FIG. 2. The 23-vertex graph with the vertices labeled by type and number. The light lines are the 20 edges of the dodecahedral graph, and the heavy lines the additional linking edges. The four cuts discussed in the Appendix are marked $\neq$.

radius being 3; what this means is that, inter alia, from each C vertex at a graph distance 3 from a particular A vertex, there is a shorter path to any third vertex of the graph than the path that passes through the A vertex. As a specific example, there are two paths of lengths 3 between A vertex number 4 and C vertex number 12, viz. $4 \to 5 \to 11 \to 12$ and $4 \to 9 \to 13 \to 12$. Similarly, from vertex 4 to C vertex number 18 we have $4 \to 20 \to 19 \to 18$ and $4 \to 9 \to 10 \to 18$. However, between vertices 12 and 18 the graph distance is 4, there being in fact three such paths ($12 \to 7 \to 8 \to 17 \to 18$, $12 \to 13 \to 20 \to 19 \to 18$, and $12 \to 11 \to 5 \to 10 \to 18$). None of these paths passes through vertex 4. This property affects the range of graph distances considered in the calculation and is largely a consequence of (1) above.

It should be noted that the independent length 3 paths described in the previous paragraph lead from the A vertex to C vertices that are in reality in different icosahedra and therefore represent distinct Coulomb interactions. However, the length 4 paths between the C vertices all lie within one icosahedron, and the interaction should thus only be counted only once. In fact this single interaction applies to all pairs of vertices at graph distance 4, irrespective of the number of paths available. (This distinction is reflected in the method of counting used in Table 3.)

Now the distribution found for the 8 silver ions over the 23 sites available is extremely unusual, with vertex occupancies O ranging from 95% down to 3%, or possibly even less. There is no grouping of the observed values around their mean (8/23 or 0.348); in fact the large gap between the 8 largest, all above 0.55, and the next group of 5, at around 0.28, led Xie and Geller to consider that the disorder might be a simple hopping of silver ions off their 8 ground state positions to neighboring tetrahedral sites. However, this interpretation, unless it includes correlated motion of the silver ions, will lead to nearest neighbor silver ion–silver ion interactions and hence a sharp increase in the energy of the system, particularly if we assume that, at that range, the screening of the charges by intermediate ions is substantially reduced, and the bulk relative permittivity does not apply.

We first examine whether it is possible with the observed distribution to avoid such nearest neighbor interactions. We can define an edge function, the occupancy sum, $O_i + O_j$, where i and j are vertices sharing a common edge. This function should have a range 0 to 2 and a mean, if random, of $16/23 = 0.696$. Figure 3 shows this function as predicted from the observed occupancies on a random basis, along with the distribution of this edge property actually observed. Its maximum value is clearly 1 rather than 2. That is not in itself enough to prove that no nearest neighbor interactions are present, but it does show it to be possible, provided there exists a combination of suitable arrangements of the silver ions sufficient to explain the observed occupancies.
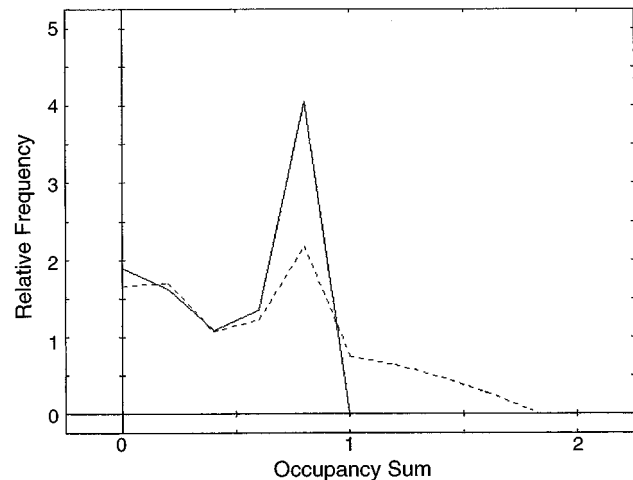

FIG. 3. The distribution of the vertex occupancy sum function. Solid line, observed; dashed line, predicted on a random basis.

Perhaps more intriguing is the mean observed for the function, at 0.601 considerably less than 16/23. What this indicates is that the silver ions tend to occupy vertices of low degree, since, if the distribution were random, the average vertex degree of an occupied site

$$\langle d \rangle = \sum_{i=1}^{23} d_i O_i / 8,$$

where d_i is the individual vertex degree, should be $74/23 = 3.22$, while the actual value is only 2.78.

This observation was confirmed by a detailed examination of the occupancies. In terms of the automorphism of the graph, there are four distinct vertex types, labeled A, B, C, and D in Fig. 2. Their degrees and average occupancies are given in Table 1.

The next step was to compile a list of those arrangements of occupied vertices such that no adjacent vertices are occupied (i.e., there are no paths between occupied vertices of length 1). The approach used applied the distance matrix D,

TABLE 1
Average Site Occupancies Observed, and Predicted by Equally Weighted Averages over Arrangements, by Vertex Type

Vertex type	Degree	Average occupancy observed	Average of 1137 arrangements	Average of 1667829 arrangements
A	4	0.064	0.389	0.396
B	4	0.092	0.139	0.138
C	3	0.425	0.371	0.369
D	2	0.805	0.646	0.653

which may be generated by standard means, in which the incidence matrix is first converted into an adjacency matrix A. (If we then construct successive powers of the adjacency matrix, the distance matrix element D_{ij} is given by n, where n is the lowest power p for which $(A^p)_{ij}$ is nonzero, while the actual value of $(A^n)_{ij}$ is the number of independent paths of length D_{ij}). The arrangements were then generated as sequences of site numbers using 8 nested loops, where the latest potential addition to a growing sequence was rejected if its graph distance to any earlier element was 1. This approach allowed the simultaneous calculation of the distribution of graph distances 2 and 3 for each arrangement, i.e., the numbers n_{2k} and n_{3k} applied in the next section.

DESCRIPTION OF THE STATISTICAL MODEL

The model assumes that the internal energy of the crystal at finite temperature includes a contribution from the arrangement of the silver ions within the tetrahedra. We approximate the complete arrangement of silver ions in the crystal using arrangements of 8 silver ions among the 23 vertices of the graph. The energy of the kth such arrangement may be assumed to be

$$E_k = \sum_{i=1}^{22} \sum_{j=i+1}^{23} (e^2/4\pi\varepsilon_0 K r_{ij}) + \sum_{i=1}^{23} \varepsilon_i,$$

where the first sum is the Coulomb energy taken over the pairs of occupied sites in the arrangement, and the second sum, over the occupied sites, is the site-specific contribution due to such effects as distortion of the iodide tetrahedra, the position of the site relative to the morpholinium ion, and the change distribution in neighboring columns. Here K is the relative permittivity of the medium.

In graph theory terms we can associate the individual distances r_{ij} within the columns with a minimum integer path length $p = 1, 2, 3, \dots$. Further, if we truncate the calculation so that at most only distances between each site and the physically nearest equivalent site of another type are considered, the relevant path lengths are simply the graph distances between the sites. Then

$$E_k = (e^2/4\pi\varepsilon_0 K) \sum_{i=1}^{22} \sum_{j=i+1}^{23} (n_{dk}/r_d) + \sum_{i=1}^{23} \varepsilon_i,$$

where n_{dk} is the number of occurrences of graph distance d in the kth arrangement.

Now the total number of arrangements of 8 indistinguishable Ag^+ ions on the 23 sites is 490,314. However, if we eliminate those high energy arrangements which have nearest neighbor ($d = 1$) interactions, we find that there are only 1137 arrangements to be considered. As a further simplifica-

tion, the Coulomb energies associated with $d = 2$ and $d = 3$ can now be written on the basis of bringing the ions together from the maximum graph distance of 4, i.e., as

$$E_i^c = (e^2/4\pi\varepsilon_0 K)(1/r_i - 1/r_4) \quad i = 2, 3$$

and the energy of the kth arrangement as

$$E_k = n_{2k}E_2^c + n_{3k}E_3^c + \mathbf{V}_k^t\boldsymbol{\varepsilon},$$

$\mathbf{V}_k$ being the vector of site occupancies in the kth arrangement, $\boldsymbol{\varepsilon}$ that of the site-specific energy terms, and the notation $\mathbf{v}^t$ indicates the transpose of the vector $\mathbf{v}$.

Using statistical mechanics, we may write the probability of the kth arrangement as

$$p_k = e^{-E_k/RT}/\sum_{k=1}^{1137} e^{-E_k/RT}$$

from which we may compute the site occupancies

$$q = \sum_{k=1}^{1137} p_k\mathbf{V}_k = \sum_{k=1}^{1137} \mathbf{V}_k\, e^{-E_k/RT}/\sum_{k=1}^{1137} e^{-E_k/RT}.$$

To have the experimental data in a suitable form for comparison, the occupancies observed by Xie and Geller were made to sum to 8 Ag^+ by assigning the missing electron density (0.027 Ag^+ or 1.3 electrons per "empty" site) equally among these remaining sites. This amount of electron density is similar to a hydrogen atom, and it would be reasonable to expect it to be undetectable experimentally in the presence of the iodine atoms, as were the hydrogen atoms in the organic cation.

The measured occupancies were then fitted to the model, minimizing the function

$$\sum_{i=1}^{23} w_i(o_i - q_i)^2 + E_2^c/\sigma(\varepsilon).$$

The weights assigned to observations were of the $1/\sigma^2$ type, using the X-ray e.s.d.'s where available, the slightly larger value of $\sigma = 0.010$ for other "partially occupied" sites, and $\sigma = 0.027$ (i.e., equal to the assigned occupancy) for the "empty" sites. The additional term in the function minimized was included to ensure that the Coulomb repulsion contributions was properly so ascribed and that their effect was not taken up by arbitrary variations in the site-specific terms. In it the quantity $\sigma(\varepsilon)$ is the estimated standard deviation of the site-specific terms relative to their mean, i.e.,

$$\sigma^2(\varepsilon) = \sum_{i=1}^{23} (\varepsilon_i - \langle\varepsilon\rangle)^2/22.$$

SIMULATION OF THE CONDUCTION PROCESS

Xie and Geller associated the higher activation energy for conduction in this system with a reduced number of pathways available for silver ion flow in the one-dimensional system. In fact, as noted above, movement of silver ions from one icosahedron to the next is restricted to four paths, the one directly through the throat AA, and those via the collar tetrahedra D. To determine whether such a flow was possible without incurring nearest neighbor interactions, the process was simulated in the following manner. Each step was considered to consist of the hop of a silver ion from an occupied vertex i to an adjacent (naturally unoccupied) vertex j, such that no nearest neighbor interactions are produced, i.e., in terms of the occupancy vectors **V**

$$\mathbf{V}_k \to \mathbf{V}_m$$

such that their difference

$$\delta = \mathbf{V}_m - \mathbf{V}_k$$

has $\delta_i = -1$, $\delta_j = 1$, and all other elements zero,

$$A_{ij} = 1,$$

and

$$V_{am} A_{ab} V_{bm} = 0 \text{ for all distinct } a, b$$

(i.e., $\mathbf{V}_m$ is one of the 1137 arrangements discussed above).

In the simulation, the probabilities of any particular hop $i \to j$ occuring next was biased to represent a field applied along the column direction, but was otherwise random. The resulting positions of the silver ions were followed as a computer display.

RESULTS

The results show it is clearly possible to derive a set of site occupancies for the silver ions which totally avoid nearest neighbor interactions and which conform to the other elements of the model. The final value of the sum

$$\sum_{i=1}^{23} w_i (o_i - q_i)^2$$

was 1.6; since the number of variables equal the number of observations, this should have a value zero if the model were capable of fitting the observations exactly. On the other hand, the observed value is much less than the value of 23 which would correspond to the errors in the X-ray results, meaning that such a precise fit to the observed data is unwarranted experimentally.

However, the results show that the nearest neighbor effect by itself is insufficient to explain the extent of the variation of occupancy with vertex type (compare columns 3 and 4 of Table 1), or why the lowest average occupancies are associated with the "central" vertices B and especially A, which latter have the highest number of second neighbors. The model achieves agreement on these features through the Coulomb terms, which comprise pairwise interactions of 4.03 kJ mol^{-1} for second neighbor silver ion sites and of 0.89 for third neighbors; by comparison $\sigma(\varepsilon)$, which indicates the variance in energy between individual sites, was found to be 2.19 kJ mol^{-1}. Since the number of second neighbors n_{2k} varies between 9 and 16 for the different arrangements, the silver ion–silver ion Coulomb terms effectively dominate their relative energies. The observed and calculated occupancies for the individual sites are given in Table 2, along with the site-specific energy contributions calculated.

The Coulomb terms applied correspond to an effective relative permittivity K of 50.4 or a polarizability of $17.2 \times 10^{-40} \text{ J}^{-1} \text{ C}^2 \text{ m}^2$. A calculation based on the electronic polarizability of iodide ions and their concentration in the columns of $1.45 \times 10^{28} \text{ m}^{-3}$ gives a polarizability of $7.3 \times 10^{-40} \text{ J}^{-1} \text{ C}^2 \text{ m}^2$, but there are distortion polarization effects to be considered also.

Figure 4 shows the distribution of these energies relative to the ground state of the system, correctly identified by Xie

TABLE 2
Observed and Calculated Site Occupancies and Site-Specific Energy Terms

| Site	O	$\sigma(O)$	q	ε (kJ mol^{-1})
1	0.285	0.008	0.287	2.09
2	0.627	0.007	0.630	− 0.73
3	0.027	0.027	0.037	0.73
4	0.027	0.027	0.025	1.83
5	0.288	0.010	0.284	− 3.56
6	0.027	0.027	0.032	1.37
7	0.621	0.007	0.621	− 0.31
8	0.154	0.007	0.155	− 3.27
9	0.100	0.010	0.100	− 0.62
10	0.027	0.027	0.029	0.74
11	0.271	0.007	0.274	1.14
12	0.289	0.007	0.295	2.36
13	0.027	0.027	0.034	1.74
14	0.278	0.006	0.280	2.41
15	0.552	0.008	0.557	0.69
16	0.945	0.007	0.945	− 4.96
17	0.027	0.027	0.019	0.95
18	0.846	0.007	0.844	− 3.66
19	0.132	0.008	0.129	− 1.76
20	0.027	0.027	0.010	− 2.03
21	0.786	0.007	0.787	1.91
22	0.693	0.010	0.689	1.85
23	0.937	0.008	0.937	1.13
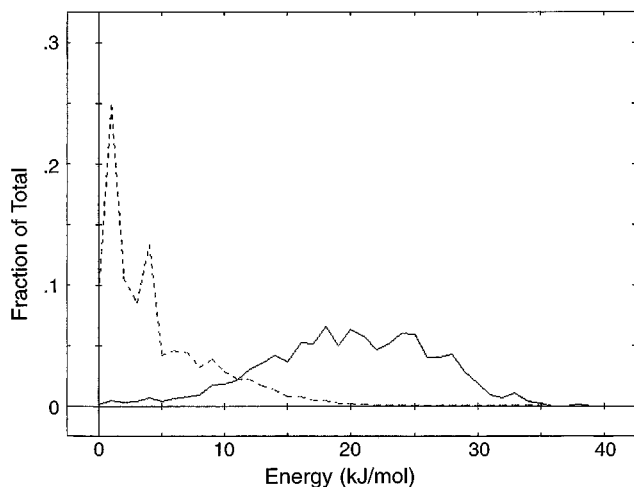
FIG. 4. The energy distribution of the 1137 arrangements. Solid line, equally weighted; dashed line, weighted by contribution to the partition function.

and Geller as that arrangement where the 8 sites with observed occupancies greater than 0.5 are all occupied. However, Fig. 4 also illustrates the relative contributions from arrangements of different energies to the partition function; it shows that the ground state arrangement is adopted only one-tenth of the time, and the hundred or so arrangements with energies within $10 \, \text{kJ} \, \text{mol}^{-1}$ of the ground state make significant contributions.

It is the large number of these low-lying arrangements that confer stability to the disordered system. Taking the relation

$$A = U - TS,$$

the contribution to the Helmholtz energy due to the silver ion arrangement, as calculated from the partition function, is $-5.85 \, \text{kJ} \, \text{mol}^{-1}$ based on two formula units or one icosahedron. This value is made up of the weighted average arrangement energy, $U = 4.79 \, \text{kJ} \, \text{mol}^{-1}$, more than doubly compensated for by a favorable entropy term, corresponding to $S = 35.7 \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1}$ assuming $T = 300 \, \text{K}$. Table 3 compares the distribution of graph distances calculated at 300 K to those in the ground state and in equally weighted averages over the 1137 selected and 490,314 total possible arrangements. The actual distribution is clearly nonrandom in favoring greater graph distances.

As for the simulation, it showed a bottleneck will occur in the flow of silver ions between adjacent iodide icosahedra unless some of them are allowed to temporarily occupy higher energy sites and arrangements, and it may well be that the additional activation energy required in this system is just such a configurational contribution.

TABLE 3
Distribution of Graph Distances between Sites in Various Models

Distribution in	Graph distance				Total[a]
	1	2	3[a]	4	
Ground state	0	9	13	6	28
Average over occupied arrangements at 300 K	0	9.94	13.51	4.91	28.36
Equally weighted average over 1137 arrangements	0	12.12	14.02	3.58	29.72
Equally weighted average over total arrangements	4.09	9.63	13.94	2.32	29.99

[a] Any excess in the total over 28 corresponds to the extra contribution when there are two independent length 3 paths between the same vertices.

APPENDIX

The representative nature of the distribution based on the 1137 arrangements chosen was tested in the following way. Using the same method as in the Analysis of the Silver Ion Distribution section above, the set of arrangements of 8 silver ions over 23 sites, with no nearest neighbors, was found for an isolated repeat unit of the structure. The underlying graph required here is formed by cutting the previous 23-vertex, 37-edge graph so that it no longer loops back on itself; i.e., it becomes planar. There are several ways of doing this, but the simplest, which also produces the smallest number of arrangements, is by making the four cuts indicated in Fig. 2. We can then combine the resulting 3369 arrangements in compatible pairs statistically, since the behavior at the joins depends solely on the occupancies of the cut vertices 4, 8, 9, 10, 13, 21, 22, and 23, to give arrangements over the 46-vertex, 74-edge graph which represents two repeat units alternating indefinately. If we also consider making such combinations using cuts above the collar as well as below and eliminate the duplicates, we produce in all 1,667,829 arrangements. Even this is not quite a complete set of those arrangements with no nearest neighbors occupied over the 46-vertex graph, since it includes only some of those arrangements where one icosahedron holds two or more silver ions more than the other. However, it does allow us to test whether the 1137 self-compatible arrangements produce a distribution representative of making all possible combinations, and the comparison shown in Table 1 confirms this is so.

REFERENCES

1. J. S. Rutherford, *Acta Crystallogr. B* **46,** 289 (1990).
2. J. S. Rutherford, *Trans. Am. Crystallogr. Assoc.* **27,** 315 (1991).
3. XIe Sishen and S. Geller, *J. Solid State Chem.* **68,** 73 (1987)
4. N. Trinajstic, "Chemical Graph Theoy," 2nd ed., CRC Press, Boca Raton, FL, 1992.