

Cite this: *CrystEngComm*, 2012, 14, 5955–5962

www.rsc.org/crystengcomm

PAPER

Structural controls of 2D sheet copper(I) ethylene and carbonyl coordination polymers directed by anions and solvents†

Masahiko Maekawa,^{*a} Toshi Tominaga,^b Kuniyoshi Sugimoto,^c Takashi Okubo,^b Takayoshi Kuroda–Sowa,^b Megumu Munakata^b and Susumu Kitagawa^d

Received 14th February 2012, Accepted 6th June 2012

DOI: 10.1039/c2ce25211b

The reactions of Cu(I) ion with {BF₄[−], ClO₄[−], or PF₆[−]} anions and 6,6′-dimethyl-4,4′-bipyrimidine (Me₂bpm) under C₂H₄ or CO in MeOH preferentially afforded three 2D sheet Cu(I)–Me₂bpm/{C₂H₄, CO} adducts [Cu₄(Me₂bpm)₃(C₂H₄)₃(MeCN)](BF₄)₄·0.33MeOH)_n (**2**), {[Cu₄(Me₂bpm)₃(C₂H₄)₃(MeOH)_{0.33}](ClO₄)₄})_n (**3**), and {[Cu₄(Me₂bpm)₃(CO)₃(MeCN)](PF₆)₄·0.33MeCN)_n (**4**), whereas the similar reaction of Cu(I) ion with a BF₄[−] anion and Me₂bpm under CO in MeOH gave the metallamacrocyclic tetranuclear Cu(I)–Me₂bpm/CO adduct [Cu₄(Me₂bpm)₄(CO)₄](BF₄)₄·4MeOH (**5**). In Cu(I)–Me₂bpm/{C₂H₄, CO} adducts **2–4**, it should be noted that the metallacalix[3]arene structures of the [Cu₃(Me₂bpm)₃]³⁺ framework are linked through another Cu atom with MeCN (**2** and **4**) or MeOH (**3**) to produce a chiral 2D sheet structure with small Cu₃ and large Cu₉ cavities. In the small triangular Cu₃ cavities, one MeOH (**2**) or MeCN (**4**) molecule is encapsulated in complexes **2** and **4**, whereas these Cu₃ cavities are empty in complex **3**. In the large Cu₉ cavities, one anion (X = BF₄[−] (**2**), ClO₄[−] (**3**) or PF₆[−] (**4**)) is surrounding by six Me groups of three Me₂bpm on the upside and three anions (X) are functionally accommodated on the downside for complexes **2–4**, respectively. In the Cu(I)–Me₂bpm/CO adduct **5**, two of the four BF₄[−] anions are accommodated in the upper and lower cavities of the [Cu₄(Me₂bpm)₄] framework. We demonstrated that the metallamacrocyclic and polymeric 2D sheet Cu(I)–Me₂bpm/{C₂H₄, CO} adducts can be reasonably self-assembled under the direction of anions and solvents.

Introduction

The use of chemical templates is now a powerful approach to the rational synthesis of inorganic and organic molecular assemblies.¹ This strategy not only enables the synthesis of molecules in a more efficient manner but also aids in the preparation of assemblies that have unusual topologies, such as macrocycles, molecular cages, interlocked species (such as catenanes and rotaxanes), and helical assemblies. In order for a template process to successfully yield the targeted product, the structural and electrostatic properties of the template need to be selected carefully. From a structural point of view, both the size and

geometry of the template have to be considered, while electrostatically the choice is restricted to neutral, positively charged or negatively charged species. Although cationic and neutral species have been widely used as templates in synthetic chemistry, the role of anion templates was scarcely exploited until the second half of the 1990s. This relative lack of an anion-templated process is partially attributable to the complicated physicochemical nature of the anions, such as their diffuse nature, variety of geometries, pH sensitivity, and relatively high solvation-free energies. However, the potential use of anion species as templates has been recently argued in a wide range of novel inorganic and organic assemblies.²

4,4′-Bipyrimidine (bpm) and its derivatives are an attractive nitrogen ligand with a bidentate site for chelation and two *exo* N-donor sites for bridging, since it can be thought of as a combination of 2,2′-bipyridine and 4,4′-bipyridine.^{3,4} It is expected to produce both finite metallamacrocyclic and infinite polymeric compounds with square/rectangular motifs. We recently reported that the combination of Cu(I) ion and bpm can produce a diversity of polymeric Cu(I)–bpm/C₂H₄ adducts and Cu(I)–bpm cage compounds by the choice of anions and solvent (Scheme 1(a)).^{4a} In particular, the reaction of the Cu(I) ion with a BF₄[−] anion and bpm under C₂H₄ in MeOH afforded the first chiral 2D sheet Cu(I)–C₂H₄ coordination polymer

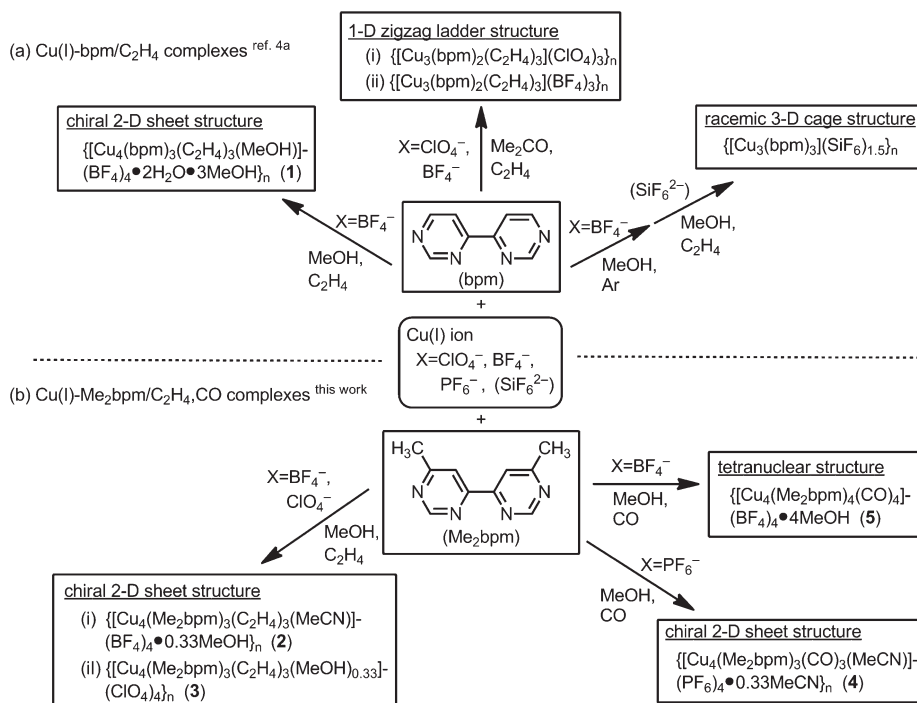
^aResearch Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan.
E-mail: maekawa@rist.kindai.ac.jp

^bDepartment of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

^cResearch and Utilization Division, Japan Synchrotron Radiation Research Institute, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

^dDepartment of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

† Electronic supplementary information (ESI) available: Crystal packing structures of complexes **3** and **4** were deposited in Fig. S1 and S2. CCDC 866528–866531 for complexes **2–5**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce25211b.



Scheme 1 Cu(I)-bpm/C₂H₄ and Cu(I)-Me₂bpm/{C₂H₄, CO} complexes.

[Cu₄(bpm)₃(C₂H₄)₃(MeOH)](BF₄)₄•2H₂O•3MeOH_n (1). However, structurally Cu(I)-C₂H₄ adducts have been poorly characterized because of the extremely labile nature of the Cu(I)-C₂H₄ interaction.^{4,5} In particular, there have been few preparative and structural reports on polynuclear and polymeric Cu(I)-C₂H₄ complexes.^{4,5e,5f} In this study, we attempted to realize a reasonably preparative approach to self-assemble 2D sheet Cu(I)-C₂H₄ adducts under the direction of anions and solvents by promoting the preliminary knowledge in Cu(I)-bpm/C₂H₄ adducts.^{4a} As a further investigation, four novel Cu(I)-Me₂bpm/{C₂H₄, CO} adducts were prepared by the combination of a Cu(I) ion with {BF₄⁻, ClO₄⁻ or PF₆⁻} anions and 6,6'-dimethyl-4,4'-bipyrimidine (Me₂bpm) as a related bpm ligand under C₂H₄ or CO (Scheme 1(b)). Their crystal structures and properties were characterized by X-ray, IR, XRPD, and TG-DTA analyses.

Experimental sections

General procedures and reagents

[Cu(MeCN)₄]X (X = PF₆ and BF₄) were prepared according to the literature.⁶ The 6,6'-dimethyl-4,4'-bipyrimidine (Me₂bpm) ligand was prepared with modifications of the literature method.⁷ Pure C₂H₄ and CO gases (>99.9%) were purchased from Sumitomo Seika Chemicals (Japan). All organic solvents were dried and distilled by the usual methods before use. All procedures were carried out using standard Schlenk techniques under C₂H₄ or CO. IR spectra were recorded with a JASCO FT-IR 430 spectrometer as KBr pellets. Thermogravimetric analysis (TG-DTA) was carried out with a RIGAKU Thermo Plus 8120 under flowing N₂ gas.

Preparation of Cu(I)-Me₂bpm/{C₂H₄, CO} complexes

[Cu₄(Me₂bpm)₃(C₂H₄)₃(MeCN)](BF₄)₄•0.33MeOH_n (2). [Cu(MeCN)₄]BF₄ (62.9 mg, 0.20 mmol) and Me₂bpm

(3.7 mg, 0.02 mmol) were reacted in MeOH (10 ml) under C₂H₄. The yellow reaction solution was filtered, and the filtrates were sealed in 7 mm φ glass tubes under C₂H₄. The reaction solution was allowed to stand for one week at -10 °C, after which red brick crystals of complex 2 were collected. After complex 2 was dried by flowing C₂H₄ gas, it was subjected immediately to elementary analysis, IR, XRPD, and TG-DTA. Anal. Calcd. for Cu₄C_{38.32}H_{43.32}N₁₃O_{0.33}B₄F₁₆: C, 35.53; H, 3.60; N, 14.05. Found: C, 35.30; H, 3.81; N, 13.83. IR (KBr, cm⁻¹): 1597(s), 1542(s, C₂H₄), 1520(m), 1468(m), 1441(m), 1420(m), 1378(m), 1346(s, C₂H₄), 1307(m), 1259(s), 1230(m), 1030(s, BF₄), 877(s), 748(m), 679(m), 553(m), 533(m), 522(m), 404(s).

[Cu₄(Me₂bpm)₃(C₂H₄)₃(MeOH)_{0.33}](ClO₄)_{4n} (3). The precursor Cu(I)-C₂H₄ complex [Cu(C₂H₄)_n]ClO₄ was prepared by the reductive reaction of Cu(ClO₄)₂•6H₂O (37.1 mg, 0.10 mmol) with Cu wire in MeOH (5 ml) under C₂H₄. A 5 ml MeOH solution of Me₂bpm (5.5 mg, 0.03 mmol) was added to the above Cu(I)-C₂H₄ solution. The C₂H₄ gas was then bubbled for 30 mins. The resultant yellow solution was filtered, and the filtrates were sealed in 7 mm φ glass tubes under C₂H₄. The reaction solution was allowed to stand at -10 °C for one week, after which red plate crystals of complex 3 were collected. After complex 3 was dried by flowing C₂H₄ gas, it was subjected immediately to elementary analysis and IR. Anal. Calcd. for Cu₄C_{36.33}H₄₂N₁₂O_{16.33}Cl₄: C, 33.43; H, 3.34; N, 12.88. Found: C, 34.15; H, 3.85; N, 12.38. IR (KBr, cm⁻¹): 1599(s), 1543(m, C₂H₄), 1525(m), 1468(w), 1425(m), 1392(w), 1360(w, C₂H₄), 1308(w), 1259(m), 1231(w), 1089-1030(s, ClO₄), 877(m), 747(m), 691(w), 679(w), 636(m), 624(s), 553(w), 536(w), 404(m).

Caution! Perchlorate salts of metal complexes with organic compounds are potentially explosive! Only small amounts of

materials should be prepared, and they should be handled with great care.

{[Cu₄(Me₂bpm)₃(CO)₃(MeCN)](PF₆)₄·0.33MeCN}_n (4). [Cu(MeCN)₄]PF₆ (37.3 mg, 0.10 mmol) and Me₂bpm (3.7 mg, 0.02 mmol) were reacted in MeOH (10 ml) under CO. The colorless reaction solution was filtered, and the filtrates were sealed in 7 mm ϕ glass tubes under CO. The reaction solution was allowed to stand for 2 weeks at $-30\text{ }^{\circ}\text{C}$, and dark reddish-brown crystals of complex **4** were obtained. After complex **4** was dried by flowing CO gas, it was subjected immediately to elementary analysis, IR, and TG-DTA. Anal. Calcd. for Cu₄C₃₇N₁₄H₃₆O₃P₄F₂₄: C, 28.51; H, 2.32; N, 12.58. Found: C, 28.18; H, 2.53; N, 12.01. IR (KBr, cm⁻¹): 2126(s, CO), 1618(s), 1550(s), 1526(s), 1479(s), 1428(s), 1402(s), 1361(m), 1311(m), 1277(m), 1193(m), 1101(m), 1053(m), 1034(s), 840(s, PF₆), 746(s), 690(m), 556(s), 421(m).

[Cu₄(Me₂bpm)₄(CO)₄](BF₄)₄·4MeOH (5). [Cu(MeCN)₄]BF₄ (31.5 mg, 0.10 mmol) and Me₂bpm (3.7 mg, 0.02 mmol) were reacted in MeOH (10 ml) under CO. The pale yellow reaction solution was filtered, and the filtrates were sealed in 7 mm ϕ glass tubes under CO. The reaction solution was allowed to stand for 2 weeks at $-30\text{ }^{\circ}\text{C}$, and yellowish-brown crystals of complex **5** were obtained. After complex **5** was dried by flowing CO gas, it was subjected immediately to elementary analysis, IR, and TG-DTA. Anal. Calcd. for Cu₄C₄₈H₅₆N₁₆O₈B₄F₁₆: C, 36.34; H, 3.56; N, 14.13. Found: C, 36.25; H, 3.22; N, 14.15. IR (KBr, cm⁻¹): 2111(s, CO), 1628(s), 1544(s), 1478(m), 1440(m), 1400(m), 1360(m), 1313(w), 1273(w), 1234(w), 1061(s, BF₄), 889(m), 851(w), 748(w), 686(w), 566(w), 518(w), 415(w).

X-ray crystal structure determinations

All measurements of Cu(I)–Me₂bpm/{C₂H₄, CO} complexes **2–5** were made on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71070\text{ \AA}$). The diffraction data were collected at $-143(2)$, $-154(2)$, $-153(2)$, and $-153(2)\text{ }^{\circ}\text{C}$ for complexes **2–5** by the ω scan mode, respectively. Of the 14 763, 9878, 20 146, and 10 806 reflections collected, 3920, 3420, 4212, and 4141 were unique ($R_{\text{int}} = 0.0232$, 0.0385, 0.0401, and 0.0245) for complexes **2–5**, respectively. Data were collected and processed using the Crystal Clear program (Rigaku). The linear absorption coefficients, μ , for Mo-K α radiation were 17.33, 19.26, 17.72, and 13.47 cm⁻¹ for complexes **2–5**, respectively. The data were corrected for Lorentz and polarization effects.

The structures were solved by a direct method (SHELXS-97) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included and were constrained to the ideal position and thermal displacement parameter. In complex **2**, the crystal structure was refined using the *TWIN* command on SHELXL-97 in order only to afford racemic twin crystal. In complexes **3–5**, the disordered ClO₄⁻ (**3**), PF₆⁻ (**4**), BF₄⁻ (**5**) anions and MeOH molecules (**5**) were restrained to the same thermal displacement parameter using the *EADP* commands on SHELXL-97. The hydrogen atoms of the disordered Me group for complex **2** and OH moiety for complex **3** were not located. The final cycle of full-matrix

least-squares refinement was based on {3920, 3908}, {3420, 3070}, {4212, 3882}, and {4141, 3900} observed reflections (all data, $I > 2\sigma(I)$) for complexes **2–5**, respectively. The un-weighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ($F_o > 4\sigma(F_o)$), and $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)]^{1/2}$ were used. The R , R_1 , and wR_2 values were {0.0273, 0.0272, and 0.0723}, {0.0574, 0.0494, and 0.1293}, {0.0639, 0.0567, and 0.1231} and {0.0442, 0.0420, and 0.1179} for complexes **2–5**, respectively. All calculations were performed using WinGX 1.80. Crystal data and details of the structure determination are summarized in Table 1.

Results and discussion

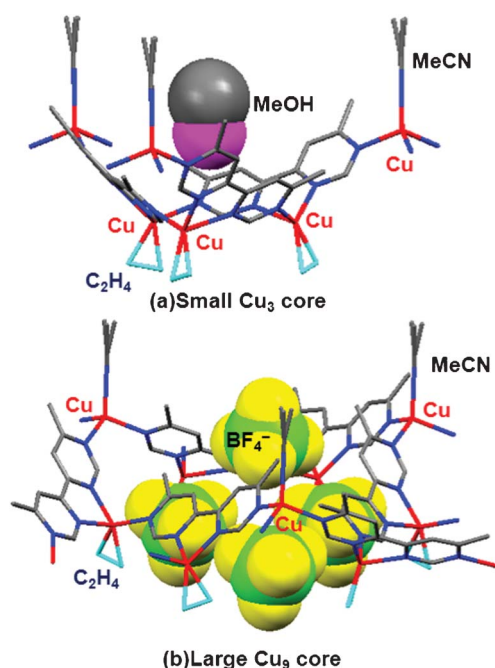
Crystal structures of Cu(I)–Me₂bpm/{C₂H₄, CO} complexes

{[Cu₄(Me₂bpm)₃(C₂H₄)₃(MeCN)](BF₄)₄·0.33MeOH}_n (2). The reaction of [Cu(MeCN)₄]BF₄ with Me₂bpm in MeOH under C₂H₄ afforded brick crystals of complex **2**. The crystal structure of Cu(I)–Me₂bpm/C₂H₄–BF₄ complex **2** is shown in Fig. 1. Each Cu atom is coordinated by three N atoms in chelate and bridging sites of Me₂bpm and the C=C bond of C₂H₄ in the distorted tetrahedral geometry. Three Cu atoms are bridged by three Me₂bpm ligands to form a metallacalix[3]arene structure with three legs of C₂H₄. Furthermore, the metallacalix[3]arene structures of the [Cu₃(Me₂bpm)₃]³⁺ framework are linked through another Cu atom with the disordered MeCN in the terminal N atom of Me₂bpm to produce a 2D sheet structure with small Cu₃ and large Cu₉ cavities. This result shows that a 2D sheet Cu(I)–C₂H₄ adduct can be reasonably produced by the combination of a Cu(I) ion with a BF₄⁻ anion and Me₂bpm in MeOH under C₂H₄ in a manner similar to the Cu(I)–bpm/C₂H₄–BF₄ complex, **1**.^{4a} Although the 2D sheet framework of complex **2** apparently resembles that of complex **1**, the structural difference between Cu(I)–C₂H₄ adducts **1** and **2** is that discrete metallacalix[3]arene structures are linked through the Cu atom with the disordered MeCN in contrast to the linkages through the Cu atom with the disordered MeOH in complex **1**. Another difference is the accommodation manner of the anions and solvents in small Cu₃ and larger Cu₉ cavities. In the small triangular Cu₃ cavity, one MeOH molecule is accommodated in contrast to the encapsulation of one BF₄⁻ anion in complex **1**. In the large Cu₉ cavity, one BF₄⁻ anion is surrounded by six Me groups of three Me₂bpm on the upside and three BF₄⁻ anions are accommodated on the downside in contrast to the encapsulation of three disordered BF₄⁻ anions in complex **1**. Consequently, the crystal packing structure of complex **2** is different from that of complex **1**: the crystallographic lattice constant was changed from hexagonal *P*6₃ (complex **1**) to trigonal *R*3 (complex **2**) and the *c*-axis length is elongated (15.2145(16) Å for **1**, and 22.6054(6) Å for **2**). As shown in Fig. 2, the repeating unit of four-layered 2D sheet structures is arranged in parallel along the *c*-axis in the unit cell in contrast to that of three-layered 2D sheet structures in complex **1**. It is suggested that these structural differences were probably caused by the steric effect of the Me group in the Me₂bpm ligand. In the coordinated C₂H₄ of complex **2**, the C=C distance of 1.340(6) Å is slightly longer than that [1.313 (exptl.) and 1.333 (calc.) Å] in the metal-free C₂H₄⁸ as well as that (1.31(2) Å) in complex **1**.^{4a}

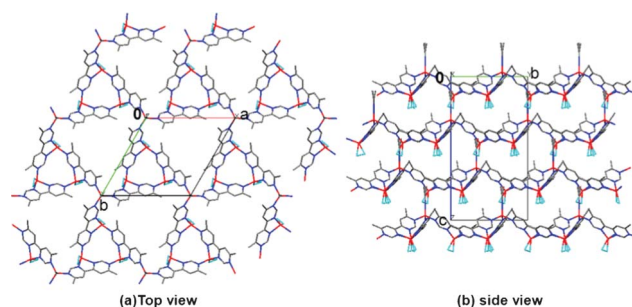
Table 1 Crystallographic data of Cu(I)–Me₂bpm/{C₂H₄, CO} complexes **2–5**

	{[Cu ₄ (Me ₂ bpm) ₃ (C ₂ H ₄) ₃ (MeCN)]–(BF ₄) ₄ ·0.33MeOH} _n (2)	{[Cu ₄ (Me ₂ bpm) ₃ (C ₂ H ₄) ₃ –(MeOH) _{0.33}](ClO ₄) ₄] _n (3)	{[Cu ₄ (Me ₂ bpm) ₃ (CO) ₃ (MeCN)]–(PF ₆) ₄ ·0.33MeCN} _n (4)	[Cu ₄ (Me ₂ bpm) ₄ (CO) ₄](BF ₄) ₄ ·4MeOH (5)
Formula	C _{38.32} H _{43.32} B ₄ Cu ₄ F ₁₆ N ₁₃ O _{0.33}	C _{36.33} H ₄₂ Cl ₄ Cu ₄ N ₁₂ O _{16.33}	C ₃₇ H ₃₀ Cu ₄ F ₂₄ N ₁₄ O ₃ P ₄	C ₄₈ H ₅₆ B ₄ Cu ₄ F ₁₆ N ₁₆ O ₈
Formula weight	1292.74	1304.06	1552.79	1586.49
Crystal system	Trigonal	Trigonal	Trigonal	Tetragonal
Space Group	R3	R3	R3	I4 ₂ d
<i>a</i> /Å	14.0511(8)	14.448(14)	14.3797(15)	12.9479(9)
<i>b</i> /Å	14.0511(8)	14.448(14)	14.3797(15)	12.9479(9)
<i>c</i> /Å	22.6054(16)	21.25(2)	23.083(3)	40.274(3)
α (°)	90.0	90.0	90.0	90.0
β (°)	90.0	90.0	90.0	90.0
γ (°)	120.0	120.0	120.0	90.0
<i>V</i> /Å ³	3865.1(4)	3841(6)	4133.6(8)	6751.9(8)
<i>Z</i>	3	3	3	4
<i>D</i> _{calc} /gcm ^{–3}	1.666	1.700	1.871	1.561
<i>F</i> (000)	1966	1976	2298	3200
μ(Mo–Kα)/cm ^{–1}	17.33	19.26	17.72	13.47
<i>T</i> /K	130(2)	119(2)	120(2)	120(1)
Observed reflections	14 763 (<i>R</i> _{int} = 0.0232)	9878 (<i>R</i> _{int} = 0.0385)	10 806 (<i>R</i> _{int} = 0.0401)	20 146 (<i>R</i> _{int} = 0.0245)
Refined reflections	3920 (all data); 3908 (<i>I</i> > 2σ(<i>I</i>))	3420 (all data); 3070 (<i>I</i> > 2σ(<i>I</i>))	4212 (all data); 3882 (<i>I</i> > 2σ(<i>I</i>))	4141 (all data); 3900 (<i>I</i> > 2σ(<i>I</i>))
<i>R</i>	0.0273 (all data)	0.0574 (all data)	0.0639 (all data)	0.0442 (all data)
<i>R</i> ₁	0.0272 (<i>I</i> > 2σ(<i>I</i>))	0.0494 (<i>I</i> > 2σ(<i>I</i>))	0.0567 (<i>I</i> > 2σ(<i>I</i>))	0.0420 (<i>I</i> > 2σ(<i>I</i>))
w <i>R</i> ₂	0.0723 (all data)	0.1293 (all data)	0.1231 (all data)	0.1179 (all data)
GOF	1.106	1.122	1.076	1.046

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|. R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| (F_o > 4\sigma(F_o)). wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}.$$

**Fig. 1** X-ray structures of complex **2** encapsulating one MeOH molecule in the small Cu₃ cavity (a) and four BF₄[–] anions in the large Cu₉ cavity (b).

{[Cu₄(Me₂bpm)₃(C₂H₄)₃(MeOH)_{0.33}](ClO₄)₄]_n (**3**). A similar reaction of [Cu(C₂H₄)]_nClO₄ with Me₂bpm in MeOH under C₂H₄ gave red plate crystals of complex **3**. The X-ray crystal structures of Cu(I)–Me₂bpm/C₂H₄–ClO₄ complex **3** are shown in Fig. 3. The crystal packing structures are deposited in Fig. S1 as ESI.† The metallacalix[3]arene structures of the [Cu₃(Me₂bpm)₃]³⁺ framework with three legs of C₂H₄ are linked through another Cu

**Fig. 2** X-ray crystal packing structures of complex **2** along the *c* (a) and *a*-axis (b). The encapsulating MeOH and BF₄[–] anions were omitted for clarity.

atom with the disordered MeOH in the terminal N atom of Me₂bpm to produce a 2D sheet structure with small Cu₃ and large Cu₉ cavities. The repeating unit of four-layered 2D sheet structures is arranged in parallel along the *c*-axis in the unit cell. Although the 2D sheet structure of complex **3** is therefore similar to that of Cu(I)–Me₂bpm/C₂H₄–BF₄ adduct **2**, the structural difference between Cu(I)–Me₂bpm/C₂H₄ adducts **2** and **3** is that the metallacalix[3]arene structures of [Cu₃(Me₂bpm)₃]³⁺ are linked through the Cu atom with the disordered MeOH in contrast to the linkages through the Cu atom with the disordered MeCN in complex **2**. It should be noted that the small triangular Cu₃ cavities with neighbouring Cu⋯Cu distances of 6.12 Å are empty. In the large Cu₉ cavity, one ClO₄[–] anion is surrounding by six Me groups on the upside and three disordered ClO₄[–] anions are accommodated on the downside. There have been few reports about the encapsulation of a ClO₄[–] anion into macrocycles and cages.⁹ This result shows that the ClO₄[–] anion can serve as anion templates in the formation of a 2D sheet Cu(I) C₂H₄ adduct while accompanying a remarkable solvent-dependent effect since the similar reaction

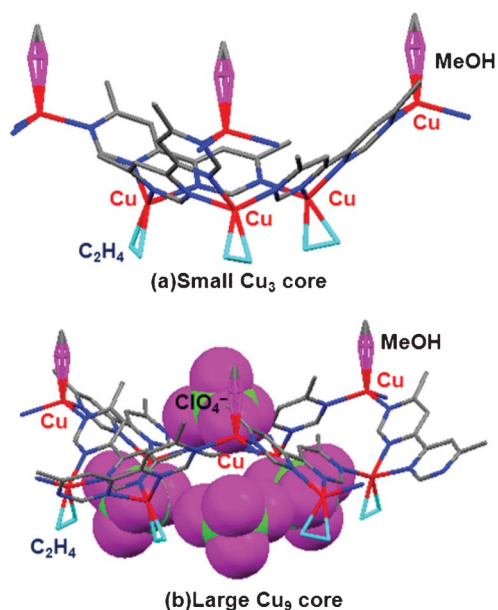


Fig. 3 X-ray structures of complex **3** encapsulating four ClO_4^- anions in the large Cu_9 cavity (b) and the vacant small Cu_3 cavity (a).

of $[\text{Cu}(\text{C}_2\text{H}_4)_n]\text{ClO}_4$ with bpm in Me_2CO under C_2H_4 afforded a 1D ladder $\text{Cu}(\text{I})\text{-bpm}/\text{C}_2\text{H}_4\text{-ClO}_4$ adduct $\{[\text{Cu}_3(\text{bpm})_2(\text{C}_2\text{H}_4)_2](\text{ClO}_4)_3\}_n$.^{4a} Based on the experimental facts in $\text{Cu}(\text{I})\text{-C}_2\text{H}_4$ adducts **1–3**, it was concluded that the reactions of $\text{Cu}(\text{I})$ ion with $\{\text{BF}_4^-$ or $\text{ClO}_4^-\}$ anions and the related bpm ligands in MeOH under C_2H_4 preferentially can produce 2D sheet $\text{Cu}(\text{I})\text{-C}_2\text{H}_4$ adducts. In the coordinated C_2H_4 , the $\text{C}=\text{C}$ distance of 1.323(10) Å is similar to those (1.31(2) for **1**; 1.340(6) Å for **2**) of related

$\text{Cu}(\text{I})\text{-C}_2\text{H}_4$ adducts **1** and **2**. The $\text{C}=\text{C}$ distance is within those (1.30(1)–1.366(6) Å) in the tetrahedral $\text{Cu}(\text{I})\text{-C}_2\text{H}_4$ complexes^{5b,j} and related $\text{Cu}(\text{I})\text{-bpm}/\text{C}_2\text{H}_4\text{-BF}_4$ complex **1**.^{4a}

$\{[\text{Cu}_4(\text{Me}_2\text{bpm})_3(\text{CO})_3(\text{MeCN})](\text{PF}_6)_4 \cdot 0.33\text{MeCN}\}_n$ (**4**). Further attempts to react $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ with Me_2bpm in MeOH under CO afforded dark reddish-brown crystals of complex **4**. The X-ray crystal structures of $\text{Cu}(\text{I})\text{-Me}_2\text{bpm}/\text{CO}\text{-PF}_6$ complex **4** are shown in Fig. 4. The crystal packing structures of complex **4** are deposited in Fig. S2, ESI.† Each Cu atom is coordinated by three N atoms in chelate and bridging sites of Me_2bpm and one CO molecule in the distorted tetrahedral geometry. Three Cu atoms are bridged by three Me_2bpm ligands to form a metallacalix[3]arene structure with three legs of CO. These metallacalix[3]arene structures are linked through another Cu atom with the disordered MeCN in the terminal N atom of Me_2bpm to produce a 2D sheet structure with small Cu_3 and large Cu_9 cavities. This result indicates that the preparative approach established in $\text{Cu}(\text{I})\text{-C}_2\text{H}_4$ adducts **1–3** can apply equally to the self-assembly of the targeted 2D sheet $\text{Cu}(\text{I})\text{-CO}$ adduct. Contrary to $\text{Cu}(\text{I})\text{-C}_2\text{H}_4$ adducts **1–3**, the structural feature of $\text{Cu}(\text{I})\text{-CO}$ adduct **4** is that metallacalix[3]arene structures of $[\text{Cu}_3(\text{Me}_2\text{bpm})_3]^{3+}$ are joined through the Cu atom with the disordered MeCN . Additionally, one MeCN molecule is accommodated in the small triangular Cu_3 cavities with neighbouring $\text{Cu}\cdots\text{Cu}$ distances of 5.98 Å. One PF_6^- anion is surrounding by six Me groups on the upside and three disordered PF_6^- anions are encapsulated on the downside in the large Cu_9 cavities. There have been few reports about the encapsulation of the PF_6^- anion into macrocycles and cages.^{9a,10} In the coordinated CO, the CO molecule is coordinative to the Cu(I) atom approximately linearly at the Cu-C-O angle of 179.8(9)°. The $\text{C}=\text{O}$ distance of 1.129(9) Å is close to that

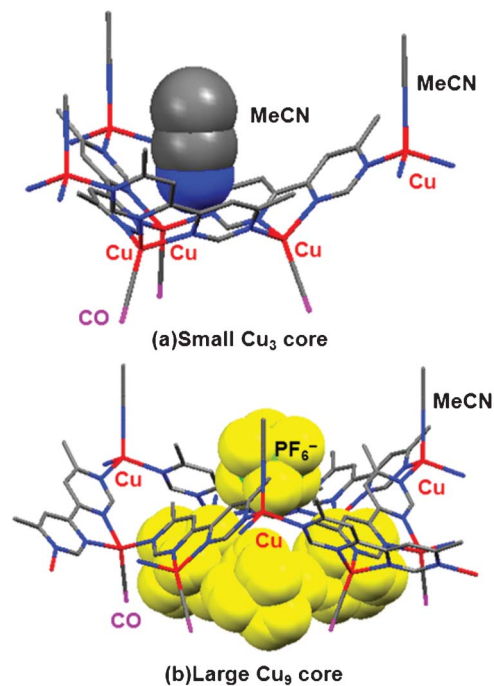


Fig. 4 X-ray structures of complex **4** encapsulating one MeCN molecule in the small Cu_3 cavity (a) and four PF_6^- anions in the large Cu_9 cavity (b).

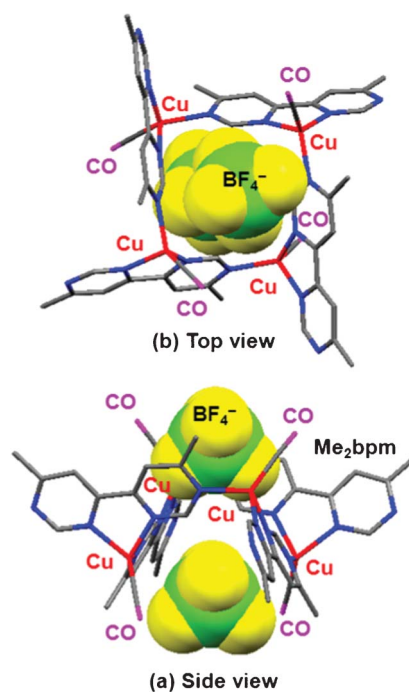


Fig. 5 X-ray structures of complex **5** encapsulating two BF_4^- anions in the Cu_4 cavity. Side (a) and top views (b).

(1.13 Å) of the metal-free CO and those (1.113(5)–1.128(5) Å) in tetrahedral Cu(I)–CO complexes with three N-donor atoms.^{4c,11}

[Cu₄(Me₂bpm)₄(CO)₄](BF₄)₄·4MeOH (5). In contrast to polymeric Cu(I)–Me₂bpm/CO–PF₆ adduct **4**, the similar reaction of [Cu(MeCN)₄]BF₄ with Me₂bpm in MeOH under CO afforded yellowish–brown crystals of complex **5**. The crystal structure of Cu(I)–Me₂bpm/CO–BF₄ complex **5** is shown in Fig. 5. Each Cu atom is coordinated by three N atoms in the chelating and bridging sites of Me₂bpm and one CO molecule in the distorted tetrahedral geometry. Four Cu atoms are bridged by four Me₂bpm to form a metallamacrocyclic tetranuclear structure. One N atom of the bridging sites in the Me₂bpm ligand is coordinatively unsaturated. Two of the four BF₄[−] anions are functionally accommodated in the upper and lower cavities of the [Cu₄(Me₂bpm)₄] framework, enhancing the stabilization of metallamacrocycles.^{4a,c,d} Therefore, the structure of Cu(I)–Me₂bpm/CO adduct **5** is largely different from those of the expected 2D Cu(I)–Me₂bpm/{C₂H₄, CO} adducts **2–4**. This result is suggested that the anion sizes and shapes were significantly recognized as a template in the formation process of Cu(I)–Me₂bpm/CO adducts: the smaller tetrahedral BF₄[−] anion preferentially can induce metallamacrocyclic Cu(I)–Me₂bpm/CO adduct **5** and the larger octahedral PF₆[−] anion can produce 2D sheet Cu(I)–Me₂bpm/CO adduct **4**. The encapsulations of the BF₄[−] anion into macrocycles and cage compounds have been limited.^{4a,4d,9a,9b,10a,12} In the coordinated CO, the Cu–C–O angle of 175.8(6)° is slightly bent. The C≡O distance of 1.092(6) Å is shorter than that (1.13 Å) of the metal-free CO as well as those (1.113(5)–1.128(5) Å) in tetrahedral Cu(I)–CO complexes with three N-donor atoms.^{4c,11}

TG-DTA curves, variable-temperature XRPD spectra, and IR spectra of Cu(I)–Me₂bpm/{C₂H₄, CO} complexes

Thermogravimetric analysis (TG-DTA) was carried out under 20 ml min^{−1} flowing N₂ gas for Cu(I)–Me₂bpm/{C₂H₄, CO} complexes **2**, **4**, and **5** except for the explosive Cu(I)–Me₂bpm/C₂H₄–ClO₄ complex **3**. The temperature was ramped at a rate of 5° min^{−1} from 20 to 400 °C. As shown in Fig. 6, the 2D sheet

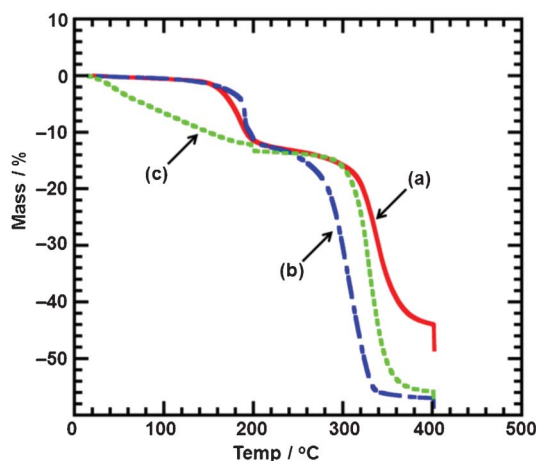


Fig. 6 TG-DTA curves of complexes **2**, **4** and **5** under flowing N₂ gas. Solid line (a) for complex **2**, dashed–dotted line (b) for complex **4** and broken line (c) for complex **5**.

Cu(I)–Me₂bpm/C₂H₄–BF₄ complex **2** displayed a mass loss of two-step curves at 20–205 °C (sharp, 11.9%) and 205–400 °C (sharp, 32.3%). The mass loss of 11.9% at the first step is correlated with the elimination of three C₂H₄, 0.33 MeOH and one CH₃CN molecules (calcd. 10.5%). The sharp curve with distinct steps suggests that complex **2** became more thermodynamically stable, in comparison to the gentle curve of the related Cu(I)–bpm/C₂H₄–BF₄ complex **1**.^{4a} The 2D sheet Cu(I)–Me₂bpm/CO–PF₆ adduct **4** showed a mass loss of two-step curves at 20–205 °C (sharp, 11.9%) and 205–360 °C (sharp, 44.6%). The mass loss of 11.9% at the first step is correlated with the elimination of three CO and two CH₃CN molecules (calcd. 10.7%). In contrast, tetranuclear Cu(I)–Me₂bpm/CO–BF₄ adduct **5** showed a mass loss of two-step curves at 20–205 °C (gentle, 13.4%) and 205–400 °C (sharp, 42.7%). The mass loss of 13.4% at the first step is correlated with the elimination of four CO and four H₂O molecules (calcd. 12.0%).

To determine the thermochemical stability of Cu(I)–Me₂bpm/{C₂H₄, CO} adducts, the variable-temperature XRPD spectra of Cu(I)–Me₂bpm/C₂H₄–BF₄ complex **2** were representatively measured with respect to each 20 °C at a rate of temperature increase of 10° min^{−1} from 30 to 290 °C (Fig. 7). The measured diffraction pattern of complex **2** is very consistent with the simulated pattern. The X-ray diffraction intensity revealed that the original diffraction pattern was changed to another diffraction pattern at 110–130 °C, and subsequently the crystalline

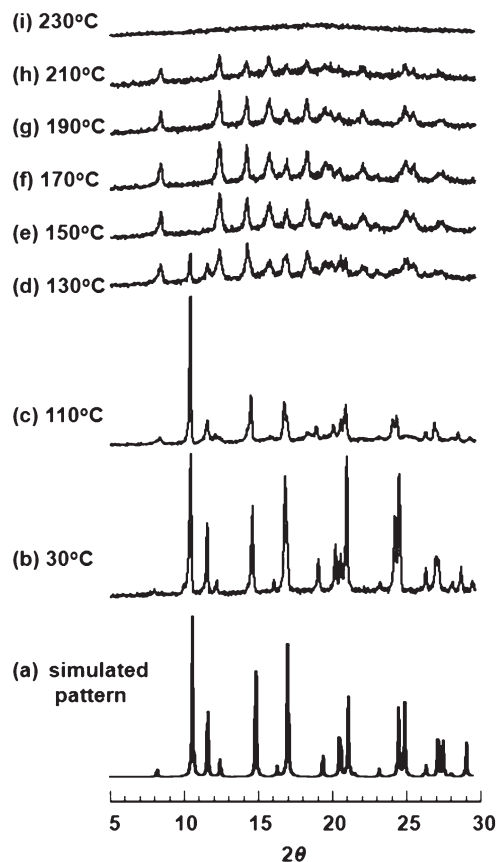


Fig. 7 The simulated XRPD pattern (a) and variable-temperature XRPD spectra (b)–(i) with respect to each 20 °C in 30–290 °C of complex **2**.

disappeared at 210–230 °C. This result shows that the 2D sheet framework of the $\{[\text{Cu}_4(\text{Me}_2\text{bpm})_3](\text{BF}_4)_4\}_n$ moiety should be maintained up to around 200 °C with the elimination of the coordinated C_2H_4 and CH_3CN molecules and the solvated MeOH molecules, although it is now difficult to describe the detailed structural changes by the elimination of individual molecules. This consideration is very consistent with the suggestions obtained from the TG-DTA curves.

The $\nu_{\text{C}=\text{C}}$ bands of $\text{Cu}(\text{I})\text{--Me}_2\text{bpm}/\text{C}_2\text{H}_4$ adducts **2** and **3** are observed at 1542 and 1543 cm^{-1} [metal-free C_2H_4 , 1623 cm^{-1}]; these values are close to that (1545 cm^{-1}) of the related $\text{Cu}(\text{I})\text{--bpm}/\text{C}_2\text{H}_4$ complex **1**.^{4a} In contrast, the $\nu_{\text{C}=\text{O}}$ bands of $\text{Cu}(\text{I})\text{--Me}_2\text{bpm}/\text{CO}$ adducts **4** and **5** appear at 2126 and 2110 cm^{-1} [metal-free CO , 2143 cm^{-1}]; these values are higher than those (2063–2119 cm^{-1}) in cationic and neutral tetrahedral $\text{Cu}(\text{I})\text{--CO}$ complexes with three N-donor atoms.^{5l,11a,b,d,e}

Conclusion

As summarized in Scheme 1, the reaction of the $\text{Cu}(\text{I})$ ion with a BF_4^- anion and Me_2bpm instead of bpm in MeOH under C_2H_4 afforded the 2D sheet $\text{Cu}(\text{I})\text{--Me}_2\text{bpm}/\text{C}_2\text{H}_4\text{--BF}_4$ complex **2** with small Cu_3 and larger Cu_9 cavities. It was proved that a 2D sheet $\text{Cu}(\text{I})\text{--Me}_2\text{bpm}/\text{C}_2\text{H}_4$ adduct can be reasonably produced by the combination of a $\text{Cu}(\text{I})$ ion with a BF_4^- anion and Me_2bpm in a manner similar to $\text{Cu}(\text{I})\text{--bpm}/\text{C}_2\text{H}_4\text{--BF}_4$ complex **1**.^{4a} Although the 2D sheet framework apparently resembles $\text{Cu}(\text{I})\text{--C}_2\text{H}_4$ adducts **1** and **2**, the accommodation manner of anions and solvents in complex **2** is different from that of complex **1** in the small Cu_3 and larger Cu_9 cavities: one MeOH molecule is accommodated in the small triangular Cu_3 cavity, and one BF_4^- anion is surrounding by six Me groups on the upside and three BF_4^- anions are accommodated on the downside in the large Cu_9 cavity. Consequently, the crystal packing structure of complex **2** is different from that of complex **1**: the repeating unit of four-layered 2D sheet structures is arranged in parallel along the c -axis in the unit cell. It is suggested that these structural differences were probably caused by the steric effect of the Me group in the Me_2bpm ligand. The reaction of $[\text{Cu}(\text{C}_2\text{H}_4)_n]\text{ClO}_4$ with Me_2bpm in MeOH under C_2H_4 gave the similar 2D sheet $\text{Cu}(\text{I})\text{--Me}_2\text{bpm}/\text{C}_2\text{H}_4\text{--ClO}_4$ complex **3** with small Cu_3 cavities and large Cu_9 cavities. It is proved that the ClO_4^- anion can serve as anion templates in the formation of a 2D sheet $\text{Cu}(\text{I})\text{--C}_2\text{H}_4$ adduct with accompanying a remarkable solvent-dependent effect since the similar reaction of $[\text{Cu}(\text{C}_2\text{H}_4)_n]\text{ClO}_4$ with bpm in Me_2CO under C_2H_4 afforded a 1D ladder $\text{Cu}(\text{I})\text{--bpm}/\text{C}_2\text{H}_4\text{--ClO}_4$ adduct.^{4a} Based on the experimental facts in $\text{Cu}(\text{I})\text{--C}_2\text{H}_4$ adducts **1–3**, it was concluded that the reactions of a $\text{Cu}(\text{I})$ ion with $\{\text{BF}_4^- \text{ or } \text{ClO}_4^-\}$ anions and the related bpm ligands in MeOH under C_2H_4 preferentially can produce 2D sheet $\text{Cu}(\text{I})\text{--C}_2\text{H}_4$ adducts under the direction of anions and solvents. As a further investigation, we attempted to self-assemble a targeted 2D sheet $\text{Cu}(\text{I})\text{--CO}$ adduct by the applications of a preparative approach established in 2D sheet $\text{Cu}(\text{I})\text{--C}_2\text{H}_4$ adducts. The reactions of $[\text{Cu}(\text{MeCN})_4]\text{X}$ ($\text{X} = \text{PF}_6^-$ or BF_4^-) with Me_2bpm in MeOH under CO anion-selectively afforded the 2D sheet $\text{Cu}(\text{I})\text{--Me}_2\text{bpm}/\text{CO--PF}_6$ complex **4** and the metallamacrocyclic tetranuclear $\text{Cu}(\text{I})\text{--Me}_2\text{bpm}/\text{CO--BF}_4$ complex **5**. It was confirmed that the anion sizes and shapes

were significantly recognized as a template in the formation process of $\text{Cu}(\text{I})\text{--Me}_2\text{bpm}/\text{CO}$ adducts. These new findings are expected to contribute to the design and architecture of not only the few 2D sheet $\text{Cu}(\text{I})\text{--C}_2\text{H}_4$ adducts but also structural and functional new inorganic anion receptors, in combination with previous results regarding the related $\text{Cu}(\text{I})\text{--}\{\text{pprd}, \text{bpm}\}/\text{C}_2\text{H}_4$ complexes.⁴

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 20550069 and 23550085) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

References

- (a) D. H. Busch, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1992, **12**, 389; (b) F. Diederich, P. J. Stang, *Templates Organic Synthesis*, Wiley-VCH, Weinheim, 2000; (c) C. A. Schalley, F. Voegtle and K. H. Doetz, *Templates in Chemistry I. Top Curr Chem.*, 2005, 248; (d) C. A. Schalley, F. Voegtle and K. H. Doetz, *Templates in Chemistry II. Top Curr Chem.*, 2005, 249.
- (a) A. Bianchi, K. Bowman-James, E. García-España, *Supramolecular Chemistry of Anions*, Wiley-VCH, Weinheim, 1997; (b) P. A. Gale, *Coord. Chem. Rev.*, 2000, **199**, 181; (c) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486; (d) P. A. Gale, *Coord. Chem. Rev.*, 2001, **213**, 79; (e) P. A. Gale, *Coord. Chem. Rev.*, 2003, **240**, 191; (f) R. Vilar, *Angew. Chem., Int. Ed.*, 2003, **42**, 1460; (g) N. Gimeno and R. Vilar, *Coord. Chem. Rev.*, 2006, **250**, 3161; (h) R. Vilar, *Struct. Bonding*, 2008, **129**, 175; (i) R. Vilar, *Eur. J. Inorg. Chem.*, 2008, 357; (j) C. Caltagirone and P. A. Gale, *Chem. Soc. Rev.*, 2009, **38**, 520.
- D. A. Beauchamp and S. J. Loeb, *Dalton Trans.*, 2007, 4760.
- (a) M. Maekawa, T. Tominaga, K. Sugimoto, T. Okubo, T. Kuroda-Sowa, M. Munakata and S. Kitagawa, *CrystEngComm*, 2012, **14**, 1345; (b) M. Maekawa, T. Tominaga, T. Okubo, T. Kuroda-Sowa and M. Munakata, *Eur. J. Inorg. Chem.*, 2009, 4225; (c) M. Maekawa, H. Konaka, T. Minematsu, T. Kuroda-Sowa, M. Munakata and S. Kitagawa, *Chem. Commun.*, 2007, 5179; (d) M. Maekawa, A. Nabei, T. Tominaga, K. Sugimoto, T. Minematsu, T. Okubo, T. Kuroda-Sowa, M. Munakata and S. Kitagawa, *Dalton Trans.*, 2009, 415.
- (a) H. V. R. Dias and J. Wu, *Eur. J. Inorg. Chem.*, 2008, 509; (b) J. S. Thompson, R. L. Harlow and J. F. Whitney, *J. Am. Chem. Soc.*, 1983, **105**, 3522; (c) J. S. Thompson and J. F. Whitney, *Inorg. Chem.*, 1984, **23**, 2813; (d) H. Masuda, N. Yamamoto, T. Taga, K. Machida, S. Kitagawa and M. Munakata, *J. Organomet. Chem.*, 1987, **322**, 121; (e) M. Munakata, T. Kuroda-Sowa, M. Maekawa and M. Nakamura, *Inorg. Chem.*, 1994, **33**, 1284; (f) J. Dai, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga and M. Munakata, *Inorg. Chem.*, 1997, **36**, 2688; (g) Y. Suenaga, L.-P. Wu, T. Kuroda-Sowa, M. Munakata and M. Maekawa, *Polyhedron*, 1997, **16**, 67; (h) B. F. Straub, F. Eiseenträger and P. Hofmann, *Chem. Commun.*, 1999, 2507; (i) X. Dai and T. H. Warren, *Chem. Commun.*, 2001, 1998; (j) H. V. R. Dias, H.-L. Lu, H.-J. Kim, S. A. Polach, T. K. H. H. Goh, R. G. Browning and C. J. Lovely, *Organometallics*, 2002, **21**, 1466; (k) H. V. R. Dias, X. Wang and H. V. K. Diyabalanage, *Inorg. Chem.*, 2005, **44**, 7322; (l) H. V. R. Dias, S. Singh and J. A. Flores, *Inorg. Chem.*, 2006, **45**, 8859; (m) G. Santiso-Quinones, A. Reisinger, J. Slattery and I. Krossing, *Chem. Commun.*, 2007, 5046; (n) J. A. Flores and H. V. R. Dias, *Inorg. Chem.*, 2008, **47**, 4448; (o) M. J. Bainbridge, J. R. L. Smith and P. H. Walton, *Dalton Trans.*, 2009, 3143; (p) J. A. Flores, V. Badarinarayana, S. Singh, C. J. Lovely and H. V. R. Dias, *Dalton Trans.*, 2009, 7648; (q) X. Kou and H. V. R. Dias, *Dalton Trans.*, 2009, 7529; (r) C. Martin, J. M. Munoz-Molina, A. Locati, E. Alvarez, F. Maseras, T. R. Belderrain and P. J. Perez, *Organometallics*, 2010, **29**, 3489.
- G. J. Gubus, *Inorg. Synth.*, 1979, **19**, 90.
- E. Ioachim, E. A. Medlycott, M. I. J. Polson and G. S. Hanan, *Eur. J. Org. Chem.*, 2005, 3775.

- 8 (a) G. J. H. v. Nes and A. Vos, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1979, **B35**, 2593; (b) I. Krossing and A. Reisinger, *Angew. Chem., Int. Ed.*, 2003, **42**, 5725 and references cited therein.
- 9 (a) R.-D. Schnebeck, E. Freisinger and B. Lippert, *Angew. Chem., Int. Ed.*, 1999, **38**, 168; (b) X.-T. Meng, Q.-S. Li, F.-B. Xu, H.-B. Song, C. E. Anson and Z.-Z. Zhang, *Inorg. Chem.*, 2006, **45**, 7986; (c) C. S. Campos-Fernández, B. L. Schottel, H. T. Chifotides, J. K. Bera, J. Bacsá, J. M. Koomen, D. H. Russell and K. R. Dunbar, *J. Am. Chem. Soc.*, 2005, **127**, 12909.
- 10 (a) R.-D. Schnebeck, E. Freisinger, F. Glahé and B. Lippert, *J. Am. Chem. Soc.*, 2000, **122**, 1381; (b) D. A. McMorran and P. J. Steel, *Angew. Chem., Int. Ed.*, 1998, **37**, 3295.
- 11 (a) K. Singh, J. R. Long and P. Stavropoulos, *Inorg. Chem.*, 1998, **37**, 1073; (b) R. R. Conry, G. Ji and A. A. Tipton, *Inorg. Chem.*, 1999, **38**, 906; (c) A. J. Blake, D. A. Carling, M. W. George, P. Hubberstey, R. L. Garcia and C. Wilson, *Acta Cryst.*, 2002, **E58**, m41; (d) M. Costas, R. Xifra, A. Llobet, M. S. J. Robles, T. Parella, H. Stoeckli-Evans and M. Neuburger, *Inorg. Chem.*, 2003, **42**, 4456; (e) H. V. R. Dias and T. K. H. H. Goh, *Polyhedron*, 2004, **23**, 273.
- 12 (a) S. Mann, G. Huttner, L. Zsolnai and K. Heinze, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2808; (b) M. Staffilani, K. S. B. Hancock, J. W. Steed, K. T. Holman, J. L. Atwood, R. K. Juneja and R. S. Burkhhalter, *J. Am. Chem. Soc.*, 1997, **119**, 6324; (c) J. S. Fleming, K. L. V. Mann, C.-A. Carraz, E. Psillakis, J. C. Jeffery, J. A. McCleverty and M. D. Ward, *Angew. Chem., Int. Ed.*, 1998, **37**, 1279; (d) C. S. Campos-Fernández, R. Clerac and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 1999, **38**, 3477; (e) H. Amouri, M. N. Rager, F. Cagnol and J. Vaissermann, *Angew. Chem., Int. Ed.*, 2001, **40**, 3636; (f) H. Amouri, L. Mimassi, M. N. Rager, B. E. Mann, C. Guyard-Duhayon and L. Raehm, *Angew. Chem., Int. Ed.*, 2005, **44**, 4543; (g) S. P. Argent, H. Adams, T. Riis-Johannessen, J. C. Jeffery, L. P. Harding, O. Mamula and M. D. Ward, *Inorg. Chem.*, 2006, **45**, 3905.