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A novel coordination polymer containing puckered rhombus grids

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The polymeric complex $[Ni(spcp)_2]_n$ ($spcp^-$ = 4-sulfanylmethyl-4′-phenylcarboxylate pyridine) with puckered rhombus grids of dimensions 11.72 × 11.09 Å was obtained from the reaction of $Ni(OAc)_2 \cdot 4H_2O$ with Na(spcp) by solvothermal methods.

Introduction

Owing to their fascinating properties and potential applications in functional materials, the construction of organic–inorganic open framework complexes with variable cavities or channels has received considerable interest in the last decade.[1,2] It has been documented that the choice of ligand plays an important role in the structure of the open framework complexes. For instance, the bidentate nitrogen containing ligand 4,4′-bipyridine and its analogues have been widely employed and have resulted in a great number of novel networks;[3–6] polycarboxylate ligands have led to the formation of moderately robust ("zeolitic") frameworks[7] and other porous coordination polymers;[8] and the use of mixed ligands has also produced many novel polymeric structures.[9–14] Although both length and flexibility of the organic ligand have great influence on the structural topology, studies on the influence of flexibility attract less attention. Recently we have begun work on the architectures of polymeric structures containing flexible ligands and a series of interesting structures has been obtained.[15,16] As part of our systematic work, in this paper we will report the synthesis and characterization of a novel long and flexible mono-anionic ligand with hybrid pyridyl and benzoic carboxylate moieties, namely 4-sulfanylmethyl-4′-phenylcarboxylate pyridine ($spcp^-$), and its nickel polymer $[Ni(spcp)_2]_n$ (**1**) which possesses puckered rhombus grids of dimensions 11.72 × 11.09 Å.

Experimental

Preparation of Na(spcp)

A mixture of the sodium salt of 4-sulfanylpyridine (0.65 g, 5 mmol) and the sodium salt of 4-(bromomethyl)phenylcarboxylate (2.15 g, 5 mmol) in CH_3OH (40 ml) was heated to 60 °C for 12 h with vigorous stirring. After cooling, $AgNO_3$ (5 mmol, 0.85 g) was added to the solution and stirred for half an hour. The reaction mixture was filtered and the resultant solution was dried to give an oil-like product, which was washed three times with H_2O (2 ml) and then extracted with CH_3OH (20 ml). Removing the CH_3OH under vacuum gave rise to crude Na(spcp). Pure Na(spcp) was obtained as a white powder by recrystallization from CH_2Cl_2/Et_2O/hexane (1 : 1 : 1) (yield 0.68 g, 51%). Elemental analyses: for $C_{13}H_{10}NNaO_2S$, calc: C, 58.42; H, 3.77; N, 5.24. Found: C, 58.36; H, 3.68; N, 5.18%. NMR (CD_3OD, 500 MHz): δ 4.36 (s, 2H, $-CH_2$), 7.31 (d, J = 6.0 Hz, 2H, $-C_5H_4N$), 8.27 (d, J = 5.5 Hz, 2H, $-C_5H_4-$), 7.44 (d, J = 8.0 Hz, 2H, $-C_6H_4-$), 7.90 (d, J = 8.5 Hz, 2H, $-C_6H_4-$). IR(KBr, cm^{-1}): 1630(s), 1589(vs), 1545(s), 1385(vs), 1109(m), 1092(m), 1018(m), 798(s), 748(s), 634(m), 536(w), 492(s).

Table 1 Crystal data for **1**

Empirical formula	$C_{26}H_{20}N_2NiO_4S_2$
Formula weight	547.27
Space group	$P\bar{1}$
a/Å	11.0854(3)
b/Å	11.1224(3)
c/Å	11.720(0)
α/°	63.373(1)
β/°	82.008(1)
γ/°	80.142(1)
V/Å^3	1269.56(5)
Z	2
ρ_{cal}/g cm^{-3}	1.432
T/K	293(2)
μ/mm^{-1}	0.963
Independent reflections	6634
Observed reflections	4446
$R(F_o)$	0.0714
$R_w(F_o)$	0.1831
S	1.051
Largest difference peak, hole/e Å^{-2}	1.075, −0.489

Preparation of $[Ni(spcp)_2]_n$ (1)

A mixture of $Ni(OAc)_2 \cdot 4H_2O$ (0.249 g, 1 mmol) and Na(spcp) (0.54 g, 2 mmol) in a metal-to-ligand ratio of 1 : 2 in 20 ml of CH_3OH/H_2O (1 : 1) was sealed in a stainless-steel reactor with a Teflon liner and heated at 90 °C for 72 h. A large quantity of green, sheet-like crystals of **1** were obtained after the solution was cooled to room temperature (0.41 g, 74%). Elemental analyses: for $C_{26}H_{20}N_2NiO_4S_2$, calc: C, 57.06; H, 3.68; N, 5.12. Found: C, 57.07; H, 3.78; N, 5.08%. IR(KBr, cm^{-1}): 1593(vs), 1541(vs), 1421(vs), 1394(vs), 1020(m), 737(s), 642(m), 503(w).

Crystallography

A single crystal of **1** with approximate dimensions 0.24 × 0.20 × 0.13 mm was used for data collection. The intensity data were collected on a Siemens Smart CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073Å) at room temperature. Empirical absorption corrections were applied by using the SADABS program for the Siemens area detector.[17] The structure of the complex was solved by direct methods[18] and all calculations were performed by using the SHELXL-97 program[19] on a Legend computer. The structure was refined by full-matrix least-squares minimizations of $\Sigma(F_o - F_c)^2$ with anisotropic thermal parameters for all atoms except H. The positions of the H atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. Table 1 summarizes the important crystal data and Table 2 gives the selected bond lengths and angles for the complex.

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Table 2 Bond lengths (Å) and angles (°) for **1**

Ni–N(1)	2.057(5)	Ni–O(1A)	2.078(4)
Ni–O(3B)	2.057(4)	Ni–O(2A)	2.170(5)
Ni–N(2)	2.065(5)	Ni–O(4B)	2.179(5)
N(1)–Ni–O(3B)	95.58(19)	O(1A)–Ni–O(4B)	105.98(17)
N(1)–Ni–N(2)	98.7(2)	O(2A)–Ni–O(4B)	88.70(18)
O(3B)–Ni–N(2)	94.0(2)	C(9)–S(1)–C(8)	104.4(3)
N(1)–Ni–O(1A)	94.71(19)	C(29)–S(2)–C(28)	104.2(3)
O(3B)–Ni–O(1A)	165.37(18)	C(5)–C(8)–S(1)	116.6(5)
N(2)–Ni–O(1A)	94.66(19)	C(13)–C(9)–S(1)	125.0(5)
N(1)–Ni–O(2A)	92.2(2)	C(10)–C(9)–S(1)	117.0(5)
O(3B)–Ni–O(2A)	107.10(18)	C(25)–C(28)–S(2)	116.6(5)
N(2)–Ni–O(2A)	155.2(2)	C(30)–C(29)–S(2)	117.7(5)
O(1A)–Ni–O(2A)	62.08(17)	C(33)–C(29)–S(2)	126.3(5)
N(1)–Ni–O(4B)	156.96(19)	N(2)–Ni–O(4B)	89.8(2)
O(3B)–Ni–O(4B)	62.30(17)		

Symmetry transformations used to generate equivalent atoms. A: *x*, *y*, *z* + 1. B: *x* − 1, *y*, *z*.

CCDC reference number 165608.

See http://www.rsc.org/suppdata/dt/b1/b108449f/ for crystallographic data in CIF or other electronic format.

Physical measurements

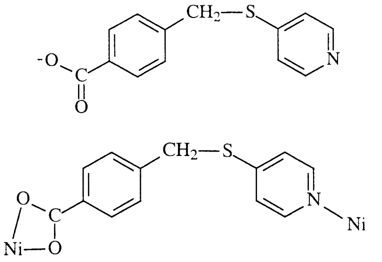
The infrared spectra were taken on a Magna 750 FTIR spectrophotometer as KBr pellets in the 4000–400 cm^{-1} region. The NMR spectrum was recorded on a Varian Inova-500 spectrophotometer at room temperature and the chemical shifts were quoted in δ (ppm) relative to the deuterated solvent used. The elementary analyses were performed on an Elementar Vario ELIII elemental analyzer. Variable-temperature magnetic susceptibility data for a polycrystalline sample of complex **1** were obtained in an external field of 10.0 kG on a Quantum Design PPMS Model 6000 magnetometer from 300 to 4 K.

Results and discussion

Syntheses

Recently, we have developed a convenient method for the syntheses of flexible organic ligands containing sulfur and nitrogen donor atoms, such as 2,4,6-tris[(4-pyridyl)methylsulfanyl]-1,3,5-triazine (tpst) and 1,2-bis[(2-pyrimidinyl)sulfanymethyl]-benzene (bpsb). By introducing these ligands during the preparation of metal complexes, we have isolated a series of novel transition metal complexes with nanometer-sized metallosupramolecular cubes, nanometer-sized tubes, single-stranded helical chains, or two-dimensional lamellar network structures.[15,16] The success prompted us to extend our work to flexible ligands containing sulfur, nitrogen and oxygen donor atoms. Thus the sodium salt of 4-(bromomethyl)phenylcarboxylate was selected as a starting material to react with the sodium salt of 4-sulfanylpyridine and Na(spcp) was obtained as a white powder in satisfactory yield.

The intriguing features of $spcp^-$ arise not only from its flexibility but also from the presence of hybrid pyridyl and benzoic carboxylate moieties that are connected by a $-CH_2S-$ spacer. As shown in Scheme 1, the ligand possesses four possible bonding sites, *i.e*, the nitrogen atom, the sulfur atom, and the two oxygen atoms of the carboxylate group. Because the carboxylate group can adopt monodentate, chelating-bidentate, bridging-bidentate and bridging-multidentate modes,[14] rich coordination modes of $spcp^-$ may be expected. If $spcp^-$ coordinates to metal ions through its carboxylate group and pyridyl nitrogen and the carboxylate group adopts a chelating-bidentate mode, it may be used as a mono-anionic singly bridging ligand. Accordingly, a grid-like structure may be expected by introducing metal ions favoring a hexa-coordination mode, with the advantage that no co-ligand is needed for saturating the coordination sphere of the metal ion owing to the chelating function of carboxylate. Thus $spcp^-$ was reacted with $Ni(OAc)_2 \cdot 4H_2O$ in a metal to ligand ratio of 1 : 2 under solvothermal conditions. As expected, complex **1** containing puckered rhombus grids was obtained in high yield.



Scheme 1 Top: $spcp^-$ ligand; bottom: coordination mode of $spcp^-$ in **1**.

Crystal structure

The crystallographic analysis reveals that complex **1** is a two-dimensional grid-like polymer. As shown in Fig. 1, each nickel ion is coordinated by two nitrogen atoms from two ligands and four oxygen atoms of the carboxylate groups from two other ligands in a highly distorted octahedral coordination geometry. One nitrogen atom [N(1)] and three oxygen atoms [O(1A), O(3B) and O(4B)] form the equatorial plane with the deviation of Ni from the mean plane of [N(1)O(1A)O(3B)O(4B)] being 0.16 Å, while the axial positions are filled by one nitrogen atom [N(2)] and one oxygen atom [O(2A)] with the N(2)–Ni–O(2A) angle being 155.2(2)°. The Ni–N and Ni–O distances range from 2.057(5) to 2.065(5) Å and 2.057(4) to 2.179(5) Å (see Table 2), respectively, similar to those in other related grid-like nickel complexes.[1,20]

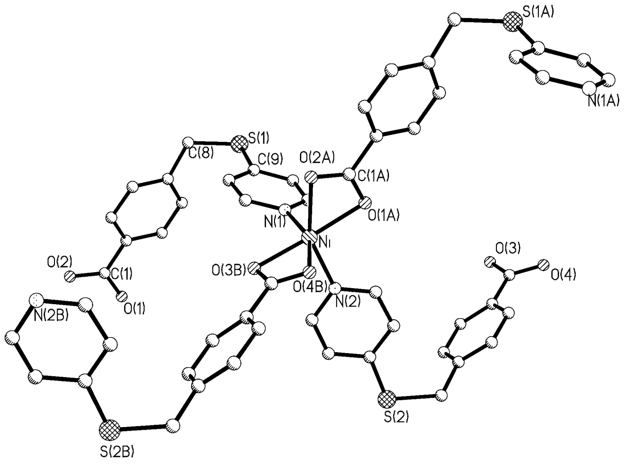


Fig. 1 The coordination environment of Ni(II) in **1**.

Each ligand acts as a single bridge linking two nickel ions through its nitrogen atom and carboxylate group (Scheme 1), and each nickel ion connects four ligands to form an infinite two-dimensional structure. The grid-like $Ni_4(spcp)_4$ species can be viewed as the basic building block of the structure, in which the apices are occupied by nickel ions and the sides are formed by $spcp^-$ ligands. Each four $Ni_4(spcp)_4$ grids are joined together through sharing the nickel apices to give the final two-dimensional layer structure consisting of puckered rhombus grids with dimensions of 11.72 × 11.09 Å based on the metal–metal distances (Fig. 2). The most intriguing feature of the structure is that the basic grid is puckered, different from previously reported grid-like structures in which the basic grids are usually coplanar or quasi-coplanar.[1,20] The puckered shape

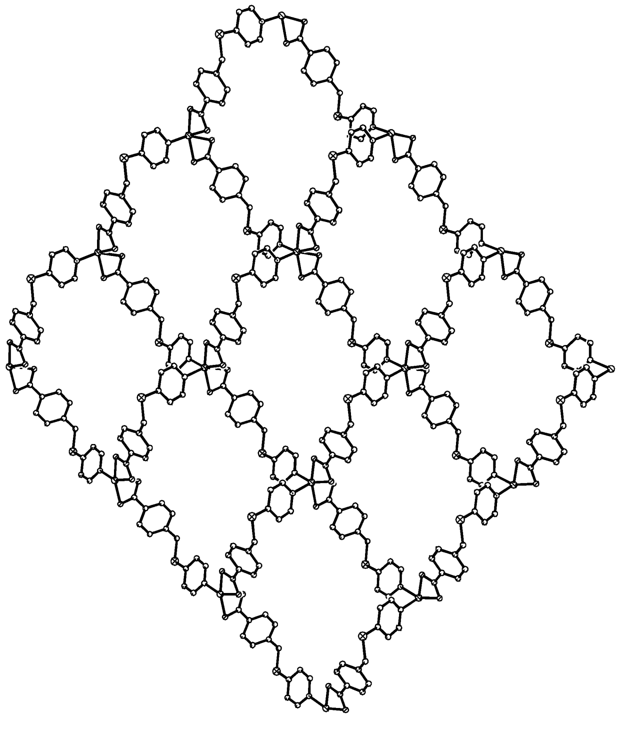


Fig. 2 The two-dimensional layer structure of **1**.

of the basic grid in **1** is understandable, because the sp^3 configurations of C and S of the $-CH_2S-$ spacer force the $spcp^-$ ligand to be non-linear, generating the non-linear grid sides and thereby the puckered grids. Actually, the C–C–S and C–S–C angles of $spcp^-$ in **1** range from 116.6(5) to 126.3(5) and 104.2(3) to 104.4(3)°, respectively; the phenyl and pyridyl rings in each ligand are almost perpendicular to each other with an average dihedral angle of 87.7(6)°. These structural data clearly depict the non-linear configuration of $spcp^-$ in **1**. It should be noted that the actual structure of the two-dimensional layer is wave-like, the convex surface of one layer is immersed into the concave surface of an adjacent layer to get a tightly packed structure without any guest molecules (Fig. 3).

Magnetic properties

Variable-temperature magnetic susceptibilities in the range of 4–300 K are shown in Fig. 4. The experimental μ_{eff} value per Ni(II) ion at room temperature is *ca.* 3.02 μ_B, within the range expected for a high-spin Ni(II) ion. Upon cooling, the magnetic moment decreases slightly to a value of 2.87 μ_B at 5.93 K. This indicates that the interaction is very weak. The χ_M^{-1} *versus* T plot is essentially linear, and least-squares fitting of the data to the Curie–Weiss law gave $C = 1.13$ cm³ mol⁻¹ K and $\theta = -0.47$ K. This Curie–Weiss behavior may arise from antiferromagnetic interactions between Ni(II) ions. Assuming an isotropic exchange between Ni(II) ions, the magnetic susceptibility per Ni(II) ion can be expressed as

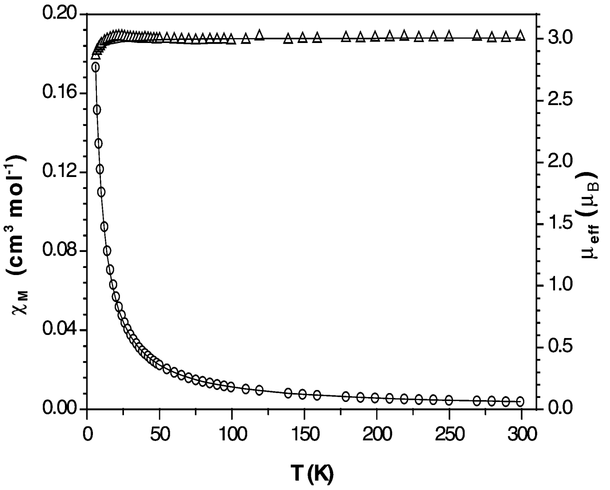


Fig. 4 Temperature-dependent magnetic susceptibility of **1**: (○) χ_M, (Δ) μ_{eff}, (—) the best fit obtained.

$$\chi_{chain} = \frac{Ng^2\beta^2}{kT}[A + Bx^2][1 + Cx + Dx^3]^{-1}$$

$$A = 0.6667, B = 2.5823, C = 3.6035, D = 39.558, x = J/kT \quad (1)$$

$$\chi_M = \frac{\chi_{chain}}{1 - (2ZJ/Ng^2\beta^2)\chi_{chain}}$$

The best fit (assuming $ZJ = 0$) of the experimental data to eqn. (1) yielded $J = -0.10$ cm⁻¹, $g = 2.13$, with an agreement factor $R = \Sigma(\chi_{obsd} - \chi_{cacld})^2/\Sigma\chi_{obsd}^2 = 2.8 \times 10^{-4}$. The J value is so small that one cannot attribute it unambiguously to an intramolecular interaction. We may conclude that the interaction *via* the $spcp^-$ bridge is very weak, suggesting that there is no efficient orbital pathway for super-exchange between Ni(II) ions through the $spcp^-$ bridge, because the sp^3 configurations of C and S of the $-CH_2S-$ spacer in $spcp^-$ make the long and flexible ligand unconjugated and unfavorable for electronic interactions.

Conclusion

In summary, a novel long and flexible mono-anionic ligand ($spcp^-$) comprising hybrid pyridyl and benzoic carboxylate moieties linked by a $-CH_2S-$ spacer was synthesized. The polymeric complex $[Ni(spcp)_2]_n$ (**1**) consisting of puckered rhombus grids with dimensions of 11.72 × 11.09 Å was obtained in the reaction of $Ni(OAc)_2 \cdot 4H_2O$ with Na(spcp) under solvothermal conditions. The non-linear configuration of $spcp^-$ induces the puckered basic grid and the wave-like two-dimensional structure of **1**.

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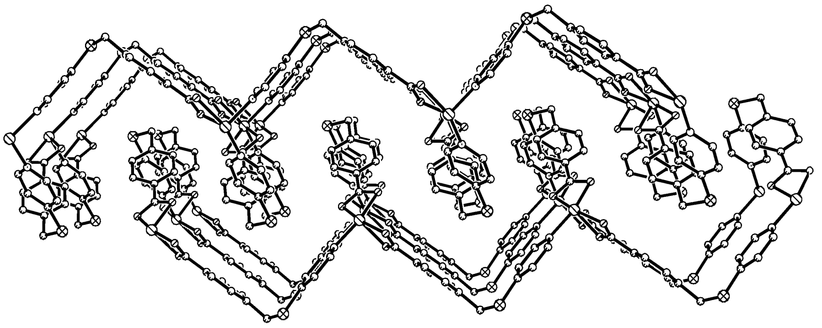

Fig. 3 The tightly packed structure of **1**, only two layers are shown for clarity.

References

1 K. Biradha and M. Fujita, *J. Chem. Soc., Dalton Trans.*, 2000, 3805.

2 *Comprehensive Supramolecular Chemistry*, ed. J.-M. Lehn, Pergamon Press, Oxford, 1996, vol. 6; T. Iwamoto (ch. 2), J. Lipowski (ch. 3); T. Iwamoto, in *Inclusion Compounds*, eds. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, London, 1991, vol. 5, ch. 2–4, pp. 172–212; C. Janiak, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1431 and references therein; S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1999, 375; M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka and K. Seki, *Angew. Chem., Int. Ed.*, 1999, **38**, 140.

3 M. J. Zaworotko, *Chem. Commun.*, 2001, 1.

4 T. Miyoshi, T. Iwamoto and Y. Sasaki, *Inorg. Chim. Acta*, 1972, **6**, 59; L. R. Macgillivray, R. H. Groeneman and J. L. Atwood, *J. Am. Chem. Soc.*, 1998, **120**, 2676.

5 M. Aoyagi, K. Biradha and M. Fujita, *Bull, Chem, Soc, Jpn.*, 2000, **73**, 1369; D. Hagrman, R. P. Hammond, R. Haushalter and J. Zubieta, *Chem, Mater.*, 1998, **10**, 79; J. Lu, T. Paliwala, S. C. Lim, C. Yu, T. Y. Niu and A. J. Jacobson, *Inorg. Chem.*, 1997, **36**, 923.

6 S. H. Park, K. M. Kim, S. Lee and O. S. Jung, *Bull. Korean Chem. Soc.*, 1998, **19**, 79; T. L. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972; M. Fujita, Y.-J. Kwon, M. Miyazawa and K. Ogura, *J. Chem. Soc., Chem. Commun.*, 1994, 1977; J. A. Real, E. Andrés, M. C. Munoz, M. Julve, T. Granier, A. Boussekou and F. Varret, *Science*, 1995, **268**, 265; Y.-B. Dong, R. C. Layland, M. D. Smith, N. G. Pschirer, U. H. F. Bunz and H.-C. zur Loye, *Inorg. Chem.*, 1997, **36**, 4292.

7 O. M. Yaghi, H. Li and T. L. Groy, *J. Am. Chem. Soc.*, 1996, **118**, 9096; C. Livage, C. Egger, M. Nogues and G. Ferey, *J. Mater. Chem.*, 1998, **8**, 2734; S. O. H. Gutschke, M. Molinier, A. K. Powell and P. T. Wood, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 991.

8 R. H. Groeneman, L. R. MacGillivray and J. L. Atwood, *Inorg. Chem.*, 1999, **38**, 208; G. Guilera and J. W. Steed, *Chem. Commun.*, 1999, 1563; L. Deakin, A. M. Arif and J. S. Miller, *Inorg. Chem.*, 1999, **38**, 5072; T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 1651.

9 M. L. Tong, X. M. Chen, X. L. Yu and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1998, 5.

10 S. Kitagawa, T. Okubo, S. Kawata, M. Kondo, M. Katada and H. Kobayashi, *Inorg. Chem.*, 1995, **34**, 4790.

11 J. Y. Lu, M. A. Lawandy, J. Li, T. Yuen and C. L. Lin, *Inorg Chem.*, 1999, **38**, 2695; L. M. Zheng, X. Fang, K. H. Li, H. H. Song, X. Q. Xin, H. K. Fun, K. Chinnaki and I. A. Razak, *J. Chem. Soc., Dalton Trans.*, 1999, 2311.

12 L. R. MacGillivray, R. H. Groeneman and J. L. Attwod, *J.Chem. Soc., Dalton Trans.*, 1998, 2676.

13 P. Lightfoot and A. Snedden, *J. Chem. Soc., Dalton Trans.*, 1999, 3549.

14 J. Tao, M. L. Tong and X. M. Chen, *J. Chem. Soc., Dalton Trans.*, 2000, 3669.

15 M. C. Hong, Y. J. Zhao, W. P. Su, R. Cao, M. Fujita, Z. Y. Zhou and A. S. C. Chan, *Angew. Chem., Int. Ed.*, 2000, **39**, 2468; M. C. Hong, Y. J. Zhao, W. P. Su, R. Cao, M. Fujita, Z. Y. Zhou and A. S. C. Chan, *J. Am. Chem. Soc.*, 2000, **122**, 4819.

16 M. C. Hong, W. P. Su, R. Cao, M. Fujita and J. X. Lu, *Chem. Eur. J.*, 2000, **6**, 427.

17 R. Blessing, *Acta Crystallogr., Sect. A.*, 1995, **51**, 33.

18 G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, 1997.

19 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, 1997.

20 K. Biradha and M. Fujita, *Chem. Commun.*, 2001, 15; K. Biradha, Y. Hongo and M. Fujita, *Angew. Chem., Int. Ed.*, 2000, **39**, 3843.