Macromol. Symp. **2004**, *209,* 119-131

Ring-Opening Polymerisation of Coordination Rings and Cages

Stuart L. James

School of Chemistry, Queens University Belfast, David Keir Building, Stranmillis Road, Belfast, Northern Ireland, BT9 5AG, UK
E-mail: s.james@qub.ac.uk

Summary: Despite the great interest in crystalline coordination polymers (sometimes called metal organic frameworks) surprisingly little is known about how they form. However, there has recently been some attention given to characterising their solution-based precursors. Of particular interest is the formal ring-opening polymerisation (ROP) relationship between the structures of some precursors and polymers, and the actual observation of ring-opened oligomers by solution state NMR spectroscopy. These points are highlighted and discussed along with related aspects of isomerism in discrete and polymeric coordination structures, and polymer-polymer interconversion.

Keywords: coordination complex; coordination polymer; metal organic framework; MOF; ring-opening polymerisation; ROP

Introduction

The study of coordination polymers has increased enormously over the past ten years.[1] Despite this widespread activity, surprisingly little has been reported on how these materials might form. Since most syntheses involve crystallisation of the polymer from solution, it is of interest in this regard to identify solution-based precursors to the polymers. In this article the recent papers for which this has been an important aspect are summarised and discussed. Also, the related aspects of 'supramolecular isomerism' (discrete and polymeric isomers prepared from the same metal and ligand blocks), and polymer-to-polymer interconversion are highlighted.

DOI: 10.1002/masy.200450508

Review and Discussion

i) Apparent ROP of Solution-based Rings and Cages upon Crystallisation

In 2001 we reported that when crystals of the dinuclear triply-bridged complex [$Ag_2(dppa)_3(OTf)_2$] (dppa = *bis*(diphenylphosphino)acetylene), which is also the main species present in solutions, were left in their supernatant for 16 weeks, they transformed by redissolution and recrystallisation into a polymeric form [$Ag_2(dppa)_3(OTf)_2$]$_\infty$.[2] The polymer consists of dinculear rings, in which the two silver ions are bridged by two diphosphines, and a third diphosphine links the rings into a one-dimensional chain (Figure 1).

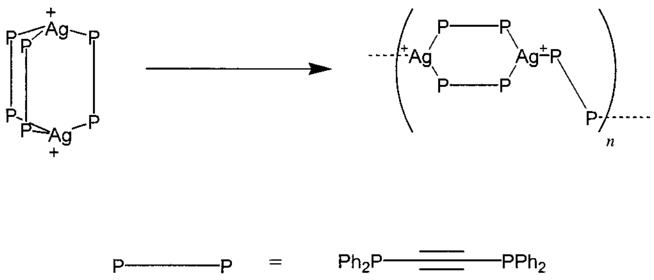

Figure 1. Apparent ring-opening polymerisation of triply-bridge disilver complexes [$Ag_2(dppa)_3(anion)_2$] to give a linear polymer.

It was intriguing that the discrete and polymeric complexes were formally related to each other by ring-opening polymerisation (ROP). Although ROP is well known in main group chemistry and for strained metallocenes it had not to our knowledge been reported previously for coordination cages. A key difference is that for the ROP of kinetically-stabilised main group rings there is direct and irreversible transformation to the polymer, whereas in these coordination complexes the formation of M-L bonds is reversible. Therefore, potentially there are many equilibira to be considered in the formation of a coordination polymer, for example those shown in Figure 2, which provide indirect routes to the observed polymer. We postulated that a direct ROP of the precursor to the polymer *could*, nevertheless, be the actual mechanism by which the polymer formed. Related work with the slightly more bulky diphosphine ligand dppet, *trans*-1,2-*bis*(diphenylphosphino)ethylene, suggested that the discrete dinuclear complexes were less stable than the dppa analogues in solution, since their NMR spectra were only resolved at low temperature, indicating that greater Ag-P dissociation occured than in the analogous dppa complexes. Consistent with this observation, the discrete complexes could not be isolated by crystallisation, and instead the polymeric form $[Ag_2(dppet)_3(SbF_6)_2]_\infty$ was obtained directly. ROP therefore appeared to be favoured by prolonged standing of crystals of the precursor in their supernatant and by steric destabilisaing of the precursor.

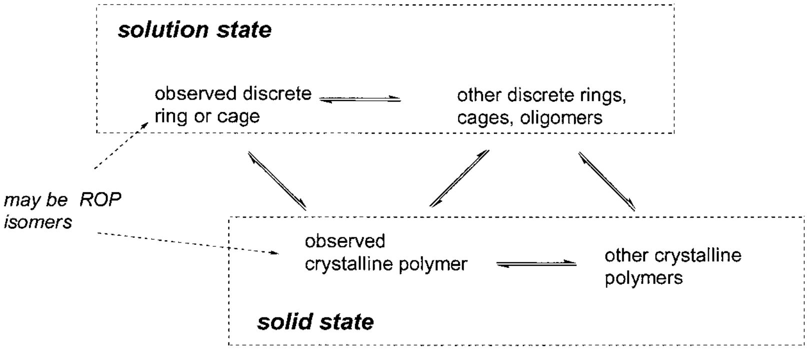

Figure 2. Some of the many potential equilibria involved in forming the observed polymeric product from a dynamic coordination system.

Simultaneously, Puddephatt and coworkers reported related coordination polymers based on gold. As well as one polymer, $[Au_2(dppet)_3](CF_3CO_2)_2$,[3] which was topologically the same as the silver-dppa and -dppet polymers we described, a chickenwire sheet polymer of formula $[Au_2(dppb)_3](AuCl_2)_2$ (dppb = 1,4-bis(diphenylphosphino)butane) was also described (Figure 3). The latter was formally related to a hypothesised solution-based triply-bridged precursor complex $[Au_2(diphosphine)_3]^{2+}$ by a double ROP process, *i.e.* by the opening of two rings in the precursor. Subsequently this group reported further on the ROP of coordination rings. [4-7] In particular, coordination rings containing two gold centres, linked by one bridging dppet diphosphine and one bridging diamine ligand, were proposed to undergo Au-N bond dissociation as a first step to oligomerisation, and ultimately to form linear polymers in which Au(I) centres were bridged alternately by the diphosphine and diamine ligands (Figure 4).[4] Such a polymer was in fact obtained with the alternative more flexible diphosphine ligand dppe, $Ph_2PCH_2CH_2PPh_2$. Variable temperature ^{31}P NMR spectroscopy was used to probe the solution structures of the complexes formed by each diphosphine. With the rigid ligand dppet, a single resonance at all temperatures was ascribed to the dinuclear ring as characterised by X-ray crystallography. However, with the more flexible linker dppe, more complex behaviour was seen which was both concentration- and temperature-dependent. Peaks resolved at low temperature were ascribed to the formation of low-molecular weight ring-opened oligomeric forms (Figure 4). The proportion of oligomers increased with the concentration. Further examples of solution-based ring structures, which transformed to polymers on crystallisation, were subsequently reported. These include mixed-ligand rings composed of the bridging diphosphine dppet and dithiols.[5] Also, use of a *bis*(pyridyl)-derived ligand, containing potentially hydrogen bonding amide functions, gave a tetranuclear ring structure when the other bridging ligand present was dppp, $Ph_2PCH_2CH_2CH_2PPh_2$, but a linear polymer when dppb, $Ph_2PCH_2CH_2CH_2CH_2PPh_2$, was used.[6] The low temperature ^{31}P NMR spectrum of the ring complex showed additional peaks which were assigned to the ring-opened form, in which anions replaced the N-donor ligands at the Au(I) centres. Other polymers based on Ag(I) and diphosphines, with a variety of topologies were also prepared and their relationships to discrete isomers discussed.[7]

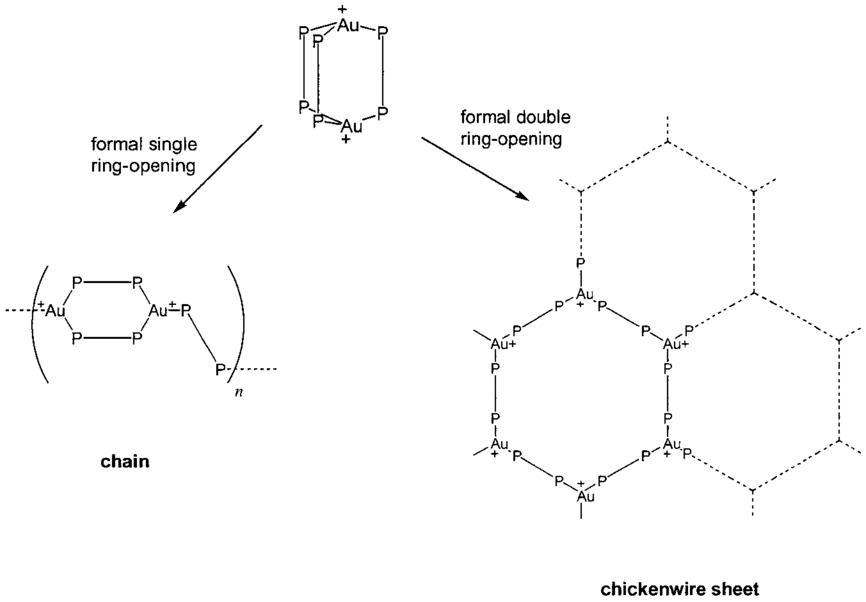

Figure 3. Formal single- and double-ring-opening relationships between a discrete triply-bridged complex and chain and chickenwire sheet polymers.

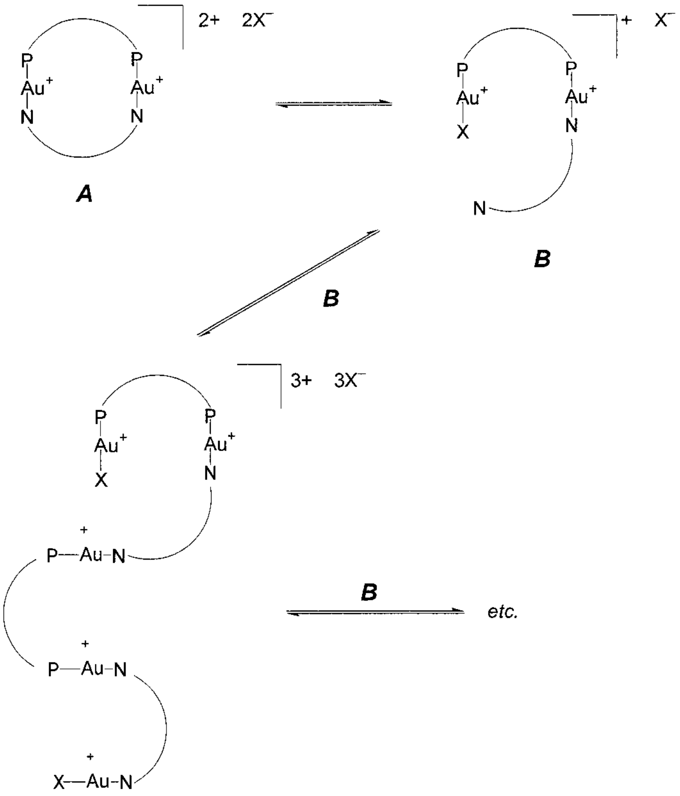

Figure 4. Proposed ROP pathway to polymers based on bridging diphosphines and bridging diamines (adapted from ref. 4, gold-gold contacts have been omitted for clarity).

Whereas the above work has involved phosphines as bridging ligands, Chung *et al.* have reported on apparent ROP of metallamacrocycles with purely N-based ligands.[8] Flexible ligands based on 1,3-*bis*(2-pyridyl)propane gave disilver macrocycles on crystallisation with silver salts. However, with 1,3-*bis*(2-pyridyl)-2-phenylpropane a linear polymer was obtained on crystallisation (Figure 5). This polymer was found to be slightly soluble in water, and ^{1}H NMR spectroscopy and solution molecular weight measurement showed that the dominant species present in solution was a dinuclear macrocycle similar to that isolated for the other ligands. The authors concluded that the polymer crystallised from a solution in which the predominant species was the discrete macrocycle.

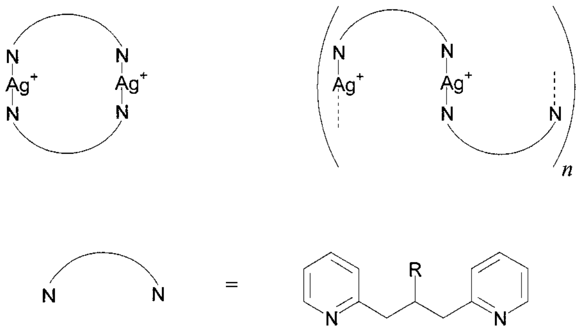

Figure 5. Discrete disilver and chain polymer structures obtained with bridging ligands based on 1,3-di(2-pyridyl)propane (anions have been omitted for clarity, in the polymeric structure they bridge between the chains).

As an interesting contrast to the study of crystalline coordination polymers, a non-crystalline system has been studied by Hill *et al.*,[9a] Gray *et al.*[9b] and Sijbesma *et al.*[9c] Reaction between $PdCl_2$ and the long chain diphosphine 1,12-*bis*(diphenylphosphino)dodecane in chloroform solvent gives mixtures of cyclic oligomers or linear polymer depending on the concentration (Figure 6). Diffusion-ordered ^{31}P NMR spectroscopy was used to identify the various cyclic oligomeric and linear polymeric species. There is a critical concentration below which only cycles are present, and above which the concentration of cycles stays constant and the amount of linear polymer increases. Slow evaporation of chloroform solutions gave viscous material containing both cyclic oligomers and linear polymer of up to 80 repeat units. However, melt polymerisation gave polymer of up to 500 repeat units.

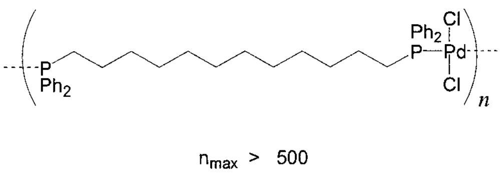

Figure 6. Cyclic coordination oligomers and high molecular weight linear polymers described by Sijbesma *et al.*[9c]

ii) Ring-opening Isomerism

The issue of ROP of coordination rings and cages is closely related to what has been called 'supramolecular isomerisim',[10] or 'supramolecular ring-opening isomerism'.[11] In these cases, the emphasis has not been on the actual mechanisms by which coordination polymers form, but instead to highlight isomeric relationships between discrete and polymeric coordination compounds. It therefore provides a way of systematising some structures. For example, the hexagonal Cu_6 ring obtained by Zaworotko *et al.*[10] is a finite isomer of the corresponding zig-zag polymer, which was also obtained by these workers under slightly different reaction conditions (Figure 7). Zur Loye et al. reported complexation of HgX_2 salts with the semi-rigid ditopic ligand 1,3-*bis*(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (bbimms) (Figure 8).[11] A discrete binuclear ring of formula $Hg_2I_4L_2$ was isolated, which consisted of a metallacycle with two bridging organic ligands and four termial I^- anions. Its polymeric counterpart, the formal ROP isomer, having a chain structure of HgI_2 centres linked by bridging organic ligands was isolated under slightly different conditions. Solution-based structures were not characterised, but attention was drawn to the 'supramolecular ring-opening isomerism' between the two complexes. The potential usefulness of this concept in predicting discrete and polymeric coordination structures was emphasised. Other examples of discrete and polymeric complexes based on bridging phosphines, which have formal mutual ROP-relationships have been described by Catalano et al.[12] in gold(I) polymers containing 3,6-bis(diphenylphosphino)pyridazine, and Wong et al. in Ag(I) complexes based on $Ph_2PC_2H_4CONHCH_2CH_2NHCOCH_2CH_2PPh_2$.[13]

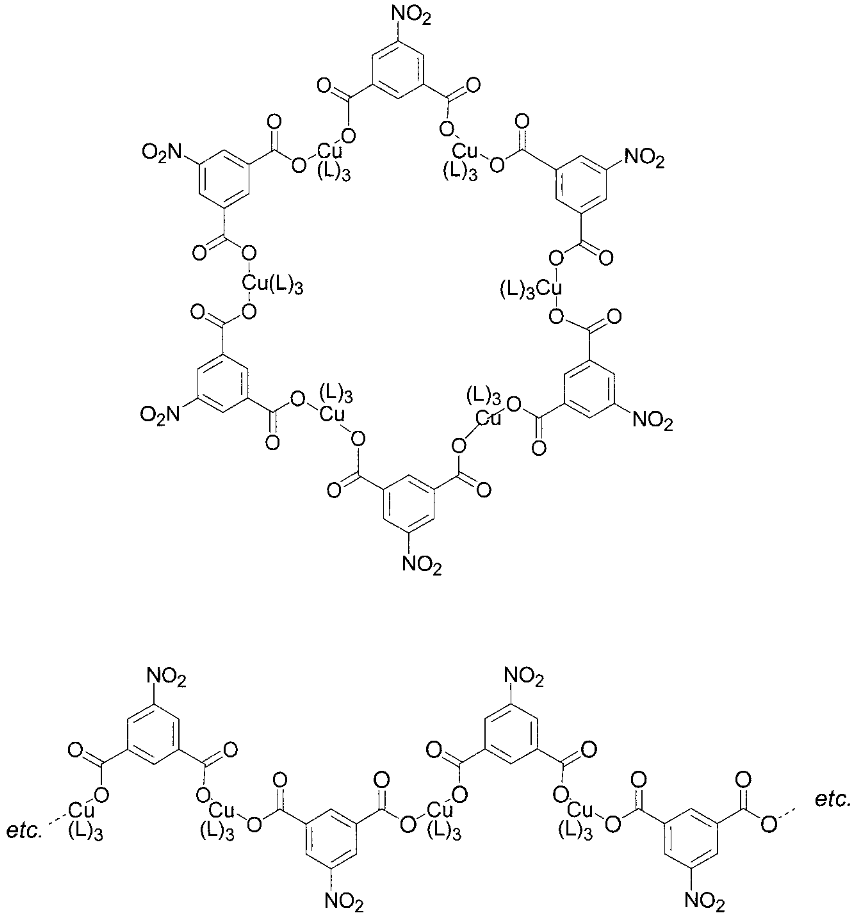

Figure 7. Discrete hexagonal and zig-zag polymeric 'supramolecular isomers' reported by Zaworotko et al.[10]

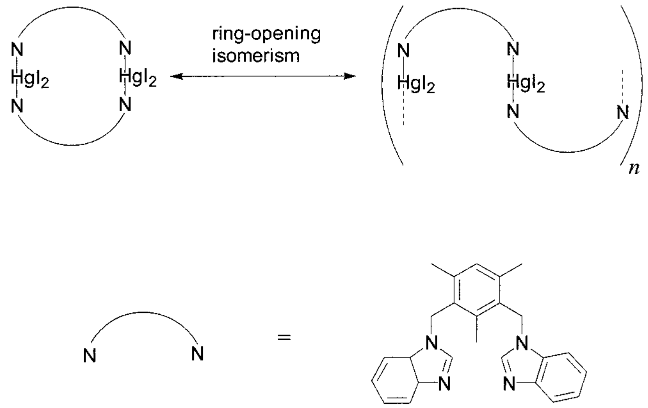

Figure 8. The ring-opening isomerism between a discrete dinuclear ring and linear polymer described by Zur Loye et al. (adapted from ref. 11).

iii) Solvent-mediated and Solid-state Interconversion of Isomeric Polymers

As well as isomerism between discrete and polymeric structures, isomerism can occur between polymers, and these polymers can sometimes also be interconverted. As well as being interesting from a structural point of view, these examples also demonstrate the high lability of the coordination systems which are often used to synthesise coordination polymers. They in fact provide examples of the various ,indirect’ equilibria shown in Figure 2. A recent example of solution-mediated polymer-to-polymer interconversion was described by Fromm et al.,[14] who obtained two coordination polymers by reacting CuCl with a *bis*(isonicotinic acid) derived ligand (Figure 9). Red crystals of one polymer, [CuCl(L)].0.5THF were obtained from an acetonitrile-THF solution of the ligand and CuCl on standing for a few hours. The structure consists of *spiro* chains of four-membered rings, defined by Cu and bridging Cl centres, alternating with larger 30-membered rings defined by Cu centres and the bridging organic ligands (Figure 9). The large rings leave sufficient space for included solvent molecules, which were modelled as disordered THF. Interestingly, when only acetonitrile was used as the crystallising solvent, red crystals were again obtained on standing for a few hours. These were then observed to redissolve and orange crystals were then obtained after a period of two months. The chain structure of the orange polymer did not contain rings, the Cu(I) centres being simply linked by bridging bidentate organic ligands, and having terminal Cl⁻ anions. It was postulated that the red crystals initially obtained from acetonitrile had the same *spiro* structure as those obtained from acetonitrile-THF. The two different chains are formally related to each other by the breaking of one Cu-N and one Cu-Cl bond, and the formation of one Cu-N bond per Cu centre. It was noted that the transformation from red to organge crystals stopped if the supernatatant was removed, showing the process to be solvent-mediated.

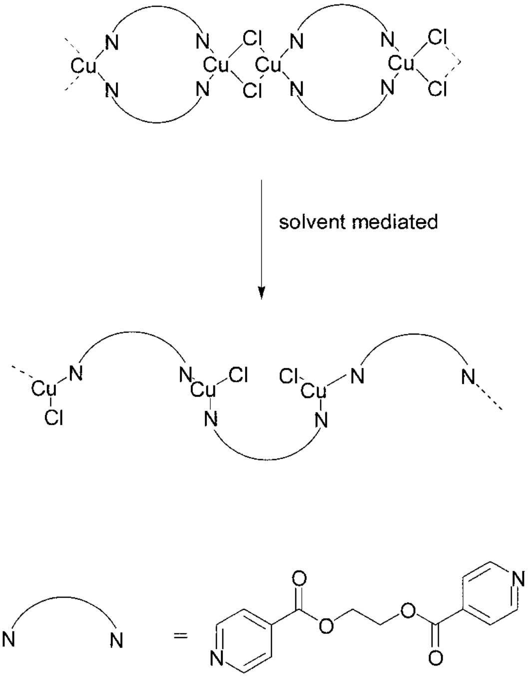

Figure 9. The solvent-mediated transformation of isomeric coordination polymers reported by Fromm et al.[14]

An example of solid-to-solid polymer interconversion was reported by Chung et al.[15] Reaction of $Co(NCS)_2$ with 1,2-dipyridylpropane gave, initially needle crystals of one polymer, followed by block crystals of another. Both had the formula $[Co(L)_2(NCS)_2]_n$ but had contrasting topologies. The first-formed consisted of interpenetrated rhombic grids with about 49% of the volume occupied by solvent molecules. The other consisted of two independent but mutually interpenetrated 3-D frameworks, both of which inteprenetrated with a 2-D grid. This polymer also had spaces occupied by solvent molecules, but accounting for only 18% of the total volume. On the basis of its greater available volume, the authors postulated that the first structure was metastable with regard to the second. They found that when crystals of the less dense polymer were removed from their supernatant, they lost solvent to become opaque, and XRPD showed that during this drying out the networks indeed transformed to the second, denser structure.

Conclusion

There are now several examples of discrete soluble species which have been found to give coordination polymers on crystallisation, and for which there is a formal ROP relationship between the precursor and the polymer.[2, 4, 5, 6, 8, 9] Opportunities and challenges in further establishing and exploiting this 'coordination ROP' include *i.* examination of precursor-polymer relationships in more cases, *ii.* evaluating the importance of potential indirect pathways to the polymer, as indicated in Figure 2, *iii.* detailed examination of the crystallisation process (potentially to get evidence of ROP at the crystal surface), *iv.* examination of how variables such as counter ion and solvent nucleophilicity, steric destabilisation and ring strain affect the ring-opening of precursors, and *v.* the deliberate design or prediction of network topologies based on the ROP principle.

[1] [1a] S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276; [1b] C. Janiak *J. Chem. Soc., Dalton Trans.* **2003**, 2781; [1c] B. Moulton, M. J. Zaworotko, *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 117; [1d] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629; [1e] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O.M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319.

[2] E. Lozano, M. Niewenhuyzen, S. L. James, *Chem. Eur. J.* **2001**, *12*, 1644.

[3] M.C. Brandys, R.J. Puddephatt, *J. Am. Chem. Soc.* **2001**, *123*, 4839.

[4] Z. Q. Qin, M. C. Jennings, R. J. Puddephatt, *Chem. Eur. J.,* **2002**, *8*, 735.

[5] W.J. Hunks, M.C. Jennings and R.J. Puddephatt *Chem. Commun.* **2002**, 1834.

[6] T. J. Burchell, D. J. Eisler, M. C. Jennings, R. J. Puddephatt, *Chem. Commun.* **2003**, 2228.

[7] M. C. Brandys, R. J. Puddephatt, *J. Am. Chem. Soc.* **2002**, *124*, 3946.

[8] D. M. Shin, I. S. Lee, Y. A. Lee, Y. K. Chung, *Inorg. Chem.* **2003**, *42*, 2977.

[9] [9a] W. E. Hill, C. McAuliffe, I. E. Niven, R. V. Parish, *Inorg. Chim. Acta* **1980**, *38*, 273; [9b] D. C. Smith, G. M. Gray, *J. Chem. Soc., Dalton Trans.* **2000**, 677. [9c] J. M. J. Paulusse, R. P. Sijbesma, *Chem. Commun.* **2003**, 1494.

[10] H. Abourahma, B. Moulton, V. Kravtsov, M. J. Zaworotko *J. Am. Chem. Soc.* **2002**, *124*, 9990.

[11] C. Y. Su, A. M. Goforth, M. D. Smith, H. C. zur Loye, *Inorg. Chem.* **2003**, *42*, 5685.

[12] V. J. Catalano, M. A. Malwitz, S. J. Horner, J. Vasquez, *Inorg. Chem.* **2003**, *42*, 2141.

[13] Y. Li, K. F. Yung, H. S. Chan, W. T. Wong, W. K. Wong, M. C. Tse, *Inorg. Chem. Commun.* **2003**, *6*, 1315.

[14] A. Y. Robin, K. M. Fromm, H. Goesmann, G. Bernadinelli, *CrystEngComm*, **2003**, *5*, 405.

[15] D. M. Shin, I. S. Lee, D. Cho, Y. K. Chung, *Inorg. Chem.* **2003**, *42*, 7722.