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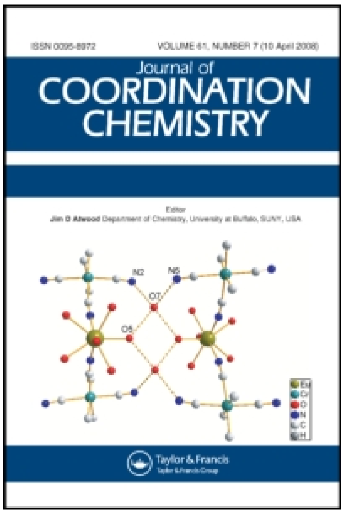

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Syntheses, structures, and reactivities of novel binuclear ruthenium(II) complexes with bis(μ-phosphinato) bridges

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Syntheses, structures, and reactivities of novel binuclear ruthenium(II) complexes with bis(μ-phosphinato) bridges

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Novel binuclear ruthenium(II) complexes with bis(μ-phosphinato-κO:$\kappa O'$) bridges, $[Ru(dpp)(bpy)_2]_2(BF_4)_2$ (**1**), $[Ru(bmp)(bpy)_2]_2(BF_4)_2$ (**2**) (Hdpp = diphenylphosphinic acid, Hbmp = bis(4-methoxyphenyl)phosphinic acid, bpy = 2,2′-bipyridine), have been prepared and characterized. The structures of **1** and **2** contain a diruthenium(II) core with two phosphinates and four bpy ligands. These are the first reported examples of such Ru(II) phosphinate structures. Oxidation of cinnamyl alcohol by molecular oxygen was carried out using **1** and **2** as catalysts and as an oxidant. In the presence of **2**, cinnamyl alcohol gave cinnamaldehyde (44% in 7 h). In CV, two reversible waves at +0.31, +0.59 V for **1** and +0.27, +0.54 V for **2** were observed.

Keywords: Ruthenium(II); Binuclear complex; Phosphinato bridge; Crystal structure; Reactivity

1. Introduction

Polynuclear ruthenium complexes with various structure types have been reported, classified as paddle wheel, hemerythrine, and poly bridging types [1–3]. In almost cases of paddle wheel and hemerythrine types, complexes have carboxylato bridges. Recently, reactions between transition metal ions and a phosphorus acid or ester in phosphate metabolism have attracted the attention of bioinorganic and inorganic chemists [4, 5]. It is expected that a diphenyl phosphinic acid would adopt the same bridging style as a carboxylate group. However, no reports of dinuclear ruthenium(II) complexes with bis(μ-phosphinato-κO:$\kappa O'$) bridges are known. In our previous studies, we described the syntheses, structures and magnetic properties of novel dinuclear oxovanadium(IV) and copper(II) complexes with phosphinato bridges [6–8]. It was found that the oxovanadium(IV) complexes catalyzed oxidation of alcohols.

The oxidation of alcohols is one of the most important reactions in organic chemistry [9]. Generally, chromic acid and DMSO are used, but recently, vanadium, complex molybdenum and ruthenium catalysts and oxygen or peroxides have been used [10–12];

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dinuclear complexes have rarely been used as catalysts. Here, we report the syntheses, crystal structures, and reactivities of $[Ru(dpp)(bpy)_2]_2(BF_4)_2$ (**1**) and $[Ru(bmp)(bpy)_2]_2(BF_4)_2$ (**2**) (Hdpp = diphenylphosphinic acid, Hbmp = bis(4-methoxyphenyl)phosphinic acid, bpy = 2,2′-bipyridine), the first examples of binuclear ruthenium(II) complexes with bis(μ-phosphinato-κO:$\kappa O'$) bridges.

2. Experimental

2.1. *Materials*

All chemicals and solvents were of reagent grade and used without further purification. The complex *cis*-$[Ru(bpy)_2Cl_2]$ was synthesized according to literature methods [13].

2.2. *Physical measurements*

Elemental analyses were obtained at the Service Center of Elemental Analysis at Kyushu University. Absorption spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer. Electrochemistry experiments were performed with a BAS100B potentiostat with a Pt electrode and an Ag/Ag^+ reference electrode.

2.3. *$[Ru(dpp)(bpy)_2]_2(BF_4)_2$ (1)*

To a solution of *cis*-$[Ru(bpy)_2Cl_2]$ (456 mg, 1 mmol) in methanol (10 cm^3) was added $AgBF_4$ (388 mg, 2 mmol). The solution was heated and stirred for 10 mins in the absence of light, and the resulting suspension centrifuged and filtered off. A solution of Hdpp (218 mg, 1 mmol) in methanol (10 cm^3) was added to the filtrate with stirring. To the resulting solution, Et_3N (101 mg, ca 1 mmol) was added. The dark purple solution was filtered and the filtrate allowed to stand for several weeks at room temperature. The dark purple crystals that formed were collected, washed with methanol and dried in air. Anal. Calcd for $C_{64}H_{54}B_2F_8N_8O_5P_2Ru_2$ (%): C, 52.91; H, 3.75; N, 7.71. Found: C, 52.60; H, 3.69; N, 7.72.

2.4. *$[Ru(bmp)(bpy)_2]_2(BF_4)_2 \cdot 3MeOH$ (2)*

The synthetic procedure was similar to that for **1** except that Hbmp was used instead of Hdpp. Anal. Calcd for $C_{68}H_{60}B_2F_8N_8O_8P_2Ru_2 \cdot 3MeOH$ (%): C, 51.47; H, 3.99; N, 6.74. Found: C, 51.64; H, 4.39; N, 6.79.

2.5. *X-ray crystallography*

Crystal data collection parameters for **1** and **2** along with the final refinement details are summarized in table 1. Diffraction data were measured on a Rigaku AFC5S automated four-circle diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71069$ Å) radiation. Structures were solved by direct methods [14] and expanded using Fourier techniques [15]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

Table 1. Crystal data and refinement details for **1** and **2**.

Formula	$C_{64}H_{54}B_2F_8N_8O_5P_2Ru_2$ (**1**)	$C_{68}H_{60}B_2F_8N_8O_8P_2Ru_2$ (**2**)
Formula weight	1452.86	1554.95
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	20.177(4)	14.344(5)
b (Å)	12.961(4)	11.640(4)
c (Å)	24.017(3)	11.654(6)
α (°)		102.16(1)
β (°)	102.80(1)	105.91(4)
γ (°)		100.14(2)
V (Å)^3	6124(2)	2228.6(14)
Z	4	2
D_c(g cm^{-3})	1.575	1.317
μ(Mo-Kα) (cm^{-1})	6.28	8.761
No. of obs. ($I > 2.00\sigma(I)$)	6787	4158
No. of variables	872	482
R	0.058	0.067
Rw	0.048	0.061
Largest diff. peak (e Å^{-3})	0.82	0.84

3. Results and discussion

3.1. *Crystal structures of 1*

The crystal structure of **1** comprises two crystallographically independent, binuclear molecules. The two units, **1A** and **1B** are shown in figures 1 and 2 with the atom numbering scheme. Selected bond lengths and angles are listed in tables 2 and 3. Each binuclear complex cations consists of two bis(bipyridyl)ruthenium(II) cores with Δ, Λ configurations, and two bridging phosphinates. Separations between Ru(II) centres in **1A** and **1B** are 4.977(1) and 5.087(1) Å, respectively. The coordination environment around each ruthenium(II) ion is a distorted octahedron. The most unusual feature of the structures of **1A** and **1B** is the dihedral angle (δ) observed between the least-squares planes through the bridging phosphinates, [O_a, P, O_b] and [O_a, O_b, Ru]. The definition of coordination modes is based on that of bridging carboxylates [8, 16]. Values of δ are 141.3 and 150.1° for **1A** [O1,P1,O2/O2,O1,Ru1 and O1,O2,Ru1′] and 145.3 and 141.0° for **1B** [O3,P2,O4/O4,O3,Ru2 and O3,O4,Ru2′], respectively. These dihedral angles show the coordination of phosphinates groups near to *syn–anti* bridging modes. Metal–metal distances in **1A** and **1B** are almost equal to those of related copper(II) and oxovanadium(IV) complexes (4.811(1) and 4.87(2) Å, respectively) with *syn–anti* coordination; copper(II) complex with *syn–syn* bridging modes have a shorter contact (3.993(8) Å) [6–8].

3.2. *Crystal structures of 2*

The structure of complex **2** is shown in figure 3 and selected bond lengths and angles are listed in table 4. The structure of **2** is almost same as that of **1** with an Ru–Ru separation of 4.9523(11) Å; δ values are 138.8° and 139.9°. Mean Ru–O(dpp or bmp) and Ru–N(bpy) distances in **1A**, **1B**, and **2** are 2.13 and 2.03 Å, respectively, and Ru–O distances are longer than those in copper(II) and oxovanadium(IV) complexes

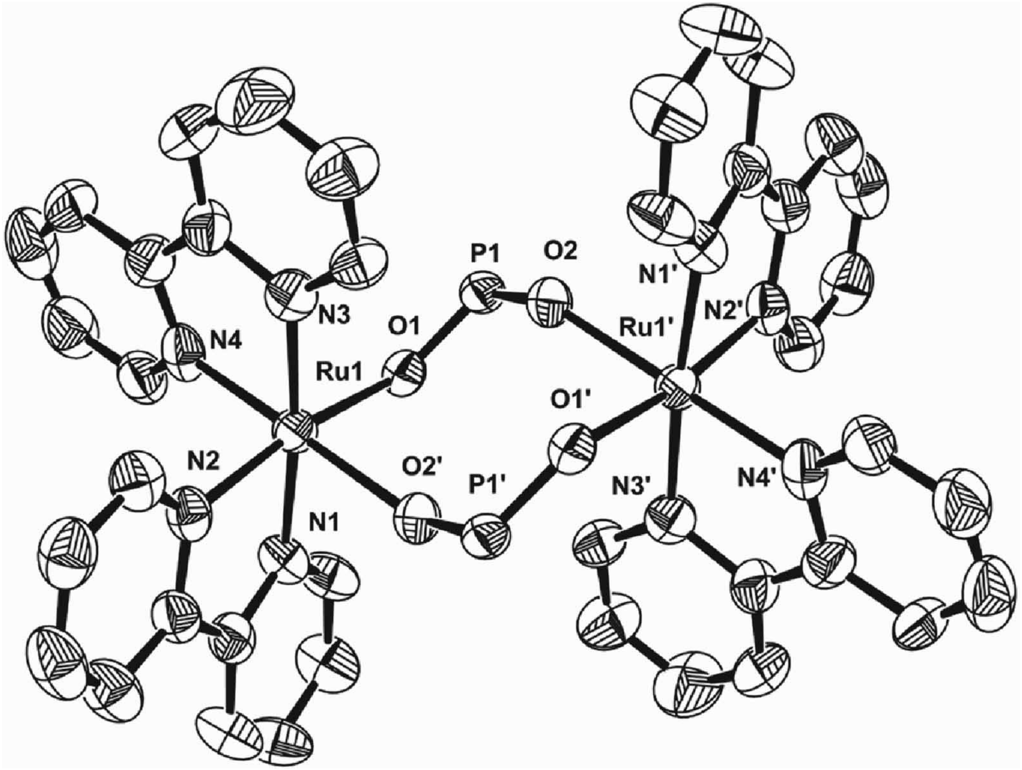

Figure 1. An ORTEP drawing at the 50% probability level of the complex cation **1A** (phenyl groups of phosphinato bridges are omitted for clarity).

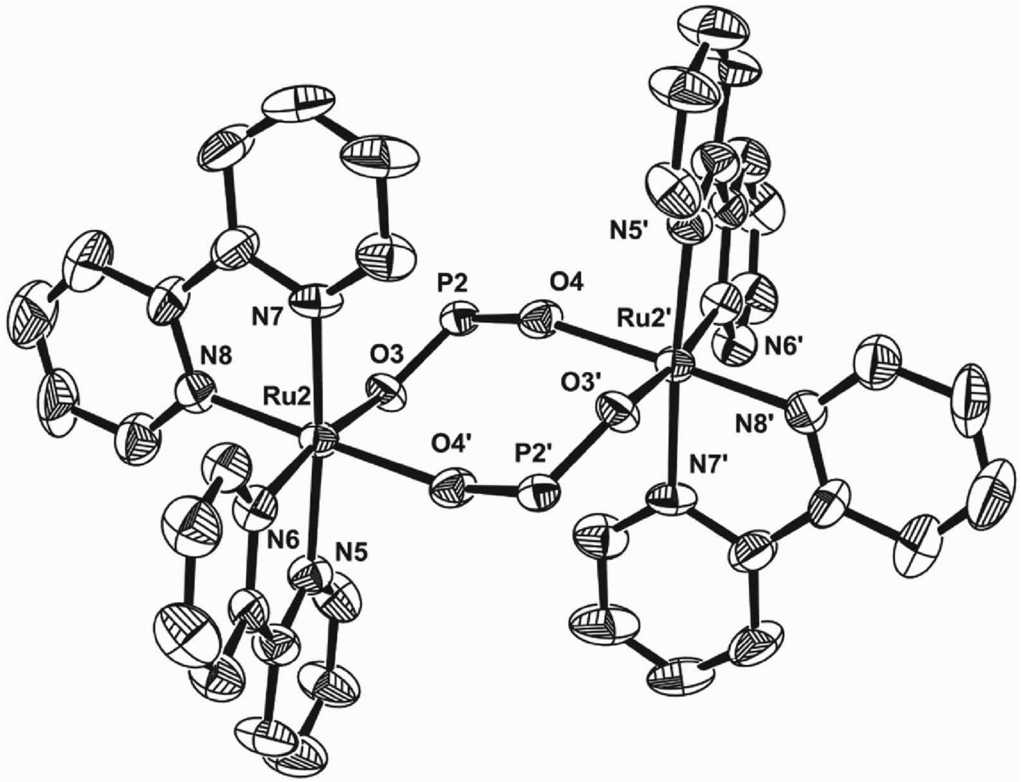

Figure 2. An ORTEP drawing at the 50% probability level of the complex cation **1B** (phenyl groups of phosphinato bridges are omitted for clarity).

Table 2. Selected bond lengths and bond angles for **1A**.

Ru1–Ru1′	4.977(1)	Ru1–O1	2.135(5)
Ru1–O2	2.125(6)	Ru1–N1	2.037(7)
Ru1–N2	2.018(7)	Ru1–N3	2.053(7)
Ru1–N4	2.006(8)	P1–O1	1.517(6)
P1–O2	1.507(7)		
N1–Ru1–N2	80.1(3)	N3–Ru1–N4	79.8(3)
N2–Ru1–N4	92.5(3)	N3–Ru1–O1	94.8(2)
O1–Ru1–O2′	89.3(2)	O2′–Ru1–N1	82.4(3)
N1–Ru1–N3	174.5(3)	N2–Ru1–O1	169.8(2)
N4–Ru1–O2′	179.5(3)	O1–P1–O2	116.4(3)

Table 3. Selected bond lengths and bond angles for **1B**.

Ru2–Ru2′	5.087(1)	Ru2–O3	2.113(5)
Ru2–O4	2.110(6)	Ru2–N5	2.052(6)
Ru2–N6	1.991(6)	Ru2–N7	2.049(7)
Ru2–N8	1.994(8)	P2–O3	1.528(6)
P2–O4	1.508(6)		
N5–Ru2–N6	80.0(3)	N7–Ru2–N8	79.1(3)
N6–Ru2–N8	93.8(3)	N7–Ru2–O3	91.6(2)
O3–Ru2–O4′	91.1(2)	O4′–Ru2–N5	84.2(3)
N5–Ru2–N7	175.4(3)	N6–Ru2–O3	171.2(2)
N8–Ru2–O4′	178.1(2)	O3–P2–O4	116.0(3)

(1.94 and 2.04 Å, respectively). Mean Ru–N(bpy) bonds distances are almost equal to those of the copper(II) complexes (2.00 Å), but shorter than those of vanadium(IV) complexes (2.16 Å). Ru–O and Ru–N distances are in agreement with those of other dinuclear ruthenium complexes of the paddle wheel, hemerythrine type, and polypyridine bridging types [1–3]. However, Ru–Ru separations are considerably longer than those in paddle wheel and hemerythrine complexes (2.32 and 3.26 Å, respectively) [1, 2] and thus the present species represent a new structure type.

3.3. *Electronic spectra*

Four major bands are observed in the electronic spectra of **1** and **2**. These are are labelled from I to IV in order of increasing energy in table 5. Bands I and II should be assigned to a $\pi^* \leftarrow d\pi(\mathrm{Ru})$ transition consistent with previous assignments for related bpy–Ru(II) complexes [3a, 13, 17]. Bands III and IV are assigned to $\pi^* \leftarrow \pi$ transitions of bpy.

3.4. *Oxidation of alcohol by the complexes*

Complex **1** or **2** (0.05 mmol) was dissolved in acetonitrile (1.5 cm^3) in a 25 cm^3 round bottomed flask under O_2 (1 atm). Cinnamyl alcohol (1.0 mmol) in acetonitrile (1.5 cm^3) was added to the flask. The mixture was stirred for 7 h at room temperature. Yields of cinnamaldehyde (table 6) were determined by GLC using an internal standard. In the absence of complex as catalyst, oxidation of cinnamyl alcohol did not take place.

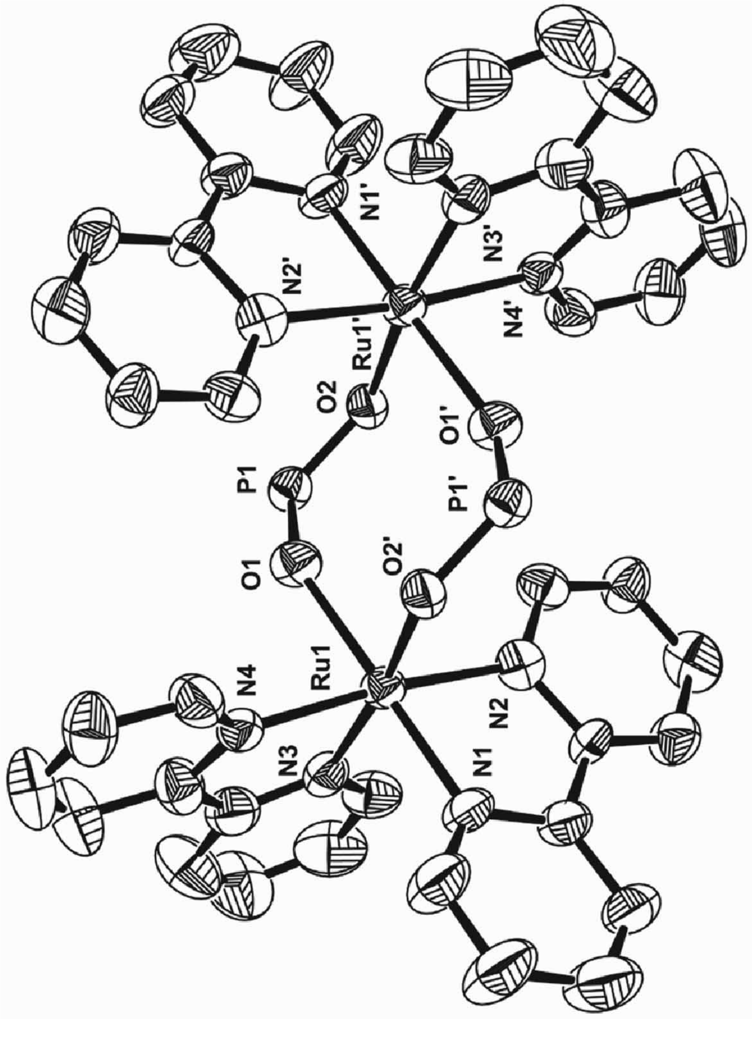

Figure 3. An ORTEP drawing at the 50% probability level of the complex cation of **2** (phenyl groups of phosphinato bridges are omitted for clarity).

Table 4. Selected bond lengths and bond angles for **2**.

Ru1–Ru1′	4.953(1)	Ru1–O1	2.133(7)
Ru1–O2	2.134(5)	Ru1–N1	1.985(9)
Ru1–N2	2.075(7)	Ru1–N3	2.055(7)
Ru1–N4	2.042(8)	P1–O1	1.499(7)
P1–O2	1.525(4)		
N1–Ru1–N2	78.7(3)	N3–Ru1–N4	79.6(3)
N2–Ru1–N4	172.8(3)	N3–Ru1–O1	88.6(3)
O1–Ru1–O2′	89.9(2)	O2′–Ru1–N1	89.9(2)
N1–Ru1–N3	91.5(3)	N1–Ru1–O1	179.8(2)
N3–Ru1–O2′	170.9(2)	O1–P1–O2	116.7(3)

Table 5. Electronic absorption data for **1** and **2** in MeCN.

	$\lambda_{\max}$, nm (ε, $10^4\,M^{-1}\,cm^{-1}$)			
Complex	**I**	**II**	**III**	**IV**
1	525(1.6)	365(1.7)	295(7.8)	245(3.8), 220sh(6.2)
2	530(1.3)	355(1.4)	290(6.6)	242(9.7), 230sh(8.1)

Table 6. Yields for oxidation of cinnamyl alcohol using **1** and **2**.

Complex	Yield of aldehyde (%)[a]
Blank	≈0
1	2
2	44
$[(VO)_2(dpp)_3(bpy)_2]NO_3{\cdot}2H_2O$[b]	21
$[(VO)_2(bmp)_3(bpy)_2]NO_3{\cdot}H_2O$[b]	66
$[Cu_2(bmp)_2(bpy)_2](NO_3)_2$[b]	5

[a] GLC yield with internal standard. [b] Ref. [7].

Oxidation was very small when **1** was used as catalyst. However, complex **2** gave a 44% yield of aldehyde. By comparison, only oxovanadium(IV) complexes of bmp give a higher yield [7].

3.5. *Electrochemistry of 1 and 2*

The redox behaviour of **1** and **2** has been studied by CV using a platinum button working electrode in MeCN containing 0.1 M $[NBu^n_4](ClO_4)$ as supporting electrolyte (table 7). For **1** and **2**, two quasi-reversible redox waves were observed. $E_{1/2}$ values of +0.31 V for **1** and +0.27 V for **2** were assigned to Ru(II,II)/Ru(II,III) and values of +0.59 V for **1** and +0.54 V for **2** were assigned to Ru(II,III)/Ru(III,III) processes. These redox potentials are in agreement with those measured for related bpy–Ru(II) complexes [3]. In the CV of **2**, two minor redox processes at −0.05 and −0.92 V were observed. The former is due to the partial decomposition of the Ru(II) complex and the latter is attributable to the reduction of bpy [3b]. The different electrochemical behaviour of **1** and **2** clearly affects their reactivity, but the reason for this effect is not clear at present.

Table 7. Electrochemical data for the dinuclear ruthenium(II) complexes in MeCN.

Complex	Ru(II,II)/Ru(II,III)			Ru(II,III)/Ru(III,III)		
	E_{pa}	E_{pc}	$E_{1/2}$[a]	E_{pa}	E_{pc}	$E_{1/2}$[a](V)
1	0.38	0.23	0.31	0.66	0.51	0.59
2	0.33	0.20	0.27	0.61	0.47	0.54

[a] $E_{1/2}$ values were calculated from the average of the anodic and cathodic peak potentials, $E_{1/2} = 0.5(E_{pa} + E_{pc})$.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, numbers CCDC Number 288279 (**1**) and 288280 (**2**). Copies of this information may be obtained free of charge free from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

References

[1] (a) M.C. Barral, R.J. Aparicio, J.L. Priego, E.C. Royer, F.A. Urbanos, U. Amador. *J. Chem. Soc., Dalton Trans.*, 863 (1997); (b) L. Bonnet, F.D. Fabio, G.-G. Pascale, M.M. Anne, J.C. Jean, M. Ibn-Elhaj, D. Guillon, A. Skoulios. *Chem. Mater.*, **6**, 31 (1994).

[2] (a) C. Sudha, S.K. Mandal, A.R. Chakravarty. *Inorg. Chem.*, **32**, 3801 (1993); (b) A. Syamala, A.R. Chakravarty. *Polyhedron*, **12**, 1545 (1993); (c) A. Syamala, M. Nethaji, A.R. Chakravarty. *Inorg. Chim. Acta*, **229**, 33 (1995); (d) Y. Mikata, N. Takeshita, T. Miyazu, Y. Miyata, T. Tanase, I. Kinoshita, A. Ichimura, W. Mori, S. Takamizawa, S. Yano. *J. Chem. Soc., Dalton Trans.*, 1969 (1998); (e) P. Neubold, K. Wieghardr, B. Nuber, J. Weiss. *Inorg. Chem.*, **28**, 459 (1989).

[3] (a) P.J. Msher, G.P.A. Yap, R.J. Crutchly. *Inorg. Chem.*, **40**, 1189 (2001); (b) P. Paul, B. Tyagi, A.K. Bilakhiya, P. Dastidar, E. Suresh. *Inorg. Chem.*, **39**, 14 (2000); (c) E. Ishow, A. Gourdon, J.-P. Launay, C. Chiorboli, F. Scandola. *Inorg. Chem.*, **38**, 1504 (1999); (d) A. Juris, V. Balzani, S. Campagna, G. Denti, S. Serroni, G. Frei, H.U. Gudel. *Inorg. Chem.*, **33**, 1491 (1994); (e) X. Hua, A. von Zelewsky. *Inorg. Chem.*, **34**, 5791 (1995).

[4] N.H. Williams, B. Takasaki, M. Wall, J. Chin. *Acc. Chem. Res.*, **32**, 485 (1999).

[5] P.E. Jurek, A.E. Martell. *Inorg. Chem.*, **38**, 6003 (1999).

[6] S. Kawasaki, M. Koikawa, T. Tokii. *Mol. Cryst. Liq. Cryst.*, **376**, 365 (2002).

[7] K. Koga, M. Makiko, M. Ueno, M. Koikawa, T. Tokii. *Inorg. Chem. Commun.*, **6**, 374 (2003).

[8] K. Koga, M. Ohtubo, Y. Yamada, M. Koikawa, T. Tokii. *Chem. Lett.*, **33**, 1606 (2004).

[9] M. Hudlicky. *Oxidation in Organic Chemistry*, American Chemical Society, Washington, DC (1990).

[10] K. Kaneda, Y. Kawanishi, K. Jitsukawa, S. Teranishi. *Tetrahedron Lett.*, **24**, 5009 (1983).

[11] K. Yamawaki, T. Yoshida, T. Suda, Y. Ishii, M. Ogawa. *Synthesis*, 59 (1983).

[12] (a) S. Kanemoto, S. Matsubara, K. Takai, K. Oshima, K. Utimoto, H. Nozaki. *Bull. Chem. Soc. Japan*, **61**, 3607 (1988); (b) K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda. *J. Am. Chem. Soc.*, **122**, 7144 (2000); (c) C. Bilgrein, S. Davis, R.S. Drago. *J. Am. Chem. Soc.*, **109**, 3786 (1987).

[13] B.P. Sullivan, D.J. Salmon, T.J. Meyer. *Inorg. Chem.*, **17**, 3334 (1978).

[14] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M. Camalli. *J. Appl. Cryst.*, **27**, 1045 (1994).

[15] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits. *The DIRDIF-99 Program System*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands (1999).

[16] H. Matsushima, E. Ishiwa, M. Koikawa, M. Nakashima, T. Tokii. *Chem. Lett.*, **2**, 129 (1995).

[17] (a) A. Garoufis, A. Koutsodimou, N. Katsaros, C.-A. Mitsopolo, N. Hadjiliadis. *Polyhedron*, **18**, 361 (1999); (b) J.E. Fergusson, G.M. Harris. *J. Chem. Soc.*, 1293 (1966).