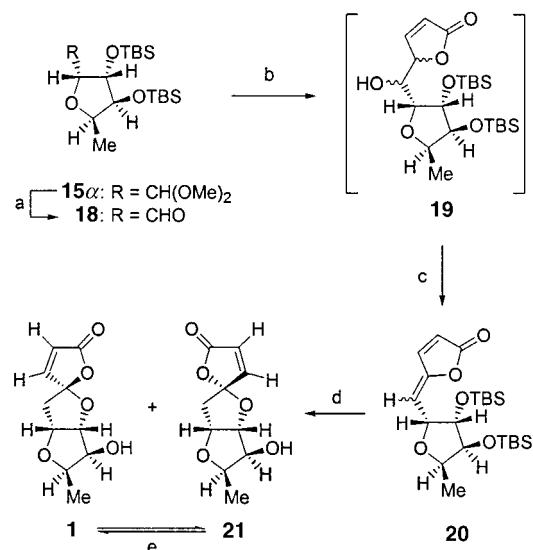




Scheme 5. a) TiCl₄, Et₂O, 0 °C, 88 %; b) 2-(trimethylsilyloxy)furan, BF₃·OEt₂, CH₂Cl₂, -78 °C; c) Burgess reagent, PhH, 55 °C, 80 % (two steps); d) 1N LiOH_{aq}, 23 °C; 16 % HF_{aq}, 23 °C, 93 % (1:1.4, **1/21**); e) 8N HCl_{aq}, THF, 23 °C, quant.

19, which was directly treated with the Burgess dehydrating agent (MeO₂CNSO₂NEt₃) to afford the unsaturated γ -lactone **20** (80 %, two steps) as a mixture of stereoisomers (2:1, *E/Z*). Formation of the spiroketal functionality and completion of the synthesis proceeded in a two-step, one-pot transformation from **20**, involving initial hydrolysis of the lactone (1N LiOH_{aq}), followed by acid-mediated (HF_{aq}) TBS-deprotection and spiroketalization to form a diastereomeric mixture of pyrenolide D (**1**) and its spiroketal epimer **21** in a 1:1.4 ratio (93 % total). Although the thermodynamic distribution of **1** and **21** exhibits essentially no selectivity, separation of the epimers by chromatography is trivial, allowing the quantitative iterative re-equilibration of **21** (8N HCl_{aq}, THF) to enhance the production of the natural product **1**. The spectral data (¹H and ¹³C NMR, FTIR) of synthetic **1** derived from tri-*O*-acetyl-D-galactal coincide with those reported by Nukina and Hirota ([α]_D²³ = +64.3 (*c* = 0.4, CHCl₃), lit.: [α]_D²³ = +79.5 (*c* = 0.9, CHCl₃)).

In summary, the first synthesis of pyrenolide D (**1**) is described, involving a short sequence beginning with tri-*O*-acetyl-D-galactal. A key feature in the synthesis includes the efficient formation of highly functionalized tetrahydrofurfural intermediates directly from glycal substrates, by employing the reagent combination of iodosylbenzene and triflic anhydride in a mixture of methanol and dichloromethane. Not only did this process lead to the efficient synthesis and absolute stereochemical assignment of **1**, but it also highlights this oxidative ring contraction strategy as one that holds promise in both natural product and C-nucleoside synthesis.

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- [1] M. Nukina, M. Ikeda, T. Sassa, *Agric. Biol. Chem.* **1980**, *44*, 2761–2762.
 [2] M. Nukina, H. Hirota, *Biosci. Biotechnol. Biochem.* **1992**, *56*, 1158–1159.
 [3] M. J. Ackland, J. R. Hanson, P. B. Hitchcock, A. H. Ratcliffe, *J. Chem. Soc. Perkin Trans. 1* **1985**, 843–847.

- [4] a) V. Di Bussolo, Y.-J. Kim, D. Y. Gin, *J. Am. Chem. Soc.* **1998**, *120*, 13515–13516; b) V. DiBussolo, J. Liu, L. G. Huffman, Jr., D. Y. Gin, *Angew. Chem.* **2000**, *112*, 210–213; *Angew. Chem. Int. Ed.* **2000**, *39*, 204–207; c) J.-Y. Kim, V. Di Bussolo, D. Y. Gin, *Org. Lett.* **2001**, *3*, 303–306.
 [5] R. L. Halcomb, S. H. Boyer, M. D. Wittman, S. H. Olson, D. J. Denhart, K. K. C. Liu, S. J. Danishefsky, *J. Am. Chem. Soc.* **1995**, *117*, 5720–5749.
 [6] a) P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, K. Mislow, *J. Am. Chem. Soc.* **1968**, *90*, 4869–4876; b) D. A. Evans, G. C. Andrews, *Acc. Chem. Res.* **1974**, *7*, 147–154.
 [7] a) A. Kaye, S. Neidle, C. B. Reese, *Tetrahedron Lett.* **1988**, *29*, 1841–1844; b) E. Bettelli, P. D'Andrea, S. Mascanzoni, P. Passacantilli, G. Piancatelli, *Carbohydr. Res.* **1998**, *306*, 221–230.
 [8] a) A. Vavoglis, *The Organic Chemistry of Polycordinated Iodine*, VCH, New York, **1992**; b) R. M. Moriarty, O. Prakash, *Org. React.* **1999**, *54*, 273–418.
 [9] A. Kirschning, *Eur. J. Org. Chem.* **1998**, 2267–2274.
 [10] A. Kirschning, *Liebigs Ann.* **1995**, 2053–2056.
 [11] R. M. Moriarty, O. Prakash, M. P. Duncan, R. K. Vaid, N. Rani, *J. Chem. Res. Synop.* **1996**, 432–433.
 [12] It is likely that the triflic acid serves to activate the PhI(OMe)₂ reagent generated in situ.
 [13] ¹H NMR analysis shows a relatively small H3–H4 proton coupling constant (*J*_{3,4} = 2.8 Hz). This is consistent with previous observations in other pyranosides incorporating vicinal *tert*-butyldimethylsilyl ethers in which *gauche* interactions between the bulky protective groups are minimized. See, for example: a) M. A. Tius, J. Busch-Peterson, *Tetrahedron Lett.* **1994**, *35*, 5181–5184; b) W. A. Roush, C. E. Bennett, *J. Am. Chem. Soc.* **1999**, *121*, 3541–3542.
 [14] This rationale assumes, among other things, that the activation of gual **12** proceeds irreversibly through a relatively late (i.e., C2-pyramidalized) transition state. For some discussions on the conformational flexibility of glycals, see: a) J. Thiem, P. Ossowski, *J. Carbohydr. Chem.* **1984**, *3*, 287–313; b) W. R. Roush, D. P. Sebesta, C. E. Bennett, *Tetrahedron* **1997**, *53*, 8825–8836.
 [15] The employment of the *tert*-butyldimethylsilyl protecting groups was crucial in achieving the desired stereoselectivity. The use of dibenzyl-D-gual with the identical oxidative ring contraction procedure led to indiscriminate facial approach of the I^{III} reagent, affording a 1:1 (α/β) mixture of the corresponding tetrahydrofurfural acetals in 82 % yield.
 [16] Formation of the minor diastereomer **15 β** might also arise from the β -approach of the oxidant onto **12** (⁵H₄), leading to a higher energy twist-boatlike transition state. Following a conformational half-chair flip, ring contraction would lead to the minor diastereomer **15 β** .

Crown-Ether-Directed Assembly of Discrete and One-Dimensional Silver Aggregates Containing Embedded Acetylenediide**

Quan-Ming Wang and Thomas C. W. Mak*

In memory of Daniel Y. Chang

Recent studies have shown that the coordination modes of the acetylide dianion (C₂²⁻, IUPAC name acetylenediide) can be classified into three categories: 1) linear end-to-end

[*] Prof. T. C. W. Mak, Q.-M. Wang
 Department of Chemistry
 The Chinese University of Hong Kong
 Shatin, New Territories, Hong Kong SAR (PR China)
 Fax: (+852) 26035057
 E-mail: tcwmak@cuhk.edu.hk

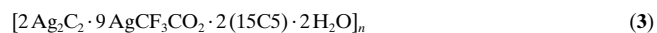
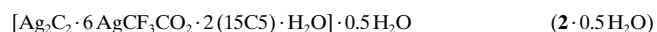
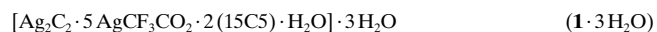
[**] Financial support from the Hong Kong Research Grants Council Earmarked Grant (CUHK 4268/00P) is gratefully acknowledged.

bridging in the $[[\text{AgC}_2]^-]_\infty$ structure of ternary alkali metal silver acetylides MAgC_2 ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$),^[1] 2) planar $\mu_4\text{-}\eta^1, \eta^2$ in the tetranuclear cation $[\text{Cu}_4(\mu\text{-dppm})_4(\text{C}_2)]^{2+}$ ($\text{dppm} = \text{bis}(\text{diphenylphosphanyl})\text{methane}$),^[2] 3) encapsulated inside a polyhedral Ag_n ($n = 6\text{--}9$) cage in a series of silver(I) double and triple salts.^[3]

Thus far all reported compounds in category 3) have either layer-type or three-dimensional network structures, in which the component $\text{C}_2@ \text{Ag}_n$ cages share common vertices or are linked by bridging anions. To obtain discrete molecules and infinite chains, our conceived strategy was to install protective cordons around the $\text{C}_2@ \text{Ag}_n$ moiety with neutral, multi-dentate ligands that can function as blocking groups or terminal stoppers.

Bearing in mind that ancillary ligation of solvent may lower the dimensionality of a coordination polymer, we introduced crown ether into silver acetylide containing systems in an attempt to prevent catenation and interlinkage of the silver polyhedra. Notably, in the context of host–guest complementarity,^[4,5] the interaction of Ag^I with crown ethers is rather weak: a) there is poor affinity between hard oxygen donor and soft cation, and consequently only a few silver(I)–crown ether complexes have been reported;^[6] b) the size of the Ag^I ion is too large to fit into the cavity of a crown ether, so that the host–guest system is necessarily forced to undergo distortion to accommodate the conflicting requirements of each partner.^[7] Accordingly, crown ethers are expected not to affect the formation of $\text{C}_2@ \text{Ag}_n$, but to act as weak capping ligands to provide ancillary ligation to the silver acetylide containing system. Herein we report the first isolation of discrete molecules and a zigzag coordination polymer containing embedded acetylide ions, for which [15]crown-5 (15C5) was employed as a structure-directing agent.

The crucial step in the synthesis of **1–3** took advantage of the fact that Ag_2C_2 readily dissolves in a concentrated aqueous solution of a silver(I) salt.^[8] Although the mechanism of the dissolution is not clear, it is presumable that the rigid lattice of Ag_2C_2 breaks down with compensation by multiple argentophilic interactions^[9] to form polyhedral species of the type $[\text{C}_2@ \text{Ag}_n]^{(n-2)+}$ ($n \geq 6$). The crown ether then influences the assembly process of these species during crystallization. Different preparative procedures have led to the isolation of discrete molecules **1** and **2** and a zigzag polymeric chain in **3**.



The sandwiched molecular structure of **1** is shown in Figure 1. The silver cage enclosing an acetylide dianion is in the shape of a pentagonal bipyramid, with its two apices (Ag6 and Ag7) slightly shifted to one side of the idealized molecular axis. The equatorial silver atoms lie within 0.205 Å of their least-squares plane. Four of the five edges of the equatorial pentagon are each bridged by one trifluoroacetate ligand (tfa), the $\text{Ag3} \cdots \text{Ag4}$ edge being the exception. Ag3 is coordinated by one aqua ligand, and the tfa

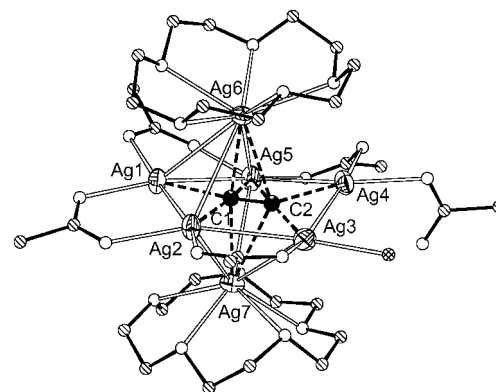


Figure 1. Crown-sandwiched molecular structure of compound **1** (the F and H atoms have been omitted for clarity). Range of metal–ligand distances [Å]: Ag–C 2.13–2.62; Ag–O 2.455–2.635 and 2.483–2.631 for the two crown ethers.

binding to Ag4 acts in a monodentate mode. Both Ag6 and Ag7 are each capped by one $\eta^5\text{-15C5}$ ligand, resulting in the first example of a discrete complex among silver acetylide containing systems.

Interestingly, the sandwich unit in **2** is very similar to that in **1**. As shown in Figure 2, it also takes the shape of a pentagonal

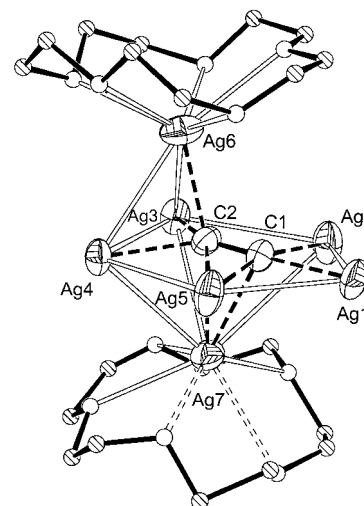


Figure 2. Sandwiched $\text{C}_2@ \text{Ag}_7$ unit in compound **2**. Metal–ligand distances [Å]: Ag–C 2.118–2.555; Ag–O (crown ether) 2.443–2.635 and 2.524–2.743 Å. Two longer Ag–O bonds that exceed 2.7 Å are represented by broken open lines.

bipyramid but the two apices (Ag6 and Ag7) undergo a much larger lateral shift. As a result of such a distortion, the C_2^{2-} ion exhibits only π interactions with Ag5 and Ag7 (C1 does not bind to Ag6). This is different from the case in **1**, where the C_2^{2-} ion has π interactions with Ag5 , Ag6 , and Ag7 . Another difference is that all edges of the equatorial pentagon in **2** are each bridged by one tfa ligand, and one corner atom is additionally coordinated by an aqua ligand. Two $[(\eta^5\text{-15C5})_2\text{-}(\text{C}_2@ \text{Ag}_7)(\mu\text{-CF}_3\text{CO}_2)_5(\text{H}_2\text{O})]$ moieties are connected through a central $[\text{Ag}_2(\text{tfa})_2]$ bridge to form a centrosymmetric hexadecanuclear supermolecule, as illustrated in Figure 3. Molecule **2** can be regarded as derived from **1** by linking two

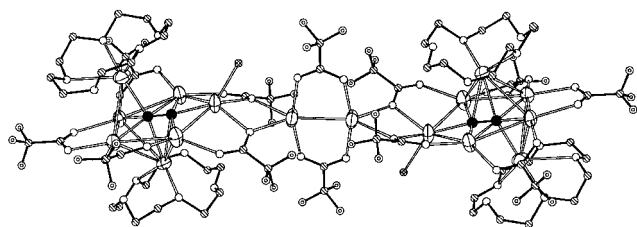


Figure 3. Centrosymmetric molecular structure of **2** (hydrogen atoms have been omitted for clarity): two sandwiched $C_2@Ag_7$ units and the central $[Ag_2(tfa)_2]$ bridge are linked by four μ_3 -tfa ligands.

$C_2@Ag_7$ units through $[Ag_2(tfa)_2]$ bridging, and steric crowding leads to serious distortion of the polyhedral cage in **2**.

In contrast to the single silver cage in **1** and **2**, compound **3** contains a novel tridecanuclear double cage composed of two distorted square antiprisms that share a common triangular face $Ag1-Ag4-Ag5$ (Figure 4). For the upper antiprism, atom

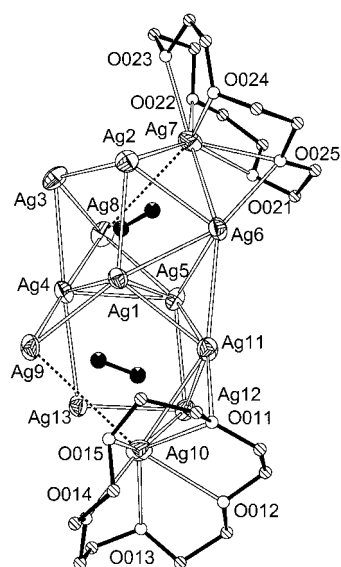


Figure 4. A sandwiched $(C_2)_2@Ag_{13}$ double-cage in **3**. Metal–ligand distances [Å]: Ag–C 2.12–2.70; Ag–O (crown ether) 2.416–2.694 and 2.437–2.696. The longer Ag...Ag distances that exceed 3.4 Å are represented by broken lines.

sets $Ag1-Ag2-Ag3-Ag4$ and $Ag5-Ag6-Ag7-Ag8$ constitute a pair of nearly parallel (dihedral angle 4.5°) tetragons, and for the lower one, the tetragons are made up of $Ag4-Ag5-Ag12-Ag13$ and $Ag1-Ag9-Ag10-Ag11$ (dihedral angle 3.5°). A unique feature is that both 15C5 ligands act in capping and bridging modes: for example, the upper 15C5 unit caps $Ag7$ and also bridges the $Ag6 \cdots Ag7$ edge through the binding of O025 to $Ag6$. Such a dual ligation mode is unprecedented in silver crown ether complexes. In the crystal structure of **3**, there are two nearly identical double cages in the asymmetric unit. As the molar ratio $15C_5/C_2^{2-}$ is 1:1 in **3**, in contrast to 2:1 in **1** and **2**, there is sufficient room around each $(C_2)_2@Ag_{13}$ double cage to allow the approach of bridging tfa groups in the assembly of an infinite zigzag chain.

The C_2^{2-} species in **1–3** all retain their triple-bond character with the C–C bond length ranging from 1.13(1) to 1.26(1) Å, which are close to those in acetylene (1.205 Å)^[10]

and CaC_2 (1.191 Å).^[11] The shortest Ag...Ag distances are 2.954(1) in **1**, 2.830(1) in **2**, and 2.847(1) Å in **3**, which are suggestive of significant argentophilic interactions.^[12]

In conclusion, the assembly process of an acetylide-encapsulating silver cluster in an aqueous system that contains Ag_2C_2 can be affected by the presence of a neutral, multidentate ligand like a crown ether, leading to the generation of unusual structures of low dimensionality. The present study has thus established a new direction in silver acetylide chemistry, showing that the $(\eta^5-15C_5)Ag$ fragment is a potentially useful building block for the synthesis of silver clusters and supramolecular systems.

Experimental Section

Ag_2C_2 was prepared as described previously.^[3] **Caution:** Thoroughly dried Ag_2C_2 detonates easily upon mechanical shock and heating, and only a small quantity should be used in any chemical reaction.

1: Ag_2C_2 was added to a concentrated aqueous solution of $AgCF_3CO_2$ (1 mL) in a plastic beaker with stirring until saturation. The excess amount of Ag_2C_2 was filtered off, and a few drops of 15C5 were added to the filtrate. The resulting suspension was transferred to a thick-walled glass tube. The tube was subsequently flame-sealed and kept in a furnace at $115^\circ C$ for 6 h, and then cooled down to room temperature at $6 K h^{-1}$. Apart from a large quantity of black unidentified material, colorless platelike crystals of **1** were isolated in about 10% yield.

2: Ag_2C_2 was added to a concentrated aqueous solution of $AgCF_3CO_2$ and $AgBF_4$ (1 mL; molar ratio $\sim 1:1$) in a plastic beaker with stirring until saturation. The excess amount of Ag_2C_2 was filtered off, and a few drops of 15C5 ether were added to the filtrate. The resulting solution was allowed to stand without disturbance, and colorless blocklike crystals of **2** were obtained in over 50% yield after several hours.

3: Excess Ag_2C_2 and $AgCN$ were added to a concentrated aqueous solution of $AgCF_3CO_2$ and $AgBF_4$ (1 mL; molar ratio $\sim 1:1$) in a plastic beaker with stirring until saturation. After filtration, a few drops of 15C5 were added to the filtrate. The resulting solution was placed in a desiccator charged with P_2O_5 . The suspension that appeared overnight was transferred to a thick-walled glass tube. The tube was subsequently flame-sealed and kept in a furnace at $115^\circ C$ for 6 h, and then cooled down to room temperature at $6 K h^{-1}$. Colorless prismatic crystals of **3** were isolated in about 30% yield.

Crystal data for **1**: $C_{32}H_{33}Ag_7F_{15}O_{24}$, $M_r = 1841.67$, monoclinic, space group $P2_1/c$ (no. 14), $a = 20.772(1)$, $b = 12.0453(7)$, $c = 22.041(1)$ Å, $\beta = 94.612(1)^\circ$, $V = 5496.8(6)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.225 \text{ Mg m}^{-3}$, $F(000) = 3524$, $\mu(\text{Mo K}\alpha) = 2.566 \text{ mm}^{-1}$. 36540 reflections measured, 13197 unique ($R_{\text{int}} = 0.0774$), final $R1 = 0.0465$, $wR2 = 0.1011$ for 4820 observed reflections ($I > 2\sigma(I)$).

Crystal data for **2**: $C_{34}H_{43}Ag_8F_{18}O_{23.5}$, $M_r = 2032.64$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.7506(5)$, $b = 20.2915(9)$, $c = 26.468(1)$ Å, $\beta = 94.225(1)^\circ$, $V = 5758.2(5)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.345 \text{ Mg m}^{-3}$, $F(000) = 3892$, $\mu(\text{Mo K}\alpha) = 2.792 \text{ mm}^{-1}$. 38492 reflections measured, 13873 unique ($R_{\text{int}} = 0.0357$), final $R1 = 0.0561$, $wR2 = 0.1610$ for 7034 observed reflections ($I > 2\sigma(I)$).

Crystal data for **3**: $C_{42}H_{44}Ag_{13}F_{27}O_{30}$, $M_r = 2944.08$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 16.533(1)$, $b = 25.235(2)$, $c = 35.007(2)$ Å, $V = 14605(2)$ Å³, $Z = 8$, $\rho_{\text{calcd}} = 2.678 \text{ Mg m}^{-3}$, $F(000) = 11120$, $\mu(\text{Mo K}\alpha) = 3.547 \text{ mm}^{-1}$. 98895 reflections measured, 35210 unique ($R_{\text{int}} = 0.0481$), final $R1 = 0.0466$, $wR2 = 0.1051$ for 19902 observed reflections ($I > 2\sigma(I)$).

Data collection was performed at 293 K on a Bruker SMART 1000 CCD diffractometer using frames of oscillation range 0.3° , with $1.5^\circ < \theta < 28^\circ$. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using the SHELXTL program.^[13]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-152945 (**1**), CCDC-152946 (**2**), and CCDC-152947 (**3**). Copies of the data can be

obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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- [1] W. Kockelmann, U. Ruschewitz, *Angew. Chem.* **1999**, *111*, 3697–3700; *Angew. Chem. Int. Ed.* **1999**, *38*, 3492–3495.
- [2] V. W.-W. Yam, W. K.-M. Fung, K.-K. Cheung, *Angew. Chem.* **1996**, *108*, 1213–1215; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1100–1103.
- [3] a) G.-C. Guo, Q.-G. Wang, G.-D. Zhou, T. C. W. Mak, *Chem. Commun.* **1998**, 339–340; b) G.-C. Guo, G.-D. Zhou, Q.-G. Wang, T. C. W. Mak, *Angew. Chem.* **1998**, *110*, 652–654; *Angew. Chem. Int. Ed.* **1998**, *37*, 630–632; c) G.-C. Guo, G.-D. Zhou, T. C. W. Mak, *J. Am. Chem. Soc.* **1999**, *121*, 3136–3141; d) Q.-M. Wang, T. C. W. Mak, *J. Am. Chem. Soc.* **2000**, *122*, 7608–7609.
- [4] J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**.
- [5] B. Dietrich, P. Viout, J.-M. Lehn, *Macrocyclic Chemistry*, VCH, Weinheim, **1993**.
- [6] P. G. Jones, T. Gries, H. Grützmacher, H. W. Roesky, J. Schimkowiak, G. M. Sheldrick, *Angew. Chem.* **1984**, *96*, 357–358; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 376; Z.-C. Liu, M.-C. Shao, *Acta Sci. Nat. Univ. Pekin.* **1987**, *6*, 17–23; P. D. Prince, J. W. Steed, *Supramol. Chem.* **1998**, *10*, 155–158.
- [7] P. D. Prince, P. J. Cragg, J. W. Steed, *Chem. Commun.* **1999**, 1179–1180.
- [8] R. Vestin, E. Ralf, *Acta Chem. Scand.* **1949**, *3*, 101–124.
- [9] a) M. A. Omary, T. R. Webb, Z. Assefa, G. E. Shankle, H. H. Patterson, *Inorg. Chem.* **1998**, *37*, 1380–1386; b) G.-C. Guo, T. C. W. Mak, *Angew. Chem.* **1998**, *110*, 3296–3299; *Angew. Chem. Int. Ed.* **1998**, *37*, 3183–3186; c) C.-M. Che, M.-C. Tse, M. C.-W. Chan, K.-K. Cheung, D. L. Phillips, K.-H. Leung, *J. Am. Chem. Soc.* **2000**, *122*, 2464–2468.
- [10] G. Herzberg, J. W. T. Spinks, *Z. Physik* **1934**, *91*, 386.
- [11] M. Atoji, *J. Chem. Phys.* **1961**, *35*, 1950–1960.
- [12] M. Jansen, *Angew. Chem.* **1987**, *99*, 1136–1149; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1098–1110.
- [13] G. M. Sheldrick, SHELXTL 5.10 for Windows NT: Structure Determination Software Programs. Bruker Analytic X-Ray Systems, Inc.: Madison, WI, **1997**.
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