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Contact Stabilization of Host Molecules during Clathrate Formation

Yurii A. Dyadin and Nikolai V. Kislykh

Institute of Inorganic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, 630090 Novosibirsk, USSR. Fax: 3832 355 903

The occurence of contact stabilization of molecules during clathration is considered; non-bonded host–guest interactions may alter considerably the structure of the host molecules and may even lead to the stabilization of host molecules that do not exist outside the clathrate.

Clathrate formation is known to involve the stabilization of a metastable or labile host framework or, more rarely, additional stabilization of a thermodynamically stable host framework through non-bonded interactions (contacts) between the guest and the host.[1,2] It has also been observed that the molecules of the guest[3] or host[4] may themselves undergo conformational transformations during clathration. Here we report, for some Schaeffer clathrates,[5] the occurrence of such stabilization, during clathration, of host molecules that are not stable at all outside the clathrate.

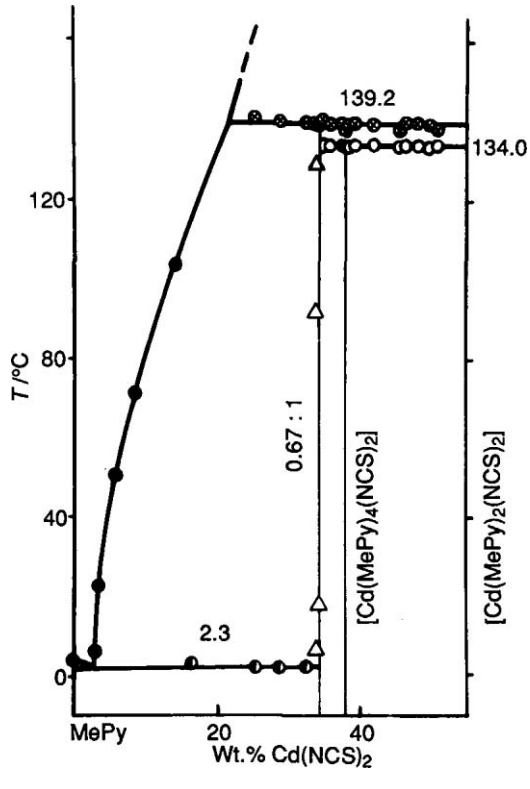

Fig. 1 Phase diagram of the $[Cu(MePy)_2(NCS)_2]$–MePy system (MePy = 4-methylpyridine). The hypothetical composition of the host system $[Cu(MePy)_4(NCS)_2]$ is designated by a dashed line; 0.67:1–$[Cu(MePy)_4(NCS)_2]\cdot 0.67(MePy)$, green clathrate; 2:1–$[Cu(MePy)_4(NCS)_2]\cdot 2(MePy)$, blue clathrate.

The phase diagram (see Fig. 1) of the system $[Cu(MePy)_2(NCS)_2]$–MePy (MePy = 4-methylpyridine) is presented on the basis of the results of differential thermal analysis (DTA) and solubility experiments and on chemical analysis of the phases (for details of the experiments see ref. 6). As can be seen from Fig. 1, two compounds are formed in the system: $[Cu(MePy)_4(NCS)_2]\cdot 2(MePy)$ (bright blue in colour) and $[Cu(MePy)_4(NCS)_2]\cdot 0.67(MePy)$ (grass green). The compounds have been isolated and their structures determined using X-ray analysis.[7]† In both cases the host coordination molecule was shown to have the gross chemical formula $[Cu(MePy)_4(NCS)_2]$. In these compounds 4-methylpyridine has a dual function, acting both as a ligand and as a guest, which is reflected in the clathrate formulae. According to the shape of the cavities and the way in which the 4-methylpyridine guests are packed with the host molecules, the two clathrates can be classified as being of the *channel* (green clathrate) or *pseudolayered* (blue) type. The channels in the former type have a variable cross section. In the broader sections (diameter ~ 8 Å) there is room to accomodate two 4-methylpyridine molecules and in the narrow parts (~ 4 Å) small molecules may be accomodated, such as those of water. This observation explains why this clathrate, as the cadmium analogue,[8] greedily absorbs even traces of water from organic solutions. In the blue clathrate the host molecules are densely packed into a layer which contains the 4-methylpyridine ligands. The isothiocyanate groups lie perpendicular to this layer, forming cages and sinuous channels to accomodate the 4-methylpyridine guest molecules. This compound does not absorb water, indicating that structural complementarity, rather than chemical affinity, is responsible for the water-binding ability of the green clathrate.

Fig. 2 shows the significant changes undergone by the host molecule on passing from one clathrate to another: in the green compound the conformation is centrosymmetric and in the blue one it is asymmetric. In addition to this, there are significant

† The structure of the blue clathrate was determined by Professor J. Lipkowski, Institute of Physical Chemistry, Warsaw, and that of the green one by N. V. Pervukhina and N. V. Podberezskaya, Institute of Inorganic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk.

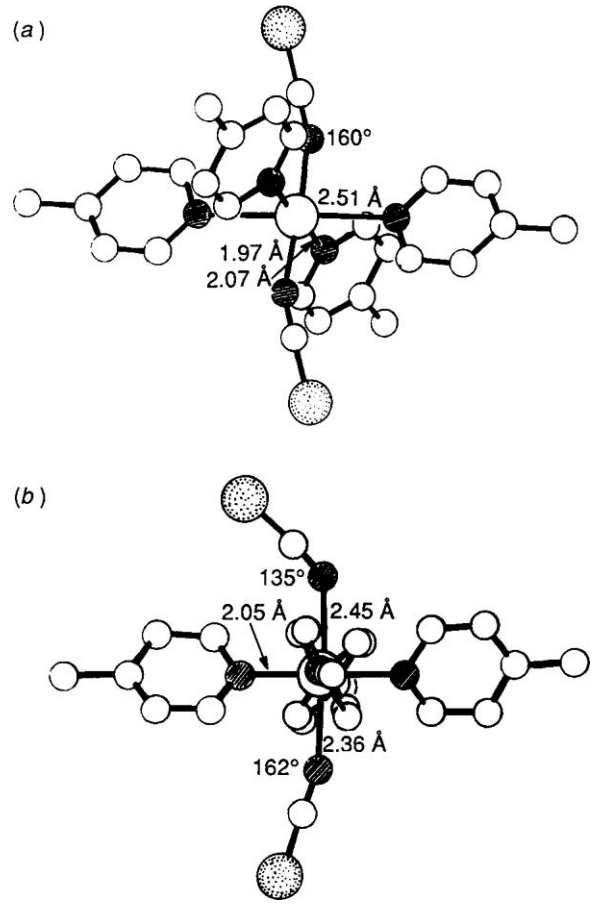

Fig. 2 Conformations of the $[Cu(MePy)_4(NCS)_2]$ host molecules in (*a*) $[Cu(MePy)_4NCS)_2]\cdot 0.67(MePy)$ clathrate; (*b*) $[Cu(MePy)_4(NCS)_2]\cdot 2(MePy)$ clathrate. Estimated standard deviations for bond lengths and angles are, respectively, <0.01 Å and 1°.

differences in the ligand environments of the copper atoms between the two compounds. In the tetragonally distorted octahedra the shorter metal–nitrogen distances (a quasisquare) are to two 4-methylpyridine ligands and two isothiocyanate groups in the green clathrate and to four 4-methylpyridine ligands in the blue clathrate. The two bonds completing the bipyramid (to two 4-methylpyridine ligands in the first case and to two isothiocyanate groups in the second) are noticeably longer. It should be noted that the green and blue clathrates both crystallize (at different temperatures) from the same green solution, from which we may conclude that the coordination environment of copper in the solution is approximately the same as that in the green clathrate [see Fig. 2(*a*)].

Thus we see that, depending on the type of packing in the host–guest system, the host molecules themselves undergo a substantial rearrangement, *i.e.* the non-bonded intermolecular interactions affect the conformation of the host molecules. Moreover, as can be seen from the phase diagram of the $[Cu(MePy)_2(NCS)_2]$–MePy system and as indicated by thermogravimetric studies of the green clathrate,[9] the host molecule does not exist at all in the absence of contacts with the guest molecules, *i.e.* without their non-bonded 'support'.

This interesting phenomenon has been given the name 'contact stabilization of molecules,' by analogy with the term 'contact conformational isomerism' introduced by Zorkii[10] to describe the coexistence in a homomolecular crystal of more than one molecular conformation, which is also determined by the packing factor.

In the $[Cd(MePy)_2(NCS)_2]$–MePy system, which we have studied previously,[8] (see Fig. 3), only one compound is formed, analogous to the green clathrate of the copper system, which

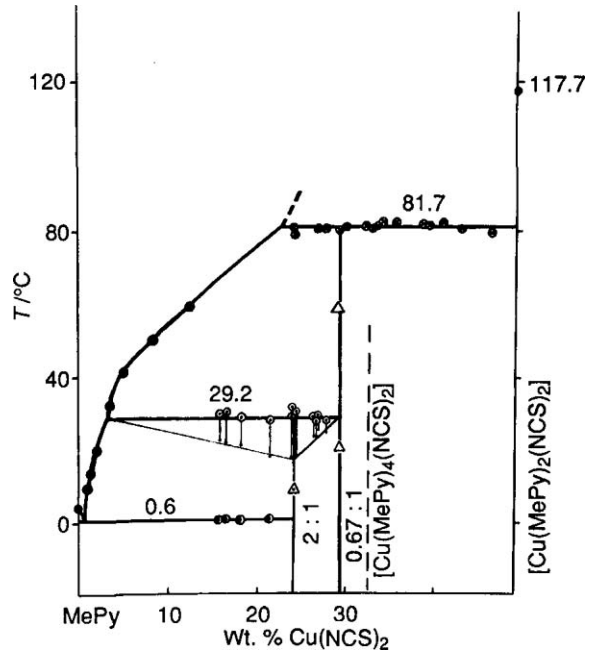

Fig. 3 Phase diagram of the $[Cd(MePy)_2(NCS)_2]$–MePy system (see notation in Fig. 1)

incongruently melts at 139.2°C to give a diisothiocyanate–bispicoline Cd^{II} complex and a liquid. The host can exist by itself but it decomposes at a lower temperature (134°C) into the clathrate and the above-mentioned diisothiocyanate–bispicoline Cd^{II} complex. *I.e.* in the temperature interval 134.0–139.2°C it exists in the clathrate only due to the contact stabilisation.

The classification of the compounds under study as clathrates is not strictly accurate since the host and the guest are so closely interdependent that the difference between the properties of the host and the guest subsystems, an essential characteristic of a clathrate, becomes very small. These compounds are approaching the 'packing complexes' of Kitaigorodskii,[11] in which the two subsystems are more or less equal.

In conclusion, it should be noted that, during the clathration process, contact stabilisation apparently occurs more frequently in the guest subsystem than in the host subsystem. An example of stabilization of guest molecules is the 'blue reaction' of iodine with amylose. In this reaction a polyiodine chain is formed in the channels; this chain cannot exist without the host. Owing to the contacts in a cavity an unstable conformation of a guest molecule may also be stabilised, as in the clathration of 3,3,6,6-tetramethyl-s-tetrathiane by the 'hexa host': the 'twist-boat' conformation that is stable without the host system changes to the 'chair' within the host cavity.[3]

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References

1 J. H. Van der Waals and J. C. Platteuw, 'Clathrate Solutions', in *Advances in Chemistry*, Interscience, New York, 1959, vol. 2, p. 1.
2 Yu. A. Dyadin and V. R. Belosludov, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.Nauk*, 1986, **2**, 72; *Chem. Abstr.*, 1986, **104**, 214062m.
3 D. D. McNicol and A. Murphy, *Tetrahedron Lett.*, 1981, **22**, 113.
4 J. Lipkowski, in *Inclusion Compounds*, Academic Press, London, 1984, vol. 1, p. 59.

Mendeleev Commun., 1991, 1(4), 135–136

5 W. D. Schaeffer, W. S. Dorsey, D. Skinner and C. Christian, *J. Am. Chem. Soc.*, 1957, **79**, 5870.
6 N. V. Kislykh, Yu. A. Dyadin, N. V. Pervykhina, I. V. Davydova and N. V. Podberezskaya, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1989, **3**, 76; *Chem. Abstr.*, 1989, **111**, 141646n.
7 J. Lipkowski, N. V. Pervukhina, I. V. Davydova, N. V. Podberezskaya, N. V. Kislykh and Yu. A. Dyadin, Third International Seminar on Inclusion Compounds, Novosibirsk, 1989, Abstract Papers, p. 76.
8 Yu. A. Dyadin, N. V. Kislykh, N. V. Podberezskaya, N. V. Pervukhina, V. A. Logvinenko and I. V. Oglezneva, *J. Incl. Phenom.*, 1984, **2**, 333.
9 E. A. Ukraintseva, N. V. Kislykh, Yu. A. Dyadin, V. A. Logvinenko, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1989, **5**, 69; *Chem. Abstr.*, 1990, **112**, 171059m.
10 P. M. Zorkii, A. E. Razumaeva, *Zh. Struct. Khim.*, 1979, **20**, 463; *Chem. Abstr.*, 1979, **91**, 174710a.
11 A. I. Kitaigorodskii, *Smeshannye kristally* (Combined crystals), Nauka, Moscow, 1983, p. 277 (in Russian).