Molecular Networks *via* Coordination Polymerization. Synthesis and Characterization of 2-D Polymeric Cobalt(II) Compounds Containing 3,3'-Dipyridyl Ether Series

Ok-Sang Jung,[*] Yun Ju Kim, Young-A Lee, Jae-Kyung Lee, and Kyung Ho Yoo[†]

Materials Chemistry Research Center and [†]Medicinal Chemistry Research Center,
*Korea Institute of Science and Technology, Seoul 136-791, Korea*
Received August 30, 1999

New coordination polymers of general form, $[CoL_2X_2]_n$ (L = 3,3'-oxybis(pyridine) (obp), 1,4-bis(3-pyridoxy)benzene (bpob); X = Cl, NCS), have been prepared via a slow diffusion method. The reaction of the present linkers with cobalt(II) ion affords infinite 2-dimensional sheet products. For $[Co(obp)_2Cl_2]_n$, the local geometry of the cobalt center is an octahedral arrangement with four nitrogen donors and two chlorine ions in *trans* positions. $[Co(bpob)_2(NCS)_2]_n$ has provided a similar structure: the local geometry of the cobalt atom is an octahedral arrangement with four pyridine units and two NCS groups in *trans* positions. The obp and bpob linkers connect two cobalt(II) ions defining the edges of 40- and 60-membered $[Co(II)]_4$ ring, respectively. Thermal analyses of the coordination polymers show significant thermal behavior associated with the characteristic structures.

Introduction

Metal-based coordination polymers are of current interest because transition metal ions exhibit various structural aspects such as oxidation states and coordination modes.[1] Furthermore, such coordination polymers have appeared as new motifs of molecular architecture due to aesthetic facets and the potential applicability as electrical conductors,[2] molecular magnets,[3] host-guest chemistry,[4] crystal bending effects,[5] molecular recognition,[6] optoelectronics,[7] and catalysis.[8] Thus, elegant coordination polymers have been constructed based on molecular design and crystal engineering technology. Their structures are mainly dependent upon the coordination geometry of central metals, the structure of spacer ligands, counter ions, and reaction conditions.[9-11] The use of unique spacers is worthy of close attention as a rational molecular design strategy. For instance, it has been found that the appropriate angular and flexible components of spacers play an important role in self-assembly *via* coordination.[12-16] Though the overall topology of coordination polymers can be controlled by means of the coordination preferences of the metal center and the structure of the linker, the prediction of the exact interactions in the crystalline phase still seems unreachable. Various spacers have been used for a wide range of molecular building blocks, but exploitation of 3,3'-bis(pyridyl)oxy units as spacers remains one of the unexplored areas. The spacers possess magic angles, which are, essentially, bent around oxygen with somewhat flexibility in contrast to linear rigid 4,4'-bipyridine analogs. Preliminary structural and thermal properties in cobalt(II) complexes of 4,4'-dipyridyl sulfide were recently reported as a communication.[17]

Our goal is the observation of subtle effects on self-assembling between potential octahedral cobalt(II) ions and 3,3-bis(pyridyl)oxy spacers. In this paper, we describe the formation of new polymeric molecular networks and related
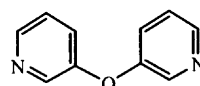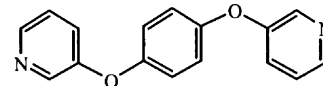
physicochemical properties of cobalt(II) complexes of two spacer ligands, 3,3-oxybis(pyridine) (obp)[18] and 1,4-bis(3-pyridoxy)benzene (bpob)[19]

Experimental Section

Materials and Measurements. $CoCl_2 \cdot 6H_2O$ and $Co(NCS)_2$ were purchased from Aldrich and used without further purification. 3,3'-Oxybis(pyridine) (obp)[18] and 1,4-bis(3-pyridoxy)benzene (bpob)[19] were prepared by the literature methods. Elemental analysis (C, H, N) was carried out at the Advanced Analysis Center in KIST. Infrared spectra were obtained in the 4000-400 cm^{-1} range on a Perkin Elmer 16F PC FTIR spectrophotometer with the sample prepared as a KBr pellet. Thermal analysis (TGA and DSC) was performed on a Stanton Red Croft TG 100 with a scanning rate of 10 ℃/min when heating.

Preparation of $[Co(obp)_2Cl_2]_n$. A methanol solution (10 mL) of $CoCl_2 \cdot 6H_2O$ (137 mg, 0.5 mmol) was slowly diffused into a chloroform solution (20 mL) of obp (172 mg, 1.0 mmol). Initially, pink crystals formed at the interface and were obtained in 1 week in 70% yield. Found (Anal. Calcd for $C_{20}H_{16}N_4O_2Cl_2Co$): C, 50.80 (50.66); H, 3.32 (3.40); N, 11.50 (11.82) %. IR (KBr, cm^{-1}): 1581 (m), 1487 (s), 1442 (s), 1262 (s), 1227 (w), 1205 (w), 1117 (w), 1038 (w), 894 (w), 844 (w), 828 (w), 709 (m), 644 (w), 594 (w).

[*]To whom correspondence should be addressed. Tel: +82-2-958-5086; Fax: +82-2-958-5089; E-mail: oksjung@kist.re.kr.

Preparation of [Co(bpob)$_2$(NCS)$_2$]$_n$. A methanol solution (20 mL) of bpob (264 mg, 1.0 mmol) was slowly diffused into an aqueous solution (10 mL) of Co(NCS)$_2$ (87 mg, 0.5 mmol). Pink crystals suitable for X-ray single crystallography were formed in 1 week in 75% yield. Found (Anal. Calcd for C$_{34}$H$_{24}$N$_6$O$_4$S$_2$Co): C, 57.80 (58.04); H, 3.27 (3.24); N,11.50 (11.94). IR (KBr, cm^{-1}): 2076 (s, v (C=N)), 1568 (m), 1496 (s), 1474 (s), 1426 (s), 1320 (w), 1258 (s), 1226 (s), 1190 (s), 1102 (m), 1048 (w), 1022 (w), 864 (m), 810 (m), 700 (s), 630 (m), 496 (w).

X-ray Crystallographic Analysis. Each pink crystal from the slow diffusion method was wedged into a Lindemann capillary with mother liquor. The X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) at ambient temperature. Axial photographs indicated monoclinic symmetry, and the unit cell dimension was based on 25 well-centered reflections by using a least-square procedure. Data were collected $\omega/2\theta$ scans within the angular range 4.0-50.0^o. During the data collection, three standard reflections monitored every hour did not show any significant intensity variation. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical ψ-scan method. The structures were solved by Patterson method (SHELXS-86) and were refined by full-matrix least squares techniques (SHELXL-93).[20] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added at calculated positions. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1.

Results and Discussion

Synthesis. A typical synthetic procedure[21] was used to form the title cobalt(II) compounds: the slow diffusion of CoX$_2$ (X = Cl, NCS) with the spacer ligands (obp, bpob) in the mole ratio of 1 : 2, respectively, afforded the following 2-dimensional coordination polymers depicted in Scheme 1. The product may depend on the mole ratio of metal-to-

● = CoX$_2$ (X = Cl, NCS)

—— = L = obp, bpob
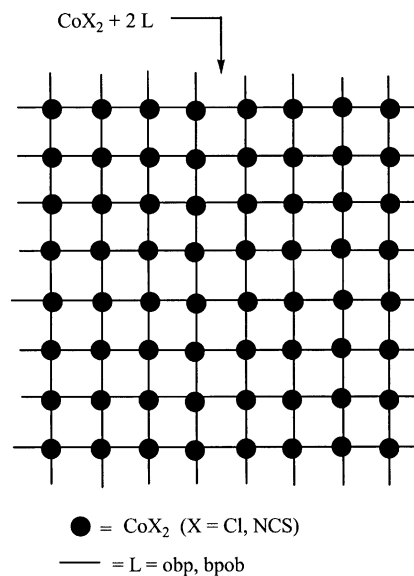
Scheme 1

ligand, but the reaction was not significantly affected by the change in the mole ratio (spacer/CoX$_2$ = 1.5-3). Though such a slow diffusion is generally susceptible to the length of the spacer ligands, the present reaction gave the same network polymers irrespective of the length of the spacers. Formation of the same structure seems to be due to the thermodynamic stability of the molecular network structure. Of course, the product may be closely dependent on the order of slow diffusion, but several attempts gave the same results. Both compounds were isolated as pink crystals without any solvate molecule or counter ion. The compounds were air-stable solids, insoluble in water and common organic solvents.

X-ray Crystal Structures. The unit and extended structures of [Co(obp)$_2$Cl$_2$]$_n$ are shown in Figures 1 and 2, respectively, and selected bond lengths and angles are listed in Table 2. The local geometry of the cobalt center is an octahedral arrangement with four obp nitrogen donors (Co-N(1), 2.169(2) Å; Co-N(2), 2.286(2) Å) and two chlorine anionic ligands in *trans* positions (Co-Cl, 2.4388(6) Å; Cl-Co-Cl,

Table 1. Crystal Data and Structure Refinement for [Co(obp)$_2$Cl$_2$]$_n$ and [Co(bpob)$_2$(NCS)$_2$]$_n$

empirical formula	C$_{20}$H$_{16}$N$_4$O$_2$Cl$_2$Co	C$_{34}$H$_{24}$N$_6$O$_4$S$_2$Co
formula weight	474.20	703.64
space group	P2$_1$/n (No. 14)	P2$_1$/c (No. 14)
a, Å	8.823(1)	9.280(1)
b, Å	13.977(3)	8.149(1)
c, Å	8.943(1)	21.404(4)
β, deg	116.95(1)	100.62(1)
V, Å^3	983.1(3)	1590.9(4)
Z	2	2
d$_{cal}$, g/cm	1.602	1.469
μ, mm^{-1}	1.170	0.720
final R [I>2σ(I)]	R1 = 0.0305	0.0366
R indices (all data)	R1 = 0.0309	0.0383
	(wR2 = 0.0800)	(wR2 = 0.0899)

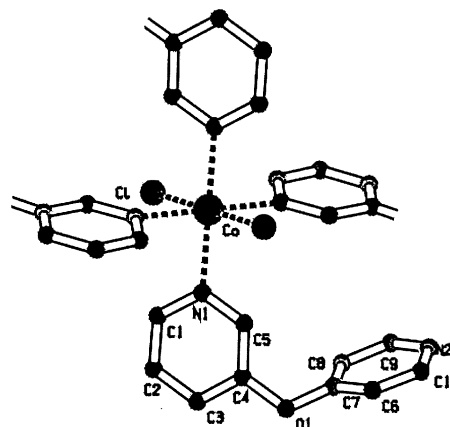**Figure 1**. The unit view of [Co(obp)$_2$Cl$_2$]$_n$ showing the cobalt(II) coordination environment. Hydrogen atoms are omitted for clarity.

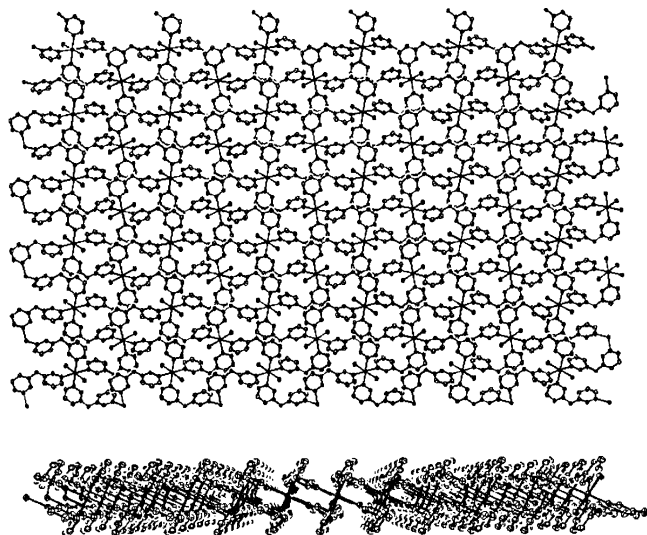**Figure 2**. Infinite molecular networks of [Co(obp)₂Cl₂]ₙ (top: top view; bottom: side view).

Table 2. Selected Bond Lengths (Å) and Angles (º) of [Co(obp)₂Cl₂]ₙ and [Co(bpob)₂(NCS)₂]ₙ

[Co(obp)₂Cl₂]ₙ		[Co(bpob)₂(NCS)₂]ₙ	
Co-N(1)	2.169(2)	Co-N(1)	2.06(2)
Co-N(1)'	2.169(2)	Co-N(2)	2.08(1)
Co-N(2)	2.286(2)	Co-N(3)	2.21(1)
Co-N(2)'	2.286(2)	Co-N(4)	2.14(2)
Co-Cl	2.4388(6)	Co-N(5)	2.27(1)
Co-Cl'	2.4388(6)	Co-N(6)	2.24(1)
N(1)-Co-N(1)'	180.0	N(1)-Co-N(2)	178.4(9)
N(1)-Co-N(2)	87.50(7)	N(1)-Co-N(6)	90.2(6)
N(1)'-Co-N(2)	92.50(7)	N(2)-Co-N(6)	90.7(6)
N(2)-Co-N(2)'	180.0	N(3)-Co-N(5)	179.6(7)
Cl-Co-Cl	180.0	N(4)-Co-N(6)	179.1(8)
C(7)-O(1)-C(4)	116.7(2)	C(4)-O(1)-C(32)'	120(2)
		C(9)-O(2)-C(13)	122(1)
		C(20)-O(3)-C(16)"	112(1)
		C(27)-O(4)-C(29)	116(1)

Figure 3. The unit view of [Co(bpob)₂(NCS)₂]ₙ showing the cobalt(II) coordination environment. Hydrogen atoms are omitted for clarity.

Figure 4. Infinite molecular networks of [Co(bpob)₂(NCS)₂]ₙ (top: top view; bottom: side view).

180.0º). The most outstanding feature is that the molecule exhibits infinite network structure. Each obp spacer is linked to the two cobalt(II) atoms *via* a bridge fashion, resulting in a 40-membered [Co(II)]₄ ring. The bent angle around the oxygen atom (C(7)-O(1)-C(4)) is 116.7(2)º. The closest intrachain Co···Co distance *via* an obp linker is 8.39 Å, whereas the shortest interchain distance of Co···Co is 8.82 Å. The dihedral angle of two pyridyl groups within the obp group is 76.9(1)º, but one pyridyl group is almost coplanar with its *trans* pyridyl group.

X-ray characterization of [Co(bpob)₂(NCS)₂]ₙ revealed a similar structure. The unit and extended structures are shown in Figures 3 and 4, respectively, and selected bond lengths and angles are listed in Table 2. The local geometry of the cobalt(II) atom is an octahedral arrangement with four bpob units (Co-N, 2.14(2)-2.27(1) Å) and two NCS groups in *trans* positions (N(1)-Co-N(2), 178.4(9)º). Each bpob linker
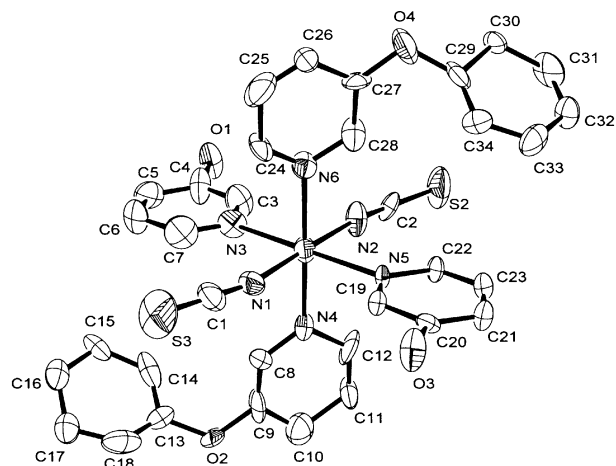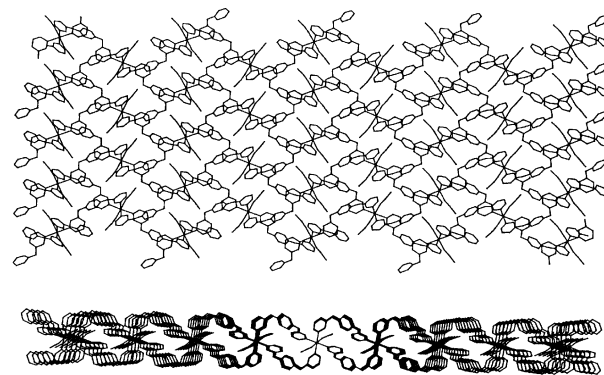
connects two cobalt(II) atoms defining the edges of a 60-membered [Co(II)]₄ ring. The bent angle around the oxygen atom (C-O-C, 112(1)-122(1)º) is very similar to that of [Co(obp)₂Cl₂]ₙ. As expected, the cobalt-cobalt separation through a bpop linker (11.4 Å) and the cobalt-cobalt distance through the interchain (9.3 Å) are longer than the corresponding lengths of [Co(obp)₂Cl₂]ₙ. An isothiocyanate mode (Co-NCS) was observed among two possible linkage isomers of the NCS group. The Co-N bond lengths involving the NCS group (2.06(2), 2.08(1) Å) are much shorter than the corresponding bonds involving the bpob ligand. The isothiocyanate group is proximity to linearity (N(1)-C(1)-S(3), 177(2); N(2)-C(2)-S(2), 174(2)º), indicating that the contribution of the resonance structure Co-N⁺≡C-S⁻ is significant.[22] The bond lengths of N(1)-C(1) (1.18(2) Å) and C(1)-S(3) (1.56(2) Å) are additional evidence of the contribution of the resonance structure.

The complexation of the appropriately long and flexible bpob linker with the cobalt(II) salts enables the interwoven structure,[17,21] but the conformation of the linker affords the non-interpenetrated sheet structure. For the complexation, the angular and conformational effects of the linker seem to be an obstacle to the formation of the interwoven sheet,
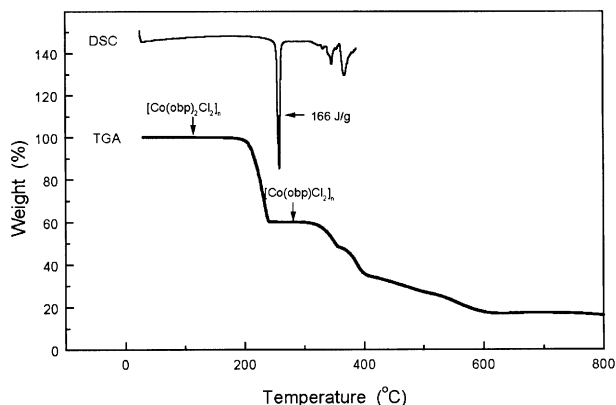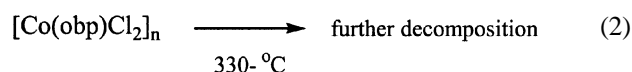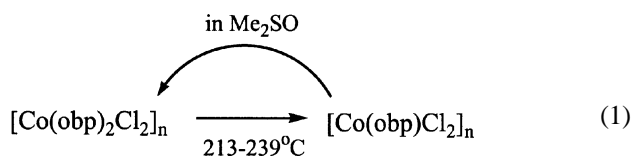
Figure 5. TGA and DSC thermograms of $[Co(obp)_2Cl_2]_n$.

instead affording the 2-dimensional infinite structure.

Thermal Analyses. Thermal analyses (TGA and DSC traces) of $[Co(obp)_2Cl_2]_n$ are shown in Figure 5. The skeletal structure is stable up to 213 °C, and the weight-loss corresponding to one obp linker was observed in the temperature range of 213-239 °C (eq. 1). The pyrolysis intermediate, $[Co(obp)Cl_2]_n$, is stable during the wide temperature range of 239-330 °C, is subsequently followed by the evaporation of the remaining spacer and coligand (eq. 2). Three endotherms at 25-400 °C are consistent with the decomposition

$$[Co(obp)_2Cl_2]_n \xrightarrow[213-239^{\circ}C]{\text{in Me}_2\text{SO}} [Co(obp)Cl_2]_n \qquad (1)$$

$$[Co(obp)Cl_2]_n \xrightarrow{330^{-}\ ^{\circ}C} \text{further decomposition} \qquad (2)$$

procedures. The structure of the pyrolysis intermediate, $[Co(obp)Cl_2]_n$, could not be clearly elucidated. When the species is recrystallized in Me_2SO, the compound returns to its mother crystal, $[Co(obp)_2Cl_2]_n$, with the liberation of the remaining $CoCl_2$. This fact shows that the formation of $[Co(obp)_2Cl_2]_n$ is favored regardless of the reaction mole ratio, whereas the structure of $[Co(obp)Cl_2]_n$ is thermody-

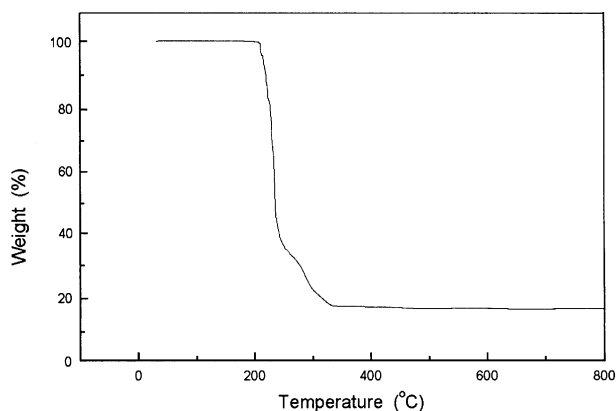**Figure 6**. TGA thermogram of $[Co(bpob)_2(NCS)_2]_n$.

namically unstable in solution. Such a pyrolysis may be developed as a rational synthetic strategy for species that cannot be synthesized by the general method. The TGA curve of $[Co(bpob)_2(NCS)_2]_n$ is depicted in Figure 6. The compound decomposes in the temperature range of 220-330 °C. This drastic decomposition reveals that the 60-membered ring sheet structure is susceptible to the expansion of the crystal-volume.

IR Spectra. The characteristic IR bands of the two compounds are consistent with their crystal structure. In particular, the relevant IR bands of $[Co(bpob)_2(NCS)_2]_n$ are those associated with the presence of the linkage isomeric NCS group. The bonding mode of the metal (iso)thiocyanate compound has been well established for whether the NCS group bonded to a thiocyanate (M-SCN) or an isothiocyanate (M-NCS).[23] The ν(C-N) band in the region of 2000-2200 cm^{-1} has been used to discern the bonding fashion of the NCS group: thiocyanate bonding mode exhibits very sharp ν(C-N) above 2100 cm^{-1}, whereas the isothiocyanate mode exhibits a relatively broad and intensive band around or below 2100 cm^{-1}. A strong band at 2076 cm^{-1} is indicative of an isothiocyanate bonding mode, which is very consistent with the X-ray crystal structure. Moreover, the single C-N stretching frequency seems to be indebted to the *trans* isomer.

Conclusion

The bpob and obp ligands are useful linkers for non-interpenetrated cobalt-based coordination polymers. The products are rare integral coordination polymers lacking any counter ions or solvate molecules. The pyrolysis of such coordination polymers may contribute to the development of a new synthetic strategy. Though the mechanism of the structural and thermal behaviors is manifestly unpredictable, the present results may be a clue to the rational synthesis of coordination polymers that have applications as molecular-based materials or molecular building blocks.

Supporting Information Available. Details of X-ray data collection parameters, atomic coordinates, anisotropic thermal parameters, and lists of bond lengths and angles are available from OSJ.

References

1. Robson, R. *Comprehensive Supramolecular Chemistry*; Macnicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon: Oxford, 1996; Vol. 6, p 733.
2. (a) Aumuller, A.; Erk, P.; Klebe, G.; Hunig, S.; von Schultz, J. U.; Werner, H.-P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 740. (b) Ermer, O. *Adv. Mater.* **1991**, *3*, 608.
3. (a) De Munno, G.; Munoz, M. C.; Julve, M. *Inorg. Chem.* **1991**, *30*, 2701. (b) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O. *Science* **1993**, *261*, 447. (c) Real, J. A.; Andres, E.; Munoz, M. C.; Julve, M.; Granier, T.; Bousseksou, A.; Varret, F. *Science* **1995**, *268*, 265. (d)

Zhao, H.; Heintz, R. A.; Dunbar, K. R.; Rogers, R. D. *J. Am. Chem. Soc*. **1996**, *118*, 12844. (e) Escuer, A.; Vicente, R.; Goher, M. A. S.; Mautner, F. A. *Inorg. Chem*. **1997**, *36*, 3440.

 4. (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc*. **1990**, *112*, 1546. (b) Yuge, H.; Iwamoto, T. *J. Chem. Soc., Dalton Trans*. **1994**, 1237. (c) Kawata, S.; Kitagawa, S.; Kondo, M.; Furuchi, I.; Munakata, M. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 1759. (d) Venkataraman, D.; Gardner, G. F.; Lee, S.; Moore, J. S. *J. Am. Chem. Soc*. **1995**, *117*, 11600.

 5. Jung, O.-S.; Pierpont, C. G. *J. Am. Chem. Soc*. **1994**, *116*, 2229.

 6. Jung, O.-S.; Park, S. H.; Kim, K. M.; Jang, H. G. *Inorg. Chem*. **1998**, *37*, 5781.

 7. (a) Braga, D.; Grepioni, F. *J. Chem. Soc., Chem. Commun*. **1998**, 911. (b) Jung, O.-S.; Park, S. H.; Park, C. H.; Park, J. K. *Chem. Lett*. **1999**, 923.

 8. Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc*. **1994**, *116*, 1151.

 9. (a) Yamaguchi, I.; Osakada, K.; Yamamoto, T. *J. Am. Chem. Soc*. **1996**, *118*, 1811. (b) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Niu, T.; Jacobson, A. J. *Inorg. Chem*. **1997**, *36*, 923.

10. (a) Kitagawa, S.; Kawata, S.; Kondo, M.; Nozaka, Y.; Munakata, M. *Bull. Chem. Soc. Jpn*. **1993**, *66*, 3387. (b) Kitagawa, S.; Munakata, M.; Tanimura, T. *Inorg. Chem*. **1992**, *31*, 1714.

11. (a) Soma, T.; Iwamoto, T. *Chem. Lett*. **1994**, 821. (b) Goodgame, D. M. L.; Menzer, S.; Smith, A. M.; Williams, D. J. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 574. (c) Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W.-S.; Schroder, M. *J. Chem. Soc., Chem. Commun*. **1997**, 1005.

12. (a) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc*. **1995**, *117*, 7287. (b) Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 972. (c) Hoskins, B. F.; Robson, R.; Slizys, D. A. *J. Am. Chem. Soc*. **1997**, *119*, 2952.

13. (a) Small, J. H.; MaCord, D. J.; Greaves, J.; Shea, K. J. *J. Am. Chem. Soc*. **1995**, *117*, 11588. (b) Li, J.; Zeng, H.; Chen, J.; Wang, Q.; Wu, X. *J. Chem. Soc., Chem. Commun*. **1997**, 1213.

14. Yaghi, O. M.; Li, H. *J. Am. Chem. Soc*. **1996**, *118*, 295.

15. Irwin, M. J.; Vittal, J. J.; Yap, G. P. A.; Puddephatt, R. J. *J. Am. Chem. Soc*. **1996**, *118*, 13101.

16. Stang, P. J.; Persky, N. E.; Manna, J. *J. Am. Chem. Soc*. **1997**, *119*, 4777.

17. Jung, O.-S.; Park, S. H.; Kim, D. C.; Kim, K. M. *Inorg. Chem*. **1998**, *37*, 610.

18. Barker, D. J.; Summers, L. A. *J. Hetrocyclic Chem*. **1983**, *20*, 1411.

19. McMorran, D. A.; Steel, P. J. *Acta Crystallogr., Sec. C* **1998**, *54*, 1132.

20. (a) Sheldrick, G. M. *SHELXS-86: A Program for Structure Determination*; University of Göttingen: Germany, 1986. (b) Sheldrick, G. M. *SHELXL-93: A Program for Structure Refinement*; University of Göttingen; Germany, 1993.

21. Park, S. H.; Kim, K. M.; Lee, S.; Jung, O.-S. *Bull. Korean Chem. Soc*. **1998**, *19*, 79.

22. Jung, O.-S.; Park, S. H.; Kim, K. M.; Kim, D. C.; Chae, H. K. *Bull. Korean Chem. Soc*. **1997**, *18*, 785.

23. Wada, M.; Okawara, R. *J. Organomet. Chem*. **1967**, *8*, 261.