

Anion-directed assembly of supramolecular zinc(II) halides with *N,N'*-bis-4-methyl-pyridyl oxalamide

Biing-Chiau Tzeng,^{*a} Bo-So Chen,^a Shih-Yang Lee,^a Wei-Hsin Liu,^a Gene-Hsiang Lee^b and Shie-Ming Peng^b

^a Department of Chemistry and Biochemistry, National Chung Cheng University, 168, University Rd., Min-Hsiung, Chia-Yi, Taiwan 621

^b Department of Chemistry, National Taiwan University, 1, Sec. 4, Roosevelt Road, Taipei, Taiwan 106

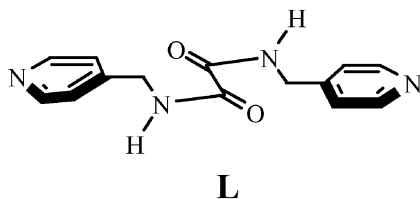
Received (in Durham, UK) 13th June 2005, Accepted 12th August 2005
First published as an Advance Article on the web 1st September 2005

We report here the supramolecular structures and solid state luminescence of zinc(II) halides with *N,N'*-bis-4-methyl-pyridyl oxalamide (**L**), where the supramolecular assembly formed is dependent on the halide, and led to the formation of one-dimensional coordination polymers for Cl ($[\text{ZnCl}_2(\text{L})]_n$) and Br ($[\text{ZnBr}_2(\text{L})]_n$) or a discrete macrocycle for I ($[\text{ZnI}_2(\text{L})]_2$), respectively. The rectangular structure of iodo compounds with pyridyl amide **L** shows an interesting nanotube framework built from $\pi \cdots \pi$ interactions in combination with hydrogen bonding. To our knowledge, these are rare examples of the anion-directed assembly of supramolecular structures. The low energy emission at *ca.* 500 nm for $[\text{ZnI}_2(\text{L})]_2$ is assigned to a ligand-to-metal charge-transfer (LMCT) transition.

Introduction

The widespread use of the coordinative bond approach in the construction of supramolecular coordination compounds with one-, two- and three-dimensional frameworks by self-assembly is well established.¹ Their functionalities² have also been reported recently. Moreover, it is possible, in parallel, to use highly directional hydrogen bonds as a means of controlling self-assembly in supramolecular systems. A variety of discrete and a wide range of infinite coordination architectures with hydrogen-bonded frameworks have been achieved in the last decade.^{3,4} In this regard, the combination of the coordinative bond approach, hydrogen bonding and/or other weak interactions has recently been recognized as a very powerful and versatile strategy in supramolecular design and materials synthesis.⁵

Organic amides have proved to be very useful in self-assembly through hydrogen bonding, and the assembled products have relevance to biological systems. Most remarkably, cyclic oligoamides can give interesting nanotube frameworks through inter-ring $\text{NH} \cdots \text{O}=\text{C}$ hydrogen bonding, as reported by Ghadiri *et al.*⁶ In this context, it prompted us to initiate a study on metal-containing cyclic amide systems which feature cyclic peptides that may be expected to self-assemble to give interesting supramolecular or nanotube structures. Puddephatt *et al.*⁷ first reported an interesting molecular triangle containing Pt(II) ions as corners and 4-NC₅H₄C(=O)NH-4-C₅H₄N units as edges, leading to a dimer of triangles formed through $\text{NH} \cdots \text{O}=\text{C}$ hydrogen bonding as well as Pt $\cdots \text{O}=\text{C}$ interactions. Although this Pt(II) complex cannot form nanotubes in the solid state, it opened up a possible opportunity for the formation of metal-containing cyclic peptides that have nanotube frameworks with functional properties.⁶



Dipyridyl amide ligands have been designed and synthesized for purposes in crystal engineering, and amide–amide hydrogen bonding has been successfully demonstrated to increase supramolecular complexity.⁸ So far, only one example regarding the Pt(IV) hydrogen-bonded polymer with *N,N'*-bis-4-methylpyridyl oxalamide (**L**) has been reported,⁹ and thus it was chosen as a building block for the construction of supramolecular coordination compounds in this work. Because it has a flexible backbone containing bifunctional binding sites (both pyridyl groups), as well as a strong capacity for hydrogen bonding of the amide groups, it is anticipated to play a vital role in the assembly of supramolecular coordination compounds. We report here the supramolecular structures and solid state luminescence of zinc(II) halides with *N,N'*-bis-4-methyl-pyridyl oxalamide, where the supramolecular assembly is dependent on the halide, leading to the formation of either a one-dimensional coordination polymer or a discrete macrocycle. To our knowledge, these are rare examples regarding anion-directed assembly of supramolecular zinc(II) halides with *N,N'*-bis-4-methyl-pyridyl oxalamide.

Experimental

General information

All solvents for syntheses (analytical grade) were used without further purification, and the metal salts (ZnCl_2 , ZnBr_2 , and ZnI_2) were commercially available. *N,N'*-bis-4-methylpyridyl oxalamide was prepared by the literature method.⁹ NMR: Bruker DPX 400 MHz; deuterated solvents were used with the usual standards. MS: Positive ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Steady state emission spectra were recorded on a SPEX Fluorolog-2 spectrophotometer.

Synthesis of $[\text{ZnCl}_2(\text{L})]_n$ (**1**), $[\text{ZnBr}_2(\text{L})]_n$ (**2**) and $[\text{ZnI}_2(\text{L})]_2$ (**3**)

1 · 2CH₃OH: ZnCl_2 (14 mg, 0.1 mmol) dissolved in CH₃OH (7 cm⁻³) was carefully layered onto an aqueous solution of **L** (27 mg, 0.1 mmol, dissolved in 7 cm⁻³ DMF). Colorless crystals

Table 1 Crystallographic data for **1**·2CH₃OH, **2**·2CH₃OH and **3**·CH₃OH

	1 ·2CH ₃ OH	2 ·2CH ₃ OH	3 ·CH ₃ OH
Empirical formula	C ₁₆ H ₂₂ Cl ₂ N ₄ O ₄ Zn	C ₁₆ H ₂₂ Br ₂ N ₄ O ₄ Zn	C ₂₉ H ₃₂ I ₄ N ₈ O ₅ Zn ₂
Formula weight	470.65	559.57	1211.01
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	<i>Pnna</i>	<i>Pnna</i>	<i>P</i> -1
<i>a</i> /Å	7.4152(2)	7.5852(11)	8.2323(1)
<i>b</i> /Å	11.8222(3)	12.1545(17)	10.9481(1)
<i>c</i> /Å	22.7057(7)	22.8290(30)	12.0332(2)
α /°	90	90	105.9078(10)
β /°	90	90	96.5427(9)
γ /°	90	90	102.9071(8)
<i>V</i> /Å ³ , <i>Z</i>	1990.47(10), 4	2104.7(5), 4	998.73(2), 1
<i>F</i> (000)/e	824	968	588
μ (Mo-K α)/mm ⁻¹	1.513	4.974	4.341
<i>T</i> /K	150(1)	295(2)	150(1)
Reflections collected	11990	12020	14409
Independent reflections	2294 (<i>R</i> _{int} = 0.055)	2547 (<i>R</i> _{int} = 0.024)	4568 (<i>R</i> _{int} = 0.038)
Observed reflections			
<i>F</i> _o ≥ 2σ(<i>F</i> _o)	2294	2547	4568
Refined parameters	122	125	229
Goodness-of-fit on <i>F</i> ²	1.103	1.033	1.044
<i>R</i> ^a , <i>R</i> _w ^b (<i>I</i> ≥ 2σ(<i>I</i>))	0.050, 0.115	0.033, 0.080	0.029, 0.072
<i>R</i> ^a , <i>R</i> _w ^b (all data)	0.089, 0.129	0.048, 0.088	0.034, 0.074
ρ _{fin} (max/min)/e Å ⁻³	0.435/−0.391	0.713/−0.370	0.821/−1.168

^a $R = \Sigma F_o - F_c / \Sigma F_o$, ^b $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

were obtained within 1 week in *ca.* 71% yield. δ_H (400 MHz, DMSO-*d*₆, 25 °C): 4.36 (4 H, d, CH₂), 7.27–8.48 (8 H, d, py) and 9.44 (2 H, t, NH). FT-IR (KBr): $\nu_{NH} = 3197$ and $\nu_{C=O} = 1691$ cm⁻¹. Found: C, 40.98; H, 3.88; N, 14.09. C₁₄H₁₄Cl₂N₄O₂Zn requires C, 41.36; H, 3.47; N, 13.78%. **2**·2CH₃OH: This compound was prepared by a similar method to **1**, except using ZnBr₂ instead of ZnCl₂, and the colorless crystals were obtained in a *ca.* 61% yield. δ_H (400 MHz, DMSO-*d*₆, 25 °C): 4.36 (4 H, d, CH₂), 7.26–8.48 (8 H, d, py) and 9.44 (2 H, t, NH). FT-IR (KBr): $\nu_{NH} = 3331$ and $\nu_{C=O} = 1694$ cm⁻¹. Found: C, 34.25; H, 2.98; N, 11.69. C₁₄H₁₄Br₂N₄O₂Zn requires: C, 33.94; H, 2.85; N, 11.31%. **3**·CH₃OH: This compound was also prepared by a similar method to **1**, except using ZnI₂ instead of ZnCl₂, and the colorless crystals were obtained in a *ca.* 54% yield. MS (FAB): *m/z* = 460 ((*M* - (2 × *I*))/2, 100%). δ_H (400 MHz, DMSO-*d*₆, 25 °C): 4.36 (4 H, d, CH₂), 7.26–8.46 (8 H, d, py) and 9.43 (2 H, t, NH). FT-IR (KBr): $\nu_{NH} = 3321$ and $\nu_{C=O} = 1668$ cm⁻¹. Found: C, 28.13; H, 2.58; N, 10.09. C₂₈H₂₈I₄N₈O₄Zn₂ requires: C, 28.52; H, 2.39; N, 9.50%.

X-Ray crystallography†

Suitable single crystals were mounted on a glass capillary. Data collection was carried out on a Bruker SMART CCD diffractometer with Mo-K α radiation at 150(1) K for **1**·2CH₃OH and **3**·CH₃OH, and at room temperature for **2**·2CH₃OH, respectively. A preliminary orientation matrix and the unit cell parameters were determined from 3 runs of 15 frames each, each frame corresponding to a 0.3° scan in 15 s, followed by spot integration and least-squares refinement. Data were measured using an ω scan of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART¹⁰ software and refined with SAINT¹¹ on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the

program SADABS.¹² The structure was solved by direct methods with the SHELX-93¹³ program and refined by full-matrix least-squares methods on *F*² with SHEXLTL-PC v 5.03.¹³ All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically-generated positions. Detailed data collection and refinement parameters of the complexes are summarized in Table 1.

Results and discussion

The dipyriddy-amide ligand *N,N'*-bis-4-methylpyridyl oxalamide has been chosen and synthesized here for the purposes of a crystal engineering study. The amide–amide hydrogen bonding has been successfully demonstrated to increase the supramolecular complexity of the Pt(IV) hydrogen-bonded polymer with *N,N'*-bis-4-methylpyridyl oxalamide,⁹ where two *N,N'*-bis-4-methylpyridyl oxalamide ligands are *trans* to each other in an octahedral geometry. The Zn(II) ion favors a tetrahedral geometry, and this geometric preference is quite different from that of the octahedral Pt(IV) ion. This may result in a dramatically different structural motif due to the different contributions from the hydrogen bonding present in both Pt(IV) and Zn(II) complexes.

A methanolic solution of ZnX₂ (X = Cl, Br, I) was carefully layered onto a DMF solution of **L**, from where the colorless crystals of **1**·2CH₃OH, **2**·2CH₃OH and **3**·CH₃OH were obtained in medium yields (50–70%) within one week, respectively.

Description of crystal structures

1, **2** and **3** have been isolated and their crystal structures determined by X-ray diffraction studies.† The chloro and bromo complexes are isomorphous and form one-dimensional coordination polymers, with tetrahedral Zn(II) centers coordinating to two halides (Cl or Br) and two bridging ligands, **L**, as shown in Fig. 1(a). Interestingly, the cavity of *ca.* 8.5 × 8.5 Å² is formed by the two interwoven chains and further stacked to give a one-dimensional channel in Fig. 1(b) (void percentage: 41.6% for **1** and 43.4% for **2**, calculated using Platon

† CCDC reference numbers CCDC 269329, 269330 and 272141. See <http://dx.doi.org/10.1039/b508293e> for crystallographic data in CIF or other electronic format.

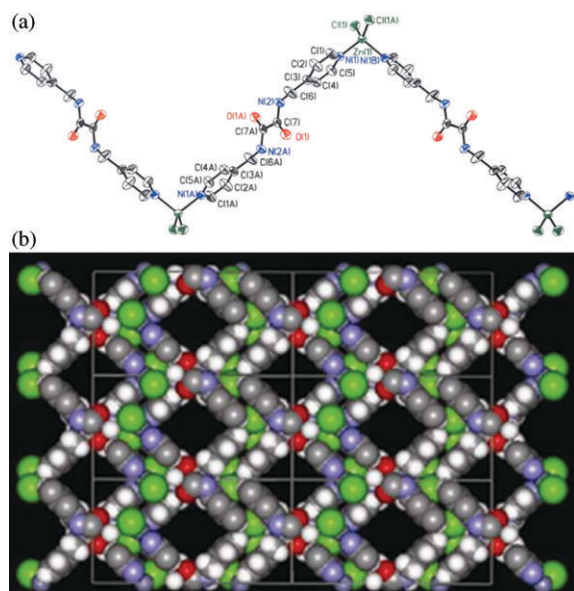


Fig. 1 (a) Molecular structure of complex **1**. ORTEP diagram showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.039(3), Zn(1)–Cl(1) 2.232(1); N(1)–Zn(1)–Cl(1) 111.39(8). (b) The extended framework showing a one-dimensional channel structure with a dimension of *ca.* 8.5 × 8.5 Å² in the solid state.

Graphics¹⁴ upon removal of the solvated methanol). Four methanol molecules sit inside each cavity for **1** and **2**, and those in **1** are highly disordered. Two slightly slipped pyridyl rings of pyridyl amide groups show the shortest distances of 3.54 Å for **1** and 3.72 Å for **2** between the C(N) and C(N) atoms (the distances between the two centroids of the pyridyl rings and the dihedral angles between them are 3.989 Å/168.4° and 4.225 Å/164.2°, respectively), indicative of the presence of weak $\pi \cdots \pi$ interactions.¹⁵ In addition, there are also some non-classical hydrogen bonds present in the solid state.¹⁶ Thus, these interesting one-dimensional channel structures for **1** and **2** may be constructed by $\pi \cdots \pi$ interactions in combination with some weak hydrogen bonding.

Unlike those of **1** and **2**, the iodo analogue **3** surprisingly forms a distinct structural motif as a molecular rectangle, shown in Fig. 2(a). Furthermore, the rectangular cavity of *ca.* 6.4 × 11.0 Å² is stacked to give one-dimensional rectangular channels in the solid state, as shown in Fig. 2(b) (void percentage: 38.7% for **3** calculated using Platon Graphics¹⁴ upon removal of the solvated methanol). Double hydrogen bonding interactions (N(3)–H(3A)···O(1): N(3)–H(3A) 0.860 Å, H(3A)···O(1) 2.224 Å, N(3)···O(1) 2.893(10) Å; N(3)–H(3A)···O(1) 134.5°) are observed in the solid state, and these are anticipated to be responsible for the one-dimensional rectangular channels. This is reminiscent of the novel nanotube frameworks for cyclic peptides reported by Ghadiri *et al.*,⁶ where the amide–amide hydrogen bonding contributes to the formation of supramolecular nanotubes. Each rectangle encapsulates a disordered CH₃OH molecule inside the cavity. TGA analysis has been conducted to examine thermostability, with the framework being thermally stable up to 250 °C and the lattice remaining intact upon solvent removal. The weight loss of 2.17% is comparable to the calculated value of 2.61% for a CH₃OH molecule, and the X-ray powder diffraction pattern upon solvent removal at 200 °C is almost the same as the one before solvent removal. The shortest distance of 3.570 Å between the C(N) atoms of the parallel pyridyl rings of **3** (the distance between the centroids of two pyridyl rings is 3.837 Å) is suggestive of the presence of $\pi \cdots \pi$ interactions. Thus, the interesting nanotube framework for **3** is built from $\pi \cdots \pi$ interactions in combination with hydrogen bonding. Additionally, the dramatic structural motif of **3** may be due to the bigger

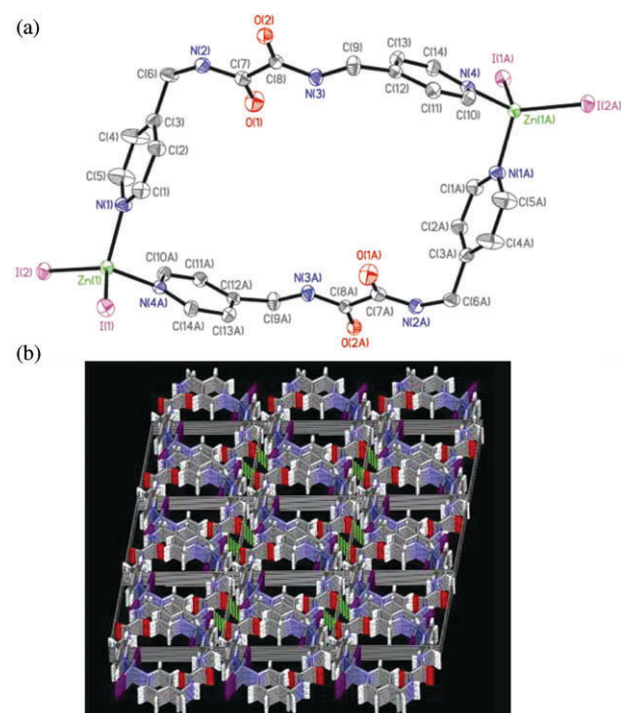


Fig. 2 (a) Molecular structure of complex **3**. ORTEP diagram showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.059(3), Zn(1)–I(1) 2.5540(4), Zn(1)–I(2) 2.5506(4); N(1)–Zn(1)–I(1) 108.8(1), N(1)–Zn(1)–I(2) 109.5(1), I(1)–Zn(1)–I(2) 120.4(2). (b) The hydrogen-bonded extended framework showing a one-dimensional channel structure with a dimension of *ca.* 6.4 × 11.0 Å² in the solid state.

iodo atom, compared with chloro and bromo atoms, inducing a delicate stacking effect on the formation of different supramolecular structures. It is noted that supramolecular synthesis of different structural frameworks, *i.e.*, coordination polymers or macrocycles, from the same ligands is not uncommon,^{7b,8a,17} but to our knowledge, the anion-directed assembly of supramolecular zinc(II) halides is rare yet represented by the examples reported here.

Solid state emission spectra

Fig. 3 shows the solid state emission spectra of **L** and **1–3** measured at room temperature. Upon photoexcitation at 350 nm, both **1** and **2** show high energy emissions with a maximum at *ca.* 395 nm, and **3** shows interesting dual emissions, with emission maxima at *ca.* 440 and 500 nm. Since **L** displays only a high energy maximum at *ca.* 440 nm, which is almost the same as the high energy one of **3**, ascribed to an intraligand transition. However, the high energy emissions at *ca.* 395 nm for **1** and **2** and the low energy one at *ca.* 500 nm for **3** are unlikely to be related to intraligand transitions. The significant red shift from **1** and **2** to **3** is tentatively assigned to a ligand-to-metal charge-transfer transition, since lower transition energies for an iodo-to-zinc(II) charge-transfer transition are known, compared to those of chloro- or bromo-to-zinc(II) transitions.¹⁸ Nevertheless, it is still possible that these ligand-to-metal transitions mix with an intraligand transition.

Conclusion

The supramolecular coordination compounds of zinc(II) halides with *N,N'*-bis-4-methyl-pyridyl oxalamide have been isolated and their crystal structures determined by X-ray diffraction studies. The supramolecular assembly is dependent on the halide, leading to the formation of either one-dimensional coordination polymers for Cl and Br or a discrete macrocycle for I, respectively. These compounds all form channel struc-

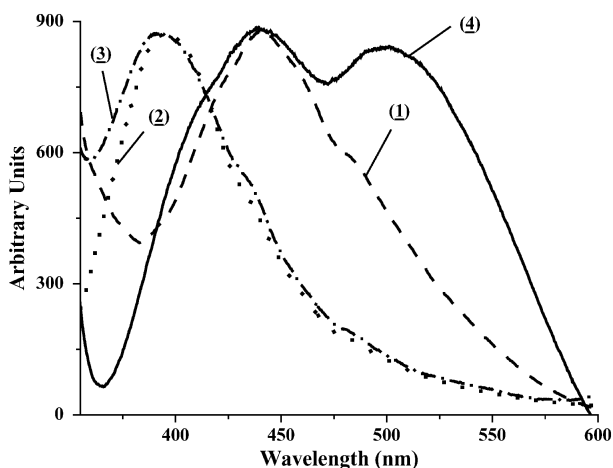


Fig. 3 The solid state emission spectra of L (1), 1 (2), 2 (3) and 3 (4) measured at room temperature with an excitation wavelength of 350 nm.

tures in the solid state with solvated methanol inside their cavities. Notably, **3** forms an interesting molecular rectangle which is reminiscent of the novel nanotube frameworks for cyclic peptides reported by Ghadiri *et al.*⁶ To our knowledge, these are rare examples of the anion-directed assembly of supramolecular structures. Additionally, the solid state luminescence has also been studied for **1–3**, where **3** shows dual emissions with emission maxima at *ca.* 440 and 500 nm. The *ca.* 440 nm emission is ascribed to an intraligand transition, and the one at *ca.* 500 nm due to an iodo-to-zinc(II) charge-transfer transition. The channel structure and hydrogen bonding functions for the rectangular structure of **3** in the solid state, as well as its low energy excited state, are anticipated to hold potential as properties of new luminescent sensory materials.

Acknowledgements

We thank the National Science Council and National Chung Cheng University of the Republic of China for financial support.

References

- (a) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; (b) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (c) B. A. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022; (d) O. M. Yaghi, H. L. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; (e) P. H. Dinolfom and J. T. Hupp, *Chem. Mater.*, 2001, **13**, 3113.
- (a) C. Janiak, *Dalton Trans.*, 2003, 2781; (b) S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276; (c) S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, **116**, 2388; (d) M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4900; (e) S.-L. Zheng and X.-M. Chen, *Aust. J. Chem.*, 2004, **57**, 703; (f) D. Maspoch, D. Ruiz-Molina and J. Veciana, *J. Mater. Chem.*, 2004, **14**, 2713; (g) S. R. Batten and K. S. Murray, *Coord. Chem. Rev.*,

- 2003, **246**, 103; (h) L. Carlucci, G. Ciani and D. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.
- (a) A. D. Burrows, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1996, 97; (b) Z.-N. Chen, H.-X. Zhang, K.-B. Yu, K.-C. Zheng, H. Cai and B.-S. Kang, *J. Chem. Soc., Dalton Trans.*, 1998, 1133; (c) C. B. Aakeröy, A. M. Beatty and B. A. Helfrich, *J. Chem. Soc., Dalton Trans.*, 1998, 1943; (d) B. R. Cameron, S. S. Corrent and S. J. Loeb, *Angew. Chem., Int. Ed.*, 1995, **34**, 2689; (e) S. B. Copp, S. Subramanian and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1992, **114**, 8719.
- (a) A. D. Burrows, D. M. P. Mingos, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1996, 3805; (b) C. M. Drain, K. C. Russell and J.-M. Lehn, *Chem. Commun.*, 1996, 337; (c) N. C. Gianneschi, E. R. T. Tiekink and L. M. Rendina, *J. Am. Chem. Soc.*, 2000, **122**, 8474.
- (a) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375; (b) A. D. Burrows, C.-W. Chan, M. W. Chowdhry, J. E. McGrady and D. M. P. Mingos, *Chem. Soc. Rev.*, 1995, **24**, 329.
- (a) J. D. Hartgerink, T. D. Clark and M. R. Ghadiri, *Chem.-Eur. J.*, 1998, **4**, 1367; (b) M. R. Ghadiri, K. Kobayashi, J. R. Granja, R. K. Chadha and D. E. McRee, *Angew. Chem., Int. Ed.*, 1995, **34**, 93.
- (a) Z. Qin, M. C. Jennings and R. J. Puddephatt, *Chem. Commun.*, 2001, 2676; (b) Z. Qin, M. C. Jennings and R. J. Puddephatt, *Inorg. Chem.*, 2003, **42**, 1956.
- (a) Z. Qin, M. C. Jennings and R. J. Puddephatt, *Chem. Commun.*, 2002, 354; (b) S. Muthu, J. H. K. Yip and J. J. Vittal, *J. Chem. Soc., Dalton Trans.*, 2002, 4561; (c) S. Muthu, J. H. K. Yip and J. J. Vittal, *J. Chem. Soc., Dalton Trans.*, 2001, 3577; (d) C. L. Schauer, E. Matwey, F. W. Fowler and J. W. Lauher, *Cryst. Eng.*, 1998, **1**, 213; (e) T. J. Burchell, D. J. Eisler and R. J. Puddephatt, *Inorg. Chem.*, 2004, **43**, 5550.
- C. S. A. Fraser, D. J. Eisler, M. C. Jennings and R. J. Puddephatt, *Chem. Commun.*, 2002, 1224.
- SMART v 4.043 Software for the CCD detector system, Siemens Analytical Instruments Division, Madison, WI, 1995.
- SAINT v4.035 Software for the CCD detector system, Siemens Analytical Instruments Division, Madison, WI, 1995.
- G. M. Sheldrick, *SHELXL-93, Program for refinement of crystal structures*, University of Göttingen, Germany, 1993.
- SHELXTL 5.03 (PC-Version), Program library for structure solution and molecular graphics, Siemens Analytical Instruments Division, Madison, WI, 1995.
- A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **A46**, 146.
- C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
- For **1**: (D–H···A, D–H, H···A, D···A, H···A) N(2)–H(2A)···Cl(1), 0.880 Å, 2.669 Å, 3.445(5) Å, 147.73°; C(1)–H(1A)···Cl(1), 0.949 Å, 2.784 Å, 3.408(6) Å, 124.13°; C(4)–H(4A)···O(1), 0.950 Å, 2.454 Å, 3.395(6) Å, 170.92°; C(6)–H(6B)···Cl(1), 0.990 Å, 2.644 Å, 3.605(6) Å, 163.97°. For **2**: (D–H···A, D–H, H···A, D···A, H···A) N(2)–H(2A)···Br(1), 0.860 Å, 2.878 Å, 3.614(3) Å, 144.75°; C(2)–H(2)···O(1), 0.930 Å, 2.490 Å, 3.413(5) Å, 171.65°; C(5)–H(5)···Br(1), 0.930 Å, 2.862 Å, 3.504(5) Å, 127.29°; C(6)–H(6A)···Br(1), 0.971 Å, 2.795 Å, 3.724(5) Å, 160.29°.
- (a) F. M. Tabellion, S. R. Seidel, A. M. Arif and P. J. Stang, *Angew. Chem., Int. Ed.*, 2001, **40**, 1529; (b) F. M. Tabellion, S. R. Seidel, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2001, **123**, 7740; (c) J. Fang, W.-Y. Sun, T.-A. Okamura, Y.-Q. Zheng, B. Sui, W.-X. Tang and N. Ueyama, *Cryst. Growth Des.*, 2004, **4**, 579; (d) R. Horikoshi, T. Mochida, M. Kurihara and M. Mikuriya, *Cryst. Growth Des.*, 2005, **5**, 243; (e) G. Zhang, G. Yang, Q. Chen and J. S. Ma, *Cryst. Growth Des.*, 2005, **5**, 661.
- M. Linhard and M. Weigel, *Z. Anorg. Chem.*, 1951, **266**, 49.