3,6-Di(2-pyridyl)-1,4,2,5-dioxadiazine and a Silver Coordination Polymer with an Unprecedented Metallosupramolecular Topology

Chris Richardson[a] **and Peter J. Steel***[a]

Keywords: Silver / Coordination polymers / Bridging ligands / N ligands

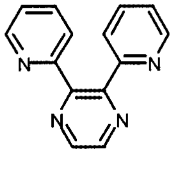
The new ligand 3,6-di(2-pyridyl)-1,4,2,5-dioxadiazine (**6**) has been prepared and reacted with silver tetrafluoroborate to form a novel coordination polymer in which adjacent chains are interdigitated and π-stacked.

Introduction

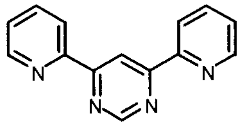
The use of bridging ligands for the controlled self-assembly of one-, two- or three-dimensional metallosupramolecular species has been the subject of enormous study in recent years.[1] Particularly stable entities can be obtained by employing ligands with chelating binding domains at the metal centres, with 2,2′-bipyridine subunits being the most commonly employed.[2] Similarly well studied are the binuclear ruthenium(II) complexes[3] of *N*,*N*′-chelating bridging ligands, such as 2,3-di(2-pyridyl)pyrazine (**1**),[4,5] 4,6-di(2-pyridyl)pyrimidine (**2**),[6] 2,5-di(2-pyridyl)pyrazine (**3**),[5] and 3,6-di(2-pyridyl)-1,2,4,5-tetrazine (**4**),[5,7] which have been the subject of detailed physicochemical studies of the fundamental nature of metal-metal interactions.

For some time now we have been involved in the synthesis of new heterocyclic ligands that incorporate less-commonly encountered heterocyclic ring systems as donors to metal acceptors. For example, we have reported a number of chelating ligands that contain tetrazole,[8] furoxan,[9] benzotriazole,[10] benzisoxazole,[11] 1,2,5-thiadiazole[12] and 1,2,3-chalcogenadiazole groups.[13] Most recently, we described a study of the binuclear ruthenium(II) complexes of 3,4-di(2-pyridyl)-1,2,5-oxadiazole (**5**),[14] which revealed remarkably strong metal-metal interactions, the magnitude of which was dependent on the specific diastereoisomer. In an attempt to probe the origin of this intriguing result, we have embarked on the synthesis of new ligands that might be used to prepare metal complexes that provide a means to test the mechanism of the observed metal-metal interactions systematically. One such issue is the role of the oxygen atom in ligand **5**.

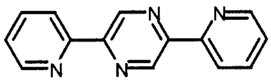
In this context, we now describe the preparation of the new ligand 3,6-di(2-pyridyl)-1,4,2,5-dioxadiazine (**6**), which is structurally similar to ligands **3** and **4** but differs by being nonaromatic and having two oxygen atoms in the central ring. We then describe a novel coordination polymer obtained from its reaction with silver tetrafluoroborate. Surprisingly, despite the fact that 3,6-diaryl-1,4,2,5-dioxadiazines are readily synthesised,[15] no coordination complexes of any ligands containing this heterocyclic ring system have previously been reported.



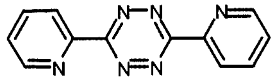
1



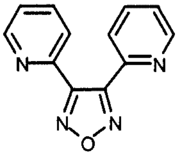
2



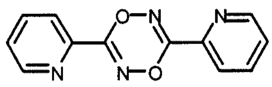
3



4



5



6

Results and Discussion

The new ligand **6** was prepared in three steps from 2-pyridinecarboxaldehyde by conversion into the oxime, chlorination to the known[16] hydroximinoyl chloride and subsequent dehydrochlorination-dimerisation to give **6** in yields that ranged between 55−60%. This reaction proceeds

---

[a] Department of Chemistry, University of Canterbury,
Christchurch, New Zealand
Fax: (internat.) + 64-3/364-2110
E-mail: p.steel@chem.canterbury.ac.nz

via a nitrile oxide intermediate.[15] The ligand was initially characterised by melting point, elemental analysis, mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy.[17] However, attempts to prepare bis(2,2′-bipyridine)ruthenium(II) complexes of **6** consistently resulted in the isolation of products containing coordinated picolinate or picolinamide ligands, as determined by FAB mass spectrometric analysis. At this point we became concerned about the integrity of the ligand itself and therefore undertook a single crystal X-ray crystal structure determination of **6**. Interestingly, a search of the Cambridge Crystallographic database located only one structure containing this heterocyclic ring system.[18]

Suitable crystals were readily obtained by slow evaporation of an ethyl acetate solution of the ligand. However, we were disappointed to discover that, although the structure solved and refined well,[19] the central ring was disordered with respect to the positions of the nitrogen and oxygen atoms of the ring, despite the fact that the outer pyridine rings did not show any such disorder (Figure 1). The molecule crystallizes about a crystallographic centre of inversion in the monoclinic space group $P2_1/n$ (see Table 1 for data collection and refinement parameters). The plane of the pyridine ring is inclined to the plane of the central ring at an angle of 21.3(1)° and the molecules pack with the typical herringbone pattern common for aromatic molecules in this space group.[20] Thus, in the crystallization process the molecules pack with the pyridine rings faithfully aligned, but with the central ring equally arranged in the two possible conformations. Notwithstanding this result, the structure of the ligand seemed assured and complexes with other transition metal precursors were sought.

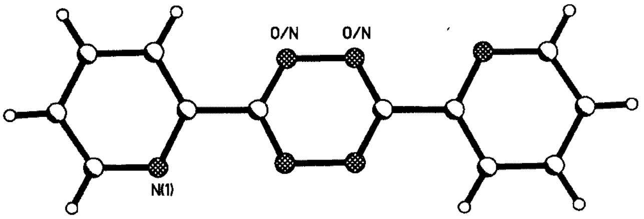


Figure 1. X-ray structure of **6** with a disordered central ring

Since we,[21] and others,[22] have found silver salts to be useful precursors to a variety of interesting metallosupramolecular compounds, including novel coordination polymers,[23] we reacted **6** with silver nitrate in methanol solution to obtain a 1:1 complex AgL(NO_3) (**7**),[24] in excellent yield (96%). All attempts to produce crystals of this product suitable for X-ray structure determination were in vain. Pleasingly, however, reaction of **6** with silver tetrafluoroborate produced the 1:1 M:L complex AgL(BF_4) (**8**),[25] that upon recystallization from acetonitrile underwent reorganisation to a 1:2 complex $AgL_2(BF_4)$, (**9**), which did furnish X-ray quality crystals.

Table 1. X-ray crystal data and details of data collections and structure refinements

Compound	6	9
Formula	$C_{12}H_8N_4O_2$	$C_{24}H_{16}AgBF_4N_8O_4$
Molecular weight	240.22	675.13
Crystal System	monoclinic	triclinic
a (Å)	6.330(2)	8.011(3)
b (Å)	5.781(2)	12.672(5)
c (Å)	14.431(5)	12.792(5)
α (°)	90	97.402(10)
β (°)	97.449(4)	99.304(18)
γ (°)	90	104.756(14)
V (Å^3)	523.6(3)	1219.4(8)
Space group	$P2_1/n$	$P\bar{1}$
Z	2	2
D_c (Mg·m^{-3})	1.524	1.839
F(000)	672	908
Temperature (K)	163(2)	163(2)
Crystal form	colourless block	colourless plate
Crystal size (mm)	0.56 × 0.44 × 0.30	0.52 × 0.20 × 0.04
μ (mm^{-1})	0.109	0.910
$2\theta_{\max}$ (°)	53	53
Unique reflections	1065	4833
Parameters	83	379
R[a] [$I > 2\sigma(I)$]	0.0383	0.0285
wR[b] (all data)	0.1058	0.0753

[a] $R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$. [b] $wR = (\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2])^{1/2}$.

This complex proved to be an intriguing coordination polymer with an unprecedented architecture. Figure 2 shows a perspective view of the contents of the asymmetric unit, along with selected atom labelling and bonding geometry. The asymmetric unit contains one silver atom, two molecules of **6** and a tetrafluoroborate counterion. One of the molecules of **6** acts as a tetradentate ligand, chelating two silver atoms separated by one unit cell translation along the a axis [8.011(1) Å]. The other acts as a bidentate ligand coordinating through only two of its four nitrogens, and has its mean plane approximately orthogonal to the first. The silver atom is chelated by three ligands, with bonds to the

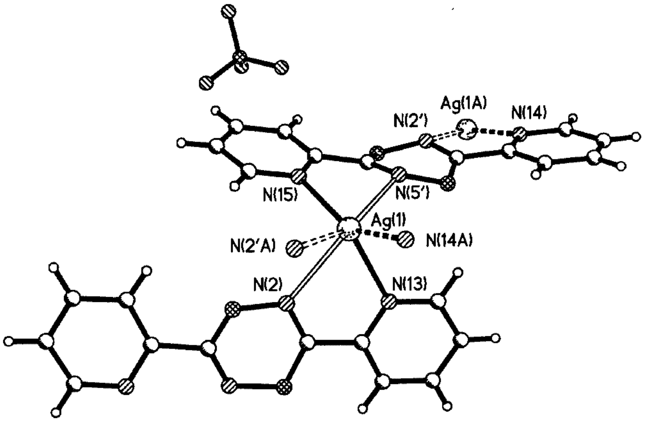


Figure 2. Perspective view and selected atom labelling of the contents of the asymmetric unit in the X-ray structure of $AgL_2(BF_4)$, (**9**); selected interatomic distances (Å) and angles(°): Ag(1)−N(15) 2.294(2), Ag(1)−N(14A) 2.296(2), Ag(1)−N(13) 2.460(2), Ag(1)−N(2) 2.619(2), Ag(1)−N(5) 2.697(2), Ag(1)−N(2′A) 2.702(2); N(15)−Ag(1)−N(14A) 147.96(7), N(15)−Ag(1)−N(13) 117.10(7), N(14A)−Ag(1)−N(13) 92.08(7), N(15)−Ag(1)−N(2) 86.31(7), N(14A)−Ag(1)−N(2) 120.16(7), N(13)−Ag(1)−N(2) 64.47(7), N(5′)−Ag(1)−N(15) 65.8(1), N(2′A)−Ag(1)−N(14A) 65.9(1)

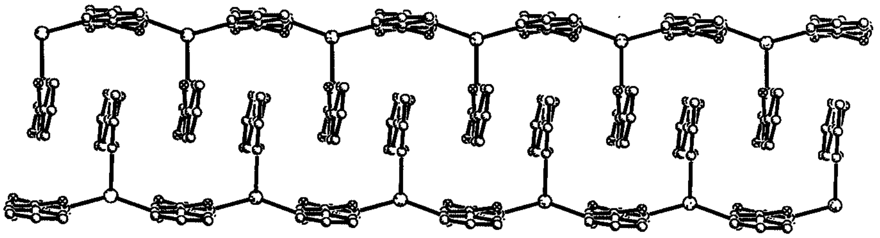


Figure 3. Projection showing the interdigitation of polymer chains

pyridine nitrogens being significantly shorter than those to the dioxadiazine nitrogens, which provide only weak interactions with the metal. These long bonds lead to small bite angles (ca. 65°) at the metal. The resulting hexacoordinate geometry at the metal is trigonal prismatic. Relatively few X-ray crystal structures have been reported that include an AgN_6 coordination environment[26] and these show various coordination geometries consistent with the filled-shell nature of the metal ion.

In both independent molecules of **6** within the complex, the central dioxadiazine ring is far from planar; these exist in boat conformations with the oxygen atoms being displaced from the planes of the carbon and nitrogen atoms by ca. 0.20 Å for the bridging ligand and ca. 0.28 Å for the terminal ligand. In the only other reported crystal structure containing this heterocyclic ring system[18] there are two independent molecules, one of which has the dioxadiazine ring in a chair form and the other in a boat form similar to that found here.

As a consequence of the bridging nature of one of the ligands, the complex extends into a fascinating coordination polymer. As shown in Figure 3, the extended structure consists of two coordination polymer chains which assemble in such a way that the terminal ligands of each chain are interdigitated as a result of π-π stacking interactions. The planes of the individual rings are separated by distances ranging between 3.0 and 3.5 Å and interacting rings have their centroids displaced at distances ranging between 3.38 and 3.81 Å. We believe that this is an unprecedented metallosupramolecular topology, in which the two sides of a ladder-like structure are separated and the rungs are held together by aromatic interactions.

In conclusion, we have shown for the first time that the dioxadiazine ring can be incorporated into chelating and bridging ligands. Studies are in progress to prepare binuclear complexes of this and related ligands with various transition metals.

Acknowledgments

We thank the Royal Society of New Zealand Marsden Fund for financial support.

---

[1] For recent reviews, see: [1a] S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853−908. [1b] G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483−3538. [1c] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629−1658. [1d] M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509−518. [1e] D. W. Johnson, K. N. Raymond, *Supramol. Chem.* **2001**, *13*, 639−659. [1f] B. J. Holliday, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2001**, *40*, 2022−2043. [1g] G. F. Swiegers, T. J. Malefetse, *Coord. Chem. Rev.* **2002**, *225*, 91−121.

[2] C. Kaes, A. Katz, M. W. Hosseini, *Chem. Rev.* **2000**, *100*, 3553−3590.

[3] [3a] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85−277. [3b] V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759−834.

[4] [4a] C. H. Braunstein, A. D. Baker, T. C. Strekas, H. D. Gafney, *Inorg. Chem.* **1984**, *23*, 857−864. [4b] Y. Fuchs, S. Lofters, T. Dieter, W. Shi, R. Morgan, T. C. Strekas, H. D. Gafney, A. D. Baker, *J. Am. Chem. Soc.* **1987**, *109*, 2691−2699. [4c] A. W. Wallace, W. R. Murphy, J. D. Petersen, *Inorg. Chim. Acta* **1989**, *166*, 47−54. [4d] K. Kalyanasundaram, M. K. Nazeeruddin, *Inorg. Chem.* **1990**, *29*, 1888−1897. [4e] R. M. Berger, *Inorg. Chem.* **1990**, *29*, 1920−1924. [4f] M. Haga, M. M. Ali, S. Koseki, A. Yoshimura, K. Nozaki, T. Ohno, *Inorg. Chim. Acta* **1994**, *226*, 17−24.

[5] [5a] S. Campagna, G. Denti, G. De Rosa, L. Sabatino, M. Ciano, V. Balzani, *Inorg. Chem.* **1989**, *28*, 2565−2570. [5b] G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano, V. Balzani, *Inorg. Chem.* **1990**, *30*, 4750−4758. [5c] A. Juris, V. Balzani, S. Campagna, G. Denti, S. Serroni, G. Frei, G. Güdel, *Inorg. Chem.* **1994**, *33*, 1491−1496. [5d] H. B. Baudin, J. Davidsson, S. Serroni, A. Juris, V. Balzani, S. Campagna, L. Hammarstroem, *J. Phys. Chem. A* **2002**, *106*, 4312−4319.

[6] [6a] X. Hua, A. von Zelewsky, *Inorg. Chem.* **1995**, *34*, 5791−5797. [6b] I. G. Phillips, P. J. Steel, *Aust. J. Chem.* **1998**, *51*, 371−382.

[7] [7a] Q. Jaradat, K. Barqawi, T. S. Akashek, *Inorg. Chim. Acta* **1986**, *116*, 63−73. [7b] S. D. Ernst, V. Kasack, W. Kaim, *Inorg. Chem.* **1988**, *27*, 1146−1148. [7c] S. D. Ernst, W. Kaim, *Inorg. Chem.* **1989**, *28*, 1520−1528. [7d] J. Poppe, M. Moscherosch, W. Kaim, *Inorg. Chem.* **1993**, *32*, 2640−2643. [7e] K. C. Gordon, A. K. Burrell, T. J. Simpson, S. E. Page, G. Kelso, M. I. J. Polson, A. Flood, *Eur. J. Inorg. Chem.* **2002**, 554−563. [7f] C. S. Araujo, M. G. B. Drew, V. Felix, L. Jack, J. Madureira, M. Newell, S. Roche, T. M. Santos, J. A. Thomas, L. Yellowlees, *Inorg. Chem.* **2002**, *41*, 2250−2259.

[8] A. J. Downard, P. J. Steel, J. Steenwijk, *Aust. J. Chem.* **1995**, *48*, 1625−1642.

[9] C. Richardson, P. J. Steel, *Aust. J. Chem.* **2000**, *53*, 93−97.

[10] C. Richardson, P. J. Steel, *J. Chem. Soc., Dalton Trans.* **2002**, in press.

[11] C. Richardson, P. J. Steel, *Inorg. Chem. Commun.* **2000**, *3*, 155−158.

[12] C. Richardson, P. J. Steel, *Acta Crystallogr., Sect. C* **2001**, *57*, 197−198.

[13] C. Richardson, P. J. Steel, *Aust. J. Chem.* **2002**, in press.

[14] C. Richardson, P. J. Steel, D. M. D'Alessandro, P. C. Junk, F. R. Keene, *J. Chem. Soc., Dalton Trans.* **2002**, 2775−2785.

[15] F. De Sarlo, *J. Chem. Soc., Perkin Trans. 1* **1974**, 1951−1953.

[16] R. H. Wiley, B. J. Wakefield, *J. Org. Chem.* **1960**, *25*, 546−551.

[17] **Preparation of 3,6-Di(2-pyridyl)-1,4,2,5-dioxadiazine (6)**: 2-Pyr-

idine hydroximinoyl chloride hydrochloride[16] (0.51 g, 2.6 mmol) was dissolved in ethanol (25 mL). Triethylamine (0.73 mL, 5.3 mmol) and pyridine (0.64 mL, 7.9 mmol) were added and the solution stirred. The resulting yellow solution was left overnight, the precipitate was filtered off, and the filtrate taken to dryness in vacuo. The resulting solid was recrystallized from water. M. p. 154−158 °C; yield 0.18 g (59%). $C_{12}H_8N_4O_2$ (240.2): calcd. C 60.00, H 3.36, N 23.32; found C 60.05, H 3.19, N 23.47. Positive-ion EI-MS: calcd. for $C_{12}H_8N_4O_2$ 240.0647; found 240.0648. *m*/*z* = 240.1 (1.8) [M^+], 120.0 (20) [$PyCNO^+$], 104.0 (100) [$PyCN^+$], 78.0 (62) [Py^+]. ^1H NMR ($CDCl_3$): δ = 7.94 (H3′), 7.80 (H4′), 7.44 (H5′), 8.73 (H6′) ppm. ^{13}C NMR ($CDCl_3$): δ = 144.66 (C2′), 123.26 (C3′), 136.99 (C4′), 126.69 (C5′), 150.30 (C6′), 160.63 (C3/C6).

[18] R. Fruttero, B. Ferrarotti, A. Gasco, G. Calestani, C. Rizzoli, *Liebigs Ann. Chem.* **1988**, 1017−1023.

[19] The crystal data, data collection and refinement parameters for the X-ray structures are listed in Table 1. Data were collected with a Siemens SMART CCD area detector, using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods, and refined on F^2 using all data by full-matrix least-squares procedures.
CCDC-191057 (**6**) and -191058 (**9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

[20] G. R. Desiraju, A. Gavezzotti, *Acta Crystallogr., Sect. B* **1989**, *45*, 473−482.

[21] [21a] C. M. Hartshorn, P. J. Steel, *Inorg. Chem.* **1996**, *35*, 6902−6903. [21b] C. M. Hartshorn, P. J. Steel, *J. Chem. Soc., Dalton Trans.* **1998**, 3927−3934. [21c] C. M. Hartshorn, P. J. Steel, *J. Chem. Soc., Dalton Trans.* **1998**, 3935−3940. [21d] R. J. Anderson, P. J. Steel, *Acta Crystallogr., Sect. C* **1998**, *54*, 223−225. [21e] B. J. O'Keefe, P. J. Steel, *Inorg. Chem. Commun.* **1998**, *1*, 147−149. [21f] C. Richardson, P. J. Steel, *Inorg. Chem. Commun.* **1998**, *1*, 260−262. [21g] C. M. Fitchett, P. J. Steel, *New J. Chem.* **2000**, *24*, 945−947. [21h] B. J. O'Keefe, P. J. Steel, *Inorg. Chem. Commun.* **2000**, *3*, 473−475. [21i] C. M. Hartshorn, P. J. Steel, *Inorg. Chem. Commun.* **2000**, *3*, 476−481. [21j] C. M. Fitchett, P. J. Steel, *Inorg. Chim. Acta* **2000**, *310*, 127−132. [21k] P. J. Steel, C. J. Sumby, *Chem. Commun.* **2002**, 322−323. [21l] P. J. Steel, C. J. Sumby, *Inorg. Chem. Commun.* **2002**, *5*, 323−327. [21m] P. J. Steel, N. C. Webb, *Eur. J. Inorg. Chem.* **2002**, 2257−2260. [21n] D. A. McMorran, P. J. Steel, *J. Chem. Soc., Dalton Trans.* **2002**, 3321−3326.

[22] M. Munakata, L. P. Wu, T. Kuroda-Sowa, *Adv. Inorg. Chem.* **1999**, *46*, 173−303.

[23] A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk, M. Schröder, *Coord. Chem. Rev.* **2001**, *222*, 155−192.

[24] **Preparation of Silver Nitrate Complex AgL(NO_3) (7):** $AgNO_3$ (22.4 mg, 0.13 mmol) dissolved in hot MeOH (3 mL) was added to ligand **6** (31.3 mg, 0.13 mmol) in warm MeOH (2 mL). A colourless precipitate formed immediately and was collected by filtration. Yield 51.4 mg (96%). $C_{12}H_8AgN_5O_5$ (410.1): calcd. C 35.15, H 1.97, N 17.07; found C 34.94, H 1.79, N 16.80.

[25] **Preparation of Silver Tetrafluoroborate Complex 9:** Ligand **6** (35.7 mg, 0.15 mmol) was dissolved in warm MeOH (3 mL) and added to $AgBF_4$ (30.1 mg, 0.16 mmol) dissolved in MeOH (1 mL). The colourless precipitate of AgL(BF_4) (**8**), that formed was collected by filtration and washed with MeOH. M.p. 189−192 °C; yield 51.5 mg (79%). $C_{12}H_8AgBF_4N_4O_2$ (434.9): calcd. C 33.14, H 1.85, N 12.88; found C 33.38, H 2.07, N 12.62. Recrystallization of the colourless solid from acetonitrile gave plate-like crystals of $AgL_2(BF_4)$ (**9**).

[26] [26a] H. Adams, N. A. Bailey, W. D. Carlisle, D. E. Fenton, G. Rossi, *J. Chem. Soc., Dalton Trans.* **1990**, 1271−1283. [26b] E. C. Constable, M. S. Khan, M. C. Liptrot, J. Lewis, P. R. Raithby, *Inorg. Chim. Acta* **1991**, *179*, 239−244. [26c] J. de Mendoza, E. Mesa, J.-C. Rodriguez-Ubis, P. Vazquez, F. Vögtle, P.-M. Windscheif, K. Rissanen, J.-M. Lehn, D. Lilienbaum, R. Ziessel, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1331−1333. [26d] C. Stockheim, K. Wieghardt, B. Nuber, J. Weiss, U. Flörke, H.-J. Haupt, *J. Chem. Soc., Dalton Trans.* **1991**, 1487−1490. [26e] H. Adams, N. A. Bailey, M. J. S. Dwyer, D. E. Fenton, P. C. Hellier, P. D. Jempstead, J. M. Latour, *J. Chem. Soc., Dalton Trans.* **1993**, 1207−1216. [26f] L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1895−1897. [26g] D. L. Reger, J. E. Collins, A. L. Rheingold, L. M. Liable-Sands, G. P. A. Yap, *Organometallics* **1997**, *16*, 349−353. [26h] M. Munakata, J. C. Zhong, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, N. Oiji, *Inorg. Chim. Acta* **2001**, *317*, 268−275. [26i] M. Jorgensen, F. C. Krebs, *Tetrahedron Lett.* **2001**, *42*, 4717−4720. [26j] A. Cingolani, Effendy, D. Martini, M. Pellei, C. Pettinari, B. W. Skelton, A. H. White, *Inorg. Chim. Acta* **2002**, *328*, 87−95.

Received August 5, 2002
[I02442]