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7. These results were presented at the 74th Annual Meeting of the Korean Chemical Society, Chungju, Chungbuk, Korea, October 1994; paper ORGN C17.

8. The difference in the observed %ee between entry 5 and 6 is due to the slow decomposition of the catalyst.

9. It took 2 days to reach at the equilibrium state [((π-allyl) Pd complex from 2b/(π-allyl)Pd complex from 3=6:94)] from the initially formed (π-allyl)Pd complexes (~3:7).

Crystal Structure and Rutile-Mimetic Framework in Cyanocadmate Clathrate [Cd{Cd(CN)₃(imH)}₂]·*p*-C₆H₄Me₂ Involving Unidentate Imidazole (imH=C₃H₄N₂) Ligand

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The structural similarity between $Cd_x(CN)_y$ and Si_xO_y in coordination and linking structures may exhibit inclusion ability for guest molecules and/or ions, and can be utilized in developing mineral-like multi-dimensional inclusion or supramolecular structures such as 1D-chains, 2D-layers and 3D-lattices. We have demonstrated such inclusion host structures as silica-mimetic 3D-lattices,[1] clay-mimetic 2D-layers[2] and zeolite-mimetic 3D-lattices[3] materialized using cyanometallates.

In contrast to the topological similarity, the Cd-CN-Cd span length of *ca.* 5.5 Å is longer by *ca.* 2.5 Å than the span length of Si-O-Si and O-H···O in silica and ice, at *ca.* 3 Å. Therefore, the $Cd_x(CN)_y$ host structures are less complicated in topography than the structures of clathrate hydrates and clathrasils upon accommodating guests. This is the remarkable feature of the $Cd_x(CN)_y$ which gives struc-

tures similar in some ways but dissimilar in others to the Si_xO_y structures occurring in nature. In addition to that the presence or absence of complementary ligand in cyanometallate systems is one of the important factors for the inclusion host structures to provide cavities appropriate in size and shape for accommodating guest molecules.[4]

One of our recent attempts is to develope mineralomimetic structures using cyanocadmate and imidazole (imH), a five-membered aromatic amine, as the complementary ligand. We reports here on the structural results that we have obtained mineral-like inclusion clathrate of 3Cd(CN)₂·2imH·*p*-C₆H₄Me₂.

Into an aqueous solution containing an equimolar mixture of $CdCl_2$ and $K_2[Cd(CN)_4]$ (10 mmol each in 100 cm³ H_2O), 10 mmol of imH was added in stirring. After filtration through a plastic membrane (Millipore, pore size of 0.45

μm), the aqueous solution was covered with an organic phase of the guest species in a glass vial; the amount of the aromatic species was much excessive, in the order of 10^2 mmol, with respect to the host moieties for the formation of clathrate. The vial was kept standing at ambient temperature for a few days to obtain single crystals formed at the interface between the aqueous and organic phases and/or the bottom of the aqueous phase. The composition of clathrate was identified by elemental analyses, infrared spectroscopy and gas chromatography. Anal. Found for clathrate: C, 30.7; H, 2.48; N, 18.8; Cd, 46.2. Calcd. for $C_{20}H_{18}N_{10}Cd_3$: C, 32.7; H, 2.47; N, 19.0; Cd, 45.8%. The clathrates are unstable under ambient conditions to release the guest molecules gradually. This crystal was subjected to the single crystal X-ray experiments.[5]

The solved crystal structures are shown in Figure 1 and 2. The host framework structure is constructed of the octahedral Cd(o) and the tetrahedral but three-handed Cd(t) $(CN)_3(imH)$ in a 1 : 2 ratio like rutile $(TiO_2$: tetragonal, $P4_2/mnm$, $a=4.59$, $c=2.96$ Å$)^6$ structure built of the octahedral six-coordinate Ti^{4+} and trigonal three-coordinate O^2 . In contrast with the tetragonal unit cell of rutile, the unit cell of clathrate is distorted into the monoclinic system of the β angle of 92.33(2)° with the b dimension of 12.835(5) Å nearly equal to the c dimension of 12.222(3) Å, and the a dimension of 8.942(2) Å. These lattice parameters give the ratio $\{(b+c)/2\}/a$ being 1.40 comparable with the a/c ratio in rutile 1.55. Hence, the parallel projection to the a axis of the unit cell as shown in Figure 1 may be compared with the parallel projection to the c axis of rutile. The octahedral Cd(o) atoms are located at every corner and the body-center of the unit cell similar to Ti^{4+} in rutile; the imH-ligated Cd(t) atoms are on the positions slightly deviated from the $(x, x, 0,$ and equivalents) of O^{2-} in rutile. However, a pseudo 4 axis may be observed along the a axis as shown in Figure 2. The voluminous space generated by the Cd(o)-NC-Cd(t)-CN-Cd(o) span $(ca.$ 5.67 Å) far longer than Ti-O-Ti $(ca.$ 1.94 and 1.99 Å) in rutile is occupied by the imH ligands and the p-xylene guest molecules.

The coordination linkage between Cd(o) and imH-ligated Cd(t) linked by CN bridges to give a three-dimensional host structure. The Cd(o) atom accepts six N atoms of the CN groups from six of the imH-ligated Cd(t) atoms like the oc-
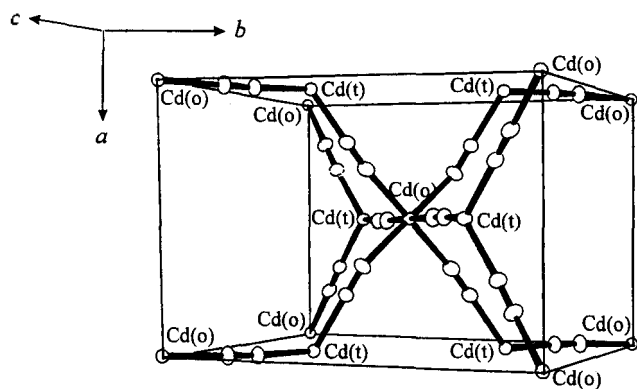

Figure 1. Rutile-mimetic host framework of the $[Cd\{Cd(CN)_3(imH)\}_2]·p$-$C_6H_4Me_2$ clathrate; each imH ligated to Cd atoms has been omitted for the sake of clarity.
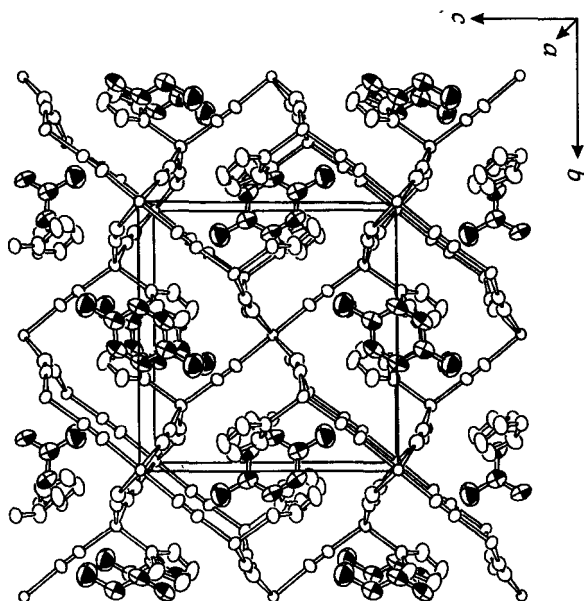
Figure 2. Perspective view of the $[Cd\{Cd(CN)_3(imH)\}_2]·p$-$C_6H_4$-$Me_2$ clathrate along the a axis; the imH ligands are perpendicular to a axis; the p-xylene guests are tilted to (100) plane.

taheral six-coordinate Ti^{4+} in rutile. Since the imH ligation at Cd(t) allows three coordination of CN groups to Cd(t), the three CN groups of imH-ligated Cd(t) atom linkages to three of the Cd(o) atoms like the trigonal three-coordinate O^2 . The imH ligands protruding from the networks cover the sides of the cavity. The guest p-xylene molecule is accommodated in the cavity witn its aromatic plane almost in sandwiched and perpendicular to the five-membered ring of imH ligated to the 3D network of the host. The bond distances and angles observed about the Cd coordination environments as well as the ring structures of the imH ligands are not unusual.

The present host structure is rather exceptional with respect to the coordination behaviour of the complementary ligand imH to the tetrahedral Cd(t) in three-dimensional hosts involving Cd(o) and Cd(t); in comparison with complementary ligands coordinate to Cd(o) in the precedent structures.[4] The imH ligand, being less bulkier than the pyridine (py) ligand, appears to be favourable for building up the three-dimensional inclusion host structure, whereas bulkier pyridine ligand gave no-guests complexes in the host structure $[Cd(py)_2Cd(CN)_4]$ with a Cd(o) : Cd(t) ratio of 1 : 1 and $[\{Cd(CN)(py)_2\}_3\{Cd_2(CN)_7\}]$ with the ratio of 3 : 2.[4a]

Newly prepared three-dimensional mineralomimetic inclusion compound with the composition $3Cd(CN)_2·2imH·p$-$C_6H_4Me_2$ has been characterized as the clathrate of the CN-bridged isopolycyanopolycadmate hosts that involve octahedral and tetrahedral Cd atoms in a 1 : 2 ratio by single crystal X-ray diffraction method. The 3D lattice of the title clathrate has a rutile-mimetic topology linked by six-coordinate Cd(o) and Cd(t)(CN)$_3$(imH) providing three bridging CN groups to the Cd(o); the expanded rutile-like lattice accommodates the guest molecule. Details of this clathrate will be reported later.

Supplementary Materials. Lists of refined atomic coordinates, selected bond distances and angles are avail-

able from the author.

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5.. The crystal data: $Cd_3C_{20}H_{28}N_{10}$, $M=735.66$, monoclinic, $P2_1/n$, $a=8.942(2)$, $b=12.835(5)$, $c=12.222(3)$ Å, $\beta=92.33(2)°$, $V=1401.5(7)$ Å^3, $Z=2$, $D_x=1.74$, $D_m=1.76(2)$ gcm^{-3}, 4588 reflections observed, 3151 ($>3\sigma(F_o)$) used, 151 parameters to $R=0.032$ and $R_w=0.042$. The diffraction data of a crystal were collected on a Rigaku AFC-5S four-circle automated diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda=0.71069$ Å) at 296 K. All data were collected with the ω-2θ scan mode in the range of $4°<2\theta<60°$. Single crystal of this clathrate coated with epoxy resin did never show any decay during the intensity measurement. The crystal structure was solved by heavy-atom method and refined by SHELX 76 and UNICS III programs.
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Sequential Radical Ring Expansion and Allylation Reactions Using 2-Bromo-3-(phenylthio)propene: Their Application to the Synthesis of Bridged Ring Systems

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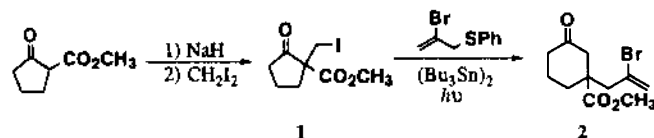†*Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, U.S.A.*
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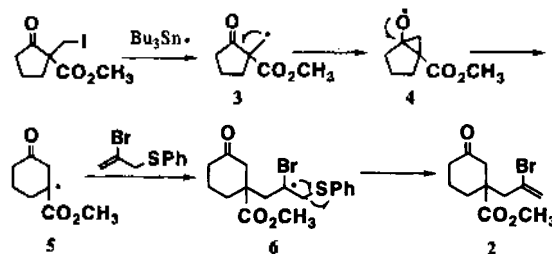*Received May 16, 1997*

In recent years we have witnessed a remarkable upsurge of the interest among synthetic organic chemists in carbon-centered radical chemistry.[1] Particularly, the development of radical-based synthetic methods for the preparation of bridged systems[2] has been stimulated by the discovery of many biologically active polycyclic natural products that contain a bridged structural unit. For example, the bicyclo[3.2.1]octane ring system has received a relatively large amount of attention due to its frequent presence in various sesqui- and diterpenes.[3]

The ability to sequence radical reactions to accomplish multiple transformations in a single step is an asset of free radical reactions in organic synthesis.[4] Ring expansion *via* an oxy radical is especially interesting because of its potential for the synthesis of medium and large rings. Dowd has shown that sequential radical reactions *via* ring expansions provide a variety of ring compounds.[5] Under these conditions, alkyl radical addition to the ketone can compete favorably with direct hydrogen atom abstraction and the location of the radical-stabilizing ester group controls the direction of fragmentation, which is itself sufficiently rapid so that an intermediate oxy radical can not be intercepted by tin hydride (Scheme 2). It is anticipated that the undesired direct reduction of alkyl radical 3 before expansion

can be minimized by using hexabutylditin for initiation instead of tributyltinhydride and trapping the ring-expanded radical 5 with allyl transfer reagent, 2-bromo-3-(phenylthio) propene 6. The ring-expanded vinyl bromide 2 thus generated is expected to undergo vinyl radical cyclization onto car-

Scheme 1.

Scheme 2.