Order of the coordinating ability of polyatomic monoanions established from their interaction with a disilver(I) metallacyclophane skeleton†

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An ordered sequence of the coordinating ability of a series of polyatomic monoanions has been established on the basis of structural parameters derived from their interaction with a disilver(I) metallacyclophane skeleton in isostructural complexes.

The study of anions in connection with host–guest chemistry, including the development of cationic receptors for anion recognition[1,2] and the design of anionic hosts for the entrapment of cations,[3] has drawn a great deal of interest during the past two decades. Anion coordination chemistry as applied to catalysis,[4a,b] templated reactions,[4c–e] ionic liquids,[4f,g] lithium batteries,[4h,i] biological processes,[4j,k] industrial chemical processing,[4l,m] environmental pollution,[4m–o] and health-related perspectives[4m] has also witnessed enormous progress. Some notable recent papers have addressed the issue of anion-controlled self-assembly.[4c–e,5,6] However, thus far only a few attempts have been made to assess and compare the coordinating ability of commonly used anions,[6] a detailed knowledge of which is a prerequisite for precise control over the course and outcome of supramolecular assembly.

The coordination diversity of di-2-pyridinylmethanone (di-2-pyridyl ketone)[7] in transition metal and supramolecular chemistry has prompted us to investigate the ligand behavior of its positional isomer 2-pyridinyl-4-pyridinylmethanone (L). Noting that the spherical d^{10} electronic configuration of silver(I) does not impose a preferred coordination geometry and number in its interaction with anionic ligands,[8] we have prepared a series of isostructural[9] dimeric silver(I) complexes classified into three types: $[Ag(L)]_2X_2$ (X = BF_4 **1**; ClO_4 **2**; NO_3 **3**; ClO_3 **4**), $\{[Ag(L)(X)]_2\}_\infty$ (X = NO_2 **5**; HCO_2 **6**; CF_3CO_2 **7**; CF_3SO_3 **8**) and $[Ag(L)(CH_3CN)_2]_2X_2$ (X = PF_6 **9**). All nine compounds possess the same flexible centrosymmetric $Ag_2L_2^{2+}$ metallacyclophane[10] skeleton, to which various polyatomic monoanions are attached to the silver atom through coordination bonds or weak electrostatic interactions, with the lone exception of **9**. With the structural parameters obtained from single-crystal X-ray analysis of this series of isostructural dinuclear silver(I) complexes,‡ together with competition experiments conducted in solution, we are able to rank the commonly used polyatomic monoanions according to their coordinating ability.

Complexes **1–6** constitute an isomorphous series, all crystallizing in space group *Pbca*. The dimeric skeletons in complexes **1–4** are stabilized by weak interactions between silver(I) and the anionic ligand atoms, as exemplified by **3** in Fig. 1a. In complexes **5–7**, the counter anions are bound to the silver atoms of the metallacycles by coordination bonds, as shown in Fig. 1b with **5** as an example. Both above-mentioned metal–ligand binding modes exist in complex **8** (Fig. 1c). The anions in complexes **5–8** also serve as bridging ligands, linking the $Ag_2L_2^{2+}$ units into one- or two-dimensional polymeric structures. Notably, in complex **9** the silver atom does not interact with the hexafluorophosphate anion but is coordinated by two acetonitrile molecules (Fig. 1d). Intramolecular Ag···π and π···π interactions also contribute to the stabilization of the dinuclear metallacycles (see Supplementary Information for details†) Our attempts at preparing similar metallacyclophane complexes with pseudo-halide and heavier halide ions (Y) were unsuccessful owing to the ready precipitation of AgY, and the use of fluoride did not lead to crystallization.

An anionic ligand with stronger coordinating ability interacts with the silver atom at a shorter distance, and *vice versa*. For the series of monoanions in the present study, the weighted averages of closest Ag···anion contacts within 2.8 Å in the complexes decrease in the sequence **1** > **2** > **8** ~ **3** > **4** > **5** ~ **6** > **7** (Chart 1). In the case of complex **9** (space group $P2_1/n$), the absence of PF_6^- in the

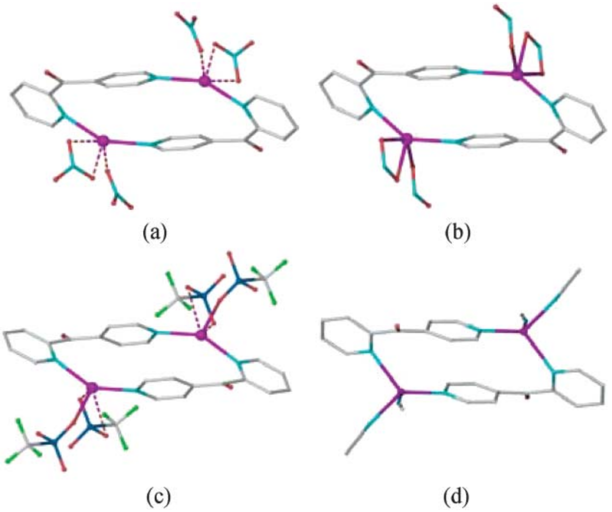

Fig. 1 Parts (a) to (d) show the cyclic $Ag_2L_2^{2+}$ skeleton stabilized by interaction of Ag(I) with NO_3^- (complex **3**), NO_2^- (**5**), $CF_3SO_3^-$ (**8**) anions and CH_3CN molecules (**9**), respectively. Color codes: purple: Ag; light gray: C; red: O; turquoise: N; green: F; deep blue: S.

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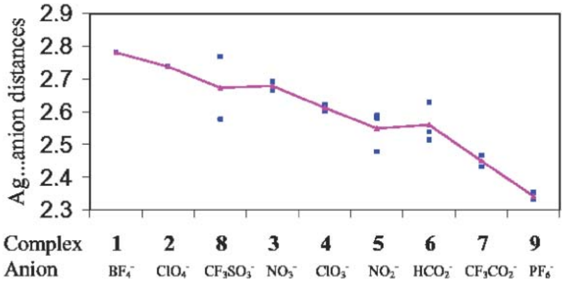
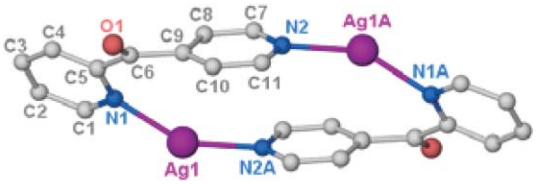


Chart 1 Trend of Ag···anion distances (Å) in complexes **1–9** based on the structural data listed in Table S1. A line is drawn through the weighted average values.

coordination sphere of the silver atom indirectly indicates that it is the weakest coordinating ligand in the list, since acetonitrile was used as a solvent in the preparation of all nine complexes. On the other hand, stronger coordination ability of the anions can reduce the plus charge on the silver atom within the metallacycle and hence increase Ag–N bond distances, being consistent with the trend **1** < **2** < **8** < **3** < **4** < **7** < **5** < **6** < **9** shown in Table 1 and Chart S1. By the same token, attachment of various anionic ligands to the metallacycle affects its geometry to different extents, so that the measured structural parameters can also be used for ranking them in the order of increasing coordinating ability. The shape of the dinuclear skeleton in complexes **1–9** gradually changes from a sharply angled parallelogram towards a rectangle (Table S2 and Chart S4), reflecting the effect of the different coordinating abilities of the complementary ligands (counter anions in **1–8** and CH_3CN in **9**). These results indicate that the $Ag_2L_2^{2+}$ system is quite malleable and responsive to minor variation in the coordinating ability of the anionic ligands.

For the monoanions in isomorphous complexes **1–6** which belong to space group *Pbca*, taking all structural information into consideration, an ordered sequence of decreasing coordinating ability can be arranged as $HCO_2^- \sim NO_2^- > ClO_3^- > NO_3^- > ClO_4^- > BF_4^-$. Although complexes **7** and **8** both crystallize in space group $P\bar{1}$, the large anions $CF_3SO_3^-$ and $CF_3CO_2^-$ do not fit into adjacent positions in the sequence. Judging from Table 1 and Chart 1, it can be inferred that NO_3^- is about the same or slightly superior to $CF_3SO_3^-$. However, one can only conclude that $CF_3CO_2^-$ has a similar coordinating ability to HCO_2^- and NO_2^-, since Table 1 indicates the order $HCO_2^- \sim NO_2^- > CF_3CO_2^-$ while Chart 1 suggests that $CF_3CO_2^- > HCO_2^- \sim NO_2^-$.

Table 1 List of Ag–N distances and N–Ag–N angles in **1–9**



Complex	Anion	Bond lengths/Å and angles/°		
		Ag–N1A	Ag–N2	N1A–Ag–N2
1	BF_4^-	2.217(4)	2.180(4)	160.2(2)
2	ClO_4^-	2.235(3)	2.200(2)	158.9(1)
8	$CF_3SO_3^-$	2.258(3)	2.234(3)	144.9(1)
3	NO_3^-	2.281(4)	2.249(4)	149.4(1)
4	ClO_3^-	2.313(4)	2.248(4)	153.5(2)
5	NO_2^-	2.327(2)	2.304(2)	139.0(1)
6	HCO_2^-	2.347(2)	2.303(2)	142.6(1)
7	$CF_3CO_2^-$	2.321(4)	2.276(4)	140.9(1)
9	PF_6^-	2.401(3)	2.248(3)	123.8(1)

Based on the X-ray structural parameters, the coordinating ability of the whole series of nine polyatomic monoanions can be arranged in the order:

$$NO_2^- \sim HCO_2^- > CF_3CO_2^- > ClO_3^- > NO_3^- > CF_3SO_3^- > ClO_4^- > BF_4^- > PF_6^-.$$

The trends of N–Ag–N bond angles (Table 1) and intramolecular Ag···π and π···π interactions (Table S2) also support this sequence but only to a more limited degree (Chart S2 and S3).

Complexes **1–9** are soluble in water and common organic solvents such as methanol and acetonitile, so we performed crystallization experiments[11] with co-existing anions under the same conditions used for preparing these complexes (Table S4), anticipating that competition between anions for preferential incorporation into the resulting crystal may provide complementary information on their relative coordinating ability. Notwithstanding the easy decomposition of $\{[Ag(L)(HCO_2)]_2\}_\infty$ **6**, the results of competition experiments involving isomorphous complexes **1–6** (space group *Pbca*) are in accord with the proposed sequence. However, poor agreement was obtained with $CF_3CO_2^-$ and $CF_3SO_3^-$ as competing anions, which may be attributed to their bulk and the crystallization of complexes **7** and **8** in a different space group $P\bar{1}$ with low symmetry.

The rapid development in supramolecular coordination chemistry over the past twenty years has witnessed great achievement in the generation of both discrete molecular and extended solid-state architectures through crystal engineering.[12] Strategies of rational design have mainly focused on spontaneous assembly by metal–ligand coordination and non-covalent interactions that include hydrogen bonding and weak electrostatic interactions.[13] In view of the crucial role of anions in supramolecular organization, the establishment of an ordered sequence of their coordinating ability is useful not only in the context of anion recognition but also in the rational construction of perceived supramolecular aggregates and infinite frameworks with diverse architectures and structure-related properties.

The present ordered sequence of polyatomic monoanions is quite different from that put forward by Jung *et al.*,[6a] which was deduced mainly from the crystal data of non-identical systems and experiments on anion exchange: $NO_3^- > CF_3CO_2^- > CF_3SO_3^- > PF_6^- > ClO_4^- > BF_4^-$. Our ordering encompasses a wider range of anions and is based on a self-consistent set of X-ray structural data of nine isostructural crystalline silver(I) complexes, of which six constitute an isomorphous series.

The generality and reliability of the present ordered sequence of coordinating ability of commonly used polyatomic monoanions should be of value in future development of the coordination and supramolecular chemistry of anions.

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Notes and references

‡ Crystal data: **1**, $C_{11}H_8BF_4N_2OAg$, M = 378.87, orthorhombic, space group $Pbca$, a = 7.8368(4), b = 15.0948(7), c = 20.606(1) Å, V = 2437.5(2) Å^3, Z = 8, 2138 unique MoKα reflections (R_{int} = 0.0426), R_1 = 0.0488, wR_2 = 0.1130 for 1773 observed reflections [$I > 2\sigma(I)$].

2, $C_{11}H_8ClN_2O_5Ag$, M = 391.51, orthorhombic, space group $Pbca$, a = 7.9427(5), b = 15.078(1), c = 20.808(1) Å, V = 2492.0(3) Å^3, Z = 8, 3005 unique MoKα reflections (R_{int} = 0.0274), R_1 = 0.0364, wR_2 = 0.1024 for 2606 observed reflections [$I > 2\sigma(I)$].

3, $C_{11}H_8N_3O_4Ag$, M = 354.07, orthorhombic, space group $Pbca$, a = 7.5654(5), b = 15.162(1), c = 20.531(1) Å, V = 2355.1(3) Å^3, Z = 8, 2819 unique MoKα reflections (R_{int} = 0.0496), R_1 = 0.0467, wR_2 = 0.1241 for 2014 observed reflections [$I > 2\sigma(I)$].

4, $C_{11}H_8ClN_2O_4Ag$, M = 375.51, orthorhombic, space group $Pbca$, a = 7.279(2), b = 15.972(3), c = 21.400(4) Å, V = 2487.9(9) Å^3, Z = 8, 2246 unique MoKα reflections (R_{int} = 0.0691), R_1 = 0.0596, wR_2 = 0.1733 for 2175 observed reflections [$I > 2\sigma(I)$].

5, $C_{11}H_8N_3O_3Ag$, M = 338.07, orthorhombic, space group $Pbca$, a = 7.1774(4), b = 15.4432(9), c = 20.659(1) Å, V = 2289.8(2) Å^3, Z = 8, 2950 unique MoKα reflections (R_{int} = 0.0286), R_1 = 0.0278, wR_2 = 0.0749 for 2600 observed reflections [$I > 2\sigma(I)$].

6, $C_{12}H_9N_2O_3Ag$, M = 337.08, orthorhombic, space group $Pbca$, a = 7.0155(3), b = 15.5043(7), c = 21.059(1) Å, V = 2290.6(2) Å^3, Z = 8, 2961 unique MoKα reflections (R_{int} = 0.0328), R_1 = 0.0303, wR_2 = 0.0816 for 2345 observed reflections [$I > 2\sigma(I)$].

7, $C_{13}H_8F_3N_2O_3Ag$, M = 405.08, triclinic, space group $P\bar{1}$, a = 7.711(2), b = 9.253(2), c = 10.785(2) Å, α = 90.692(5), β = 93.506(5), γ = 112.214(4)°, V = 710.5(3) Å^3, Z = 2, 2475 unique MoKα reflections (R_{int} = 0.0271), R_1 = 0.0403, wR_2 = 0.1028 for 2067 observed reflections [$I > 2\sigma(I)$].

8, $C_{12}H_8F_3N_2O_4SAg$, M = 441.13, triclinic, space group $P\bar{1}$, a = 9.159(1), b = 9.289(1), c = 10.193(1) Å, α = 88.633(3), β = 70.997(2), γ = 64.430(2) °, V = 732.7(2) Å^3, Z = 2, 2543 unique MoKα reflections (R_{int} = 0.0293), R_1 = 0.0312, wR_2 = 0.0827 for 2200 observed reflections [$I > 2\sigma(I)$].

9, $C_{15}H_{14}F_6N_4OPAg$, M = 519.14, monoclinic, space group $P2_1/n$, a = 13.6369(7), b = 7.0728(4), c = 20.142(1) Å, β = 90.196(1)°, V = 1942.7(2) Å^3, Z = 4, 4676 unique MoKα reflections (R_{int} = 0.0371), R_1 = 0.0440, wR_2 = 0.1257 for 3391 observed reflections [$I > 2\sigma(I)$].

CCDC 264193–264201 for **1–9**. See http://dx.doi.org/10.1039/b505919d for crystallographic data in CIF or other electronic format.

1 *Supramolecular Chemistry of Anions*, ed. A. Bianchi, K. Bowman-James and E. García-España, Wiley-VCH, New York, 1997.

2 (*a*) M. W. Hosseini, *Coord. Chem. Rev.*, 2003, **240**, 157–166; (*b*) J. M. Llinares, D. Powell and K. Bowman-James, *Coord. Chem. Rev.*, 2003, **240**, 57–75; (*c*) J. L. Sessler, S. Camiolo and P. A. Gale, *Coord. Chem. Rev.*, 2003, **240**, 17–55; (*d*) V. Amendola, L. Fabbrizzi, C. Mangano, P. Pallavicini, A. Poggi and A. Taglietti, *Coord. Chem. Rev.*, 2001, **219–221**, 821–837; (*e*) J. J. Bodwin, A. D. Cutland, R. G. Malkani and V. L. Pecoraro, *Coord. Chem. Rev.*, 2001, **216–217**, 489–512; (*f*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486–516.

3 T. N. Parac, D. L. Caulder and K. N. Raymond, *J. Am. Chem. Soc.*, 1998, **120**, 8003–8004 and references therein.

4 (*a*) T. Chivers, *Top. Curr. Chem.*, 2003, **229**, 143–159; (*b*) R. Guilard, S. Brandès, C. Tardieux, A. Tabard, M. L'Her, C. Miry, P. Gouerec, Y. Knop and J. P. Collman, *J. Am. Chem. Soc.*, 1995, **117**, 11721–11729; (*c*) M. R. Sambrook, P. D. Beer, J. A. Wisner, R. L. Paul and A. R. Cowley, *J. Am. Chem. Soc.*, 2004, **126**, 15364–15365; (*d*) J. A. Wisner, P. D. Beer, M. G. B. Drew and M. R. Sambrook, *J. Am. Chem. Soc.*, 2002, **124**, 12469–12476; (*e*) C. S. Campos-Fernández, R. Clérac and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 1999, **38**, 3477–3479 and references therein; (*f*) K. A. Fletcher, S. N. Baker, G. A. Baker and S. Pandey, *New J. Chem.*, 2003, **27**, 1706–1712; (*g*) R. A. Brown, P. Pollet, E. McKoon, C. A. Eckert, C. L. Liotta and P. G. Jessop, *J. Am. Chem. Soc.*, 2001, **123**, 1254–1255; (*h*) A. Blazejczyk, W. Wieczorek, R. Kovarsky, D. Golodnitsky, E. Peled, L. G. Scanlon, G. B. Appetecchi and B. Scrosati, *J. Electrochem. Soc.*, 2004, **151**, A1762–A1766; (*i*) H. S. Lee, Z. F. Ma, X. Q. Yang, X. Sun and J. McBreen, *J. Electrochem. Soc.*, 2004, **151**, A1429–A1435; (*j*) M. Haranczyk and M. Gutowski, *J. Am. Chem. Soc.*, 2005, **127**, 699–706; (*k*) N. Sakai and S. Matile, *J. Am. Chem. Soc.*, 2003, **125**, 14348–14356; (*l*) P. Gili and P. A. Lorenzo-Luis, *Coord. Chem. Rev.*, 1999, **193–195**, 747–768; (*m*) S. Mason, T. Clifford, L. Seib, K. Kuczera and K. Bowman-James, *J. Am. Chem. Soc.*, 1998, **120**, 8899–8900 and references therein; (*n*) P. D. Beer and J. B. Cooper, *Calixarenes in Action*, ed. L. Mandolini and R. Ungaro, Imperial College Press, London, UK, 2000, pp. 111–143; (*o*) A. F. D. de Namor and M. Shehab, *J. Phys. Chem. A*, 2004, **108**, 7324–7330.

5 (*a*) L. P. Harding, J. C. Jeffery, T. Riis-Johannessen, C. R. Rice and Z. T. Zeng, *Dalton Trans.*, 2004, 2396–2397; (*b*) S. J. Hong, J. Y. Ryu, J. Y. Lee, C. Kim, S.-J. Kim and Y. Kim, *Dalton Trans.*, 2004, 2697–2701; (*c*) L. P. Harding, J. C. Jeffery, T. Riis-Johannessen, C. R. Rice and Z. T. Zeng, *Chem. Commun.*, 2004, 654–655; (*d*) R. Vilar, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1998, **37**, 1258–1261; (*e*) N. Schultheiss, D. R. Powell and E. Bosch, *Inorg. Chem.*, 2003, **42**, 8886–8890; (*f*) S. Sailaja and M. V. Rajasekharan, *Inorg. Chem.*, 2003, **42**, 5675–5684; (*g*) N.-H. Hu, T. Norifusa and K. Aoki, *Dalton Trans.*, 2003, 335–341; (*h*) M. Du, X.-H. Bu, Y.-M. Guo, H. Liu, S. R. Batten, J. Ribas and T. C. W. Mak, *Inorg. Chem.*, 2002, **41**, 4904–4908; (*i*) J. A. R. Navarro, J. M. Salas, M. A. Romero and R. Faure, *Dalton Trans.*, 1998, 901–904.

6 (*a*) O.-S. Jung, Y. J. Kim, Y.-A. Lee, K.-M. Park and S. S. Lee, *Inorg. Chem.*, 2003, **42**, 844–850; (*b*) Y. J. Kim, K. H. Yoo, K.-M. Park, J. Hong and O.-S. Jung, *Bull. Korean Chem. Soc.*, 2002, **23**, 1744–1748; (*c*) M. W. Glenny, A. J. Blake, C. Wilson and M. Schröder, *Dalton Trans.*, 2003, 1941–1951; (*d*) A. P. Cote and G. K. H. Shimizu, *Coord. Chem. Rev.*, 2003, **245**, 49–64; (*e*) C. Janiak, L. Uehlin, H.-P. Wu, P. Klüfers, H. Piotrowski and T. G. Scharmann, *Dalton Trans.*, 1999, 3121–3131; (*f*) H.-P. Wu, C. Janiak, G. Rheinwald and H. Lang, *Dalton Trans.*, 1999, 183–190; (*g*) M. G. Hill, W. M. Lamanna and K. R. Mann, *Inorg. Chem.*, 1991, **30**, 4687–4960.

7 G. S. Papaefstathiou and S. P. Perlepes, *Comments Inorg. Chem.*, 2002, **23**, 249–274 and references therein.

8 G.-C. Guo and T. C. W. Mak, *Chem. Commun.*, 1999, 813–814.

9 (*a*) L. Fábián and A. Kálmán, *Acta Crystallogr., Sect. B*, 1999, **B55**, 1099–1108; (*b*) L. Fábián and A. Kálmán, *Acta Crystallogr., Sect. B*, 2004, **B60**, 547–558.

10 Some examples of metallacyclophanes: (*a*) B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022–2043; (*b*) C.-Y. Su, Y.-P. Cai, C.-L. Chen, M. D. Smith, W. Kaim and H.-C. zur Loye, *J. Am. Chem. Soc.*, 2003, **125**, 8595–8613; (*c*) M. Munakata, G. L. Ning, Y. Suenaga, T. Kuroda-Sowa, M. Maekawa and T. Ohta, *Angew. Chem., Int. Ed.*, 2000, **39**, 4555–4557.

11 Competition experiments were performed under the same conditions as the preparation of compounds **1–9** (solvent: methanol–acetonitrile; molar ratio: L : AgX_1 : AgX_2 = 2 : 1 : 1 or 1 : 1 : 1), and the products were identified by IR (KBr) and elemental analyses. In a typical run, L (74 mg, 0.4 mmol), $AgNO_2$ (31 mg, 0.2 mmol) and $AgClO_3$ (38 mg, 0.2 mmol) were dissolved in a mixed solvent of 4 ml CH_3CN and 4 ml CH_3OH with stirring at room temperature. After filtration, the resulting solution was allowed to stand overnight to give 20 mg yellow crystals which were identified as complex **5**.

12 (*a*) D. Braga, *Chem. Commun.*, 2003, 2751–2754; (*b*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853–908; (*c*) P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502–518; (*d*) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638–2684; (*e*) D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975–982; (*f*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460–1494; (*g*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417–425.

13 (*a*) H. W. Roesky and M. Andruh, *Coord. Chem. Rev.*, 2003, **236**, 91–119; (*b*) D. Braga, L. Maini, M. Polito, E. Tagliavini and F. Grepioni, *Coord. Chem. Rev.*, 2003, **246**, 53–71; (*c*) D. Braga and F. Grepioni, *Acc. Chem. Res.*, 2000, **33**, 601–608.