

Synthesis, crystal structure determination, spectroscopic and electrochemical studies of *trans*-[Ru(PPh₃)₂(bbpH₂)Cl]Cl·CHCl₃·H₂O (bbpH₂ = 2,6-bis(benzimidazolyl)pyridine) – an infinite double columnar supramolecule in the solid state

Dipankar Mishra, Subhendu Naskar and Shyamal K. Chattopadhyay*

Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah 711 103, India

Milan Maji

National Institute of Technology, Durgapur 713209, India

Parbati Sengupta, Rupam Dinda and Saktiprasad Ghosh

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

Thomas C.W. Mak

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, People's Republic of China

Received 27 August 2004; accepted 25 October 2004

Abstract

The synthesis, crystal structure, redox and spectroscopic properties of *trans*-[Ru(bbph₂)(PPh₃)₂Cl]Cl are reported. In the crystalline solvate *trans*-[Ru(bbph₂)(PPh₃)₂Cl]Cl·CHCl₃·H₂O, the molecular components are connected by strong intermolecular hydrogen bonding to form an infinite double column.

Introduction

Ruthenium(II) complexes with diimine ligands have been studied in great detail [1–13], because of their exciting electronic, photochemical and photophysical properties and their possible applications in solar energy conversions and catalysis. The most extensively studied [1–8] ligand systems include the imine nitrogens as part of pyridine rings; *e.g.* bipyridine and phenanthroline and their derivatives. Much less attention has been given [9–13] to systems where a donor nitrogen is part of an imidazole ring. In this communication we report the synthesis, X-ray crystal structure and spectroscopic characterization of a ruthenium(II) complex containing the tridentate ligand 2,6-bis(benzimidazolyl)pyridine (bbpH₂).

Experimental

Materials

RuCl₃ was purchased from Arora Matthey, India and processed by dissolving in HCl, evaporating to dryness and repeating the process thrice. Finally it was dried over solid NaOH. Ru(PPh₃)₃Cl₂ was prepared by a

reported procedure [14]. 2,6-Bis(benzimidazolyl)pyridine was obtained from Aldrich. All other chemicals and solvents were obtained from Merck (India) or SRL (India).

Measurements

Cyclic voltammetry was carried out using a PAR Versastat instrument driven by E-chem software. A three electrode configuration with Pt working and auxiliary electrodes, calomel reference electrode and TEAP as supporting electrolyte, were used. The potentials were calibrated against a ferrocene/ferrocenium couple. UV-vis spectra were recorded using a JASCO7850 spectrophotometer while luminescence spectra were obtained using a Perkin Elmer LS55 fluorescence spectrophotometer.

Syntheses of *trans*-[Ru(bbph₂)(PPh₃)₂Cl]Cl (1)

To a hot MeOH solution (30 cm³) of 2,6-bis(benzimidazolyl)pyridine (0.12 g, 37.5 mmol) solid Ru(PPh₃)₂Cl₂ (0.36 g, 37.5 mmol) was added and the mixture was boiled under reflux for 2.5 h. The resulting brown red solution was concentrated on a rotary evaporator to *ca.* 10 cm³. Addition of Et₂O led to a brown shiny precipitate, which was filtered and washed thoroughly with Et₂O. The complex was finally recrystallised

* Author for correspondence

from $\text{CHCl}_3\text{-Et}_2\text{O}$. Yield 87%. Found: C, 58.6; H, 4.2; N, 6.3. $\text{C}_{56}\text{H}_{46}\text{N}_5\text{Cl}_5\text{OP}_2$ Ru($\text{CHCl}_3\text{-H}_2\text{O}$ solvate) calcd. C, 58.7; H, 4.0; N, 6.1%.

Crystallography

A dark red-brown crystal of (*I*). $\text{CHCl}_3\text{-H}_2\text{O}$ ($0.40 \times 0.12 \times 0.12 \text{ mm}^3$) was chosen for the X-ray diffraction study. The compound crystallized in the triclinic P-1 space group. Intensity data were collected at 293 K on a Bruker Smart CCD area detector system using graphite monochromated Mo- K_α radiation. The structure was solved by the direct method. All non-hydrogen atoms were refined anisotropically by full matrix least squares, with a riding model for the hydrogen atoms, using the SHELXTL package.

Crystallographic data

Empirical formula: $\text{C}_{56}\text{H}_{46}\text{Cl}_5\text{N}_5\text{OP}_2\text{Ru}$, $M = 1145.24$. Triclinic, space group P-1, $a = 11.949(1) \text{ \AA}$, $b = 12.292(1) \text{ \AA}$, $c = 19.778(2) \text{ \AA}$, $\alpha = 105.765(2)^\circ$, $\beta = 92.601(2)^\circ$, $\gamma = 108.019(2)^\circ$, $U = 2631.8(5) \text{ \AA}^3$, $Z = 2$, calculated density = 1.445 g cm^{-3} , temperature: 293(2) K, $\lambda(\text{Mo-}\text{K}_\alpha) = 0.71073 \text{ \AA}$. Absorption coefficient = 0.656 mm^{-1} , $F(000) = 1168$, θ range: $1.08\text{--}28.04^\circ$, limiting indices $-15 \leq h \leq 15$, $-15 \leq k \leq 16$, $-22 \leq l \leq 26$. Reflections collected/unique 18102/12477, Data/restraints/parameters 12477/0/631, Goodness-of-fit on $F^2 = 0.923$, Final R indices [$I > 2\sigma(I)$] $R1 = 0.0578$, $wR2 = 0.1211$, R indices (all data) $R1 = 0.1133$, $wR2 = 0.1439$, largest diff. peak and hole are 1.183 and 0.834 e \AA^{-3} , respectively.

Selected bond distances and angles are given in Table 1. Crystallographic information has been deposited in the CCDC with deposition number CCDC216282.

Computation

All calculations were done using the commercially available HYPERCHEM 7.0^R, software [15] and implemented in Windows XP platform, and using default parameters of the programme.

Results and discussion

Synthesis and description of the structure

The title compound *trans*-[Ru(bbpH_2)(PPh_3) $_2$ Cl]Cl (*I*) was synthesized by reacting [Ru(PPh_3) $_3$ Cl] $_2$ with 2,6-bis-(benzimidazolyl)pyridine in a 1:1 molar proportion in refluxing MeOH. Recrystallization from a $\text{CHCl}_3\text{-Et}_2\text{O}$ mixture gave red-brown crystals of *trans*-[Ru(bbpH_2)(PPh_3) $_2$ Cl]Cl- $\text{CHCl}_3\text{-H}_2\text{O}$.

The asymmetric unit of compound (*I*). $\text{CHCl}_3\text{-H}_2\text{O}$ (Figure 1) consists of the monomeric *trans*-

Table 1. Selected bond distances (\AA) and bond angles ($^\circ$) for *trans*-[Ru(bbpH_2)(PPh_3) $_2$ Cl]Cl- $\text{CHCl}_3\text{-H}_2\text{O}$

Bond distances	
Ru–N1	1.981(3)
Ru–N4	2.106(3)
Ru–N2	2.115(3)
Ru–P1	2.4079(12)
Ru–P2	2.4141(12)
Ru–C11	2.4472(12)
Bond angles	
N1–Ru–N4	78.62(14)
N1–Ru–N2	78.25(14)
N4–Ru–N2	156.87(14)
N1–Ru–P1	89.31(10)
N4–Ru–P1	93.13(9)
N2–Ru–P1	86.73(9)
N1–Ru–P2	91.16(10)
N4–Ru–P2	90.76(10)
N2–Ru–P2	89.58(9)
P1–Ru–P2	176.10(4)
N1–Ru–Cl1	177.97(10)
N4–Ru–Cl1	99.35(10)
N2–Ru–Cl1	103.77(10)
P1–Ru–Cl1	90.65(4)
P2–Ru–Cl1	89.01(4)

[Ru(bbpH_2)(PPh_3) $_2$ Cl] $^+$ cation, a chloride anion, and one each of co-crystallized chloroform and water molecules. All three Ru–N distances are dissimilar, with the Ru– N_{py} distance (1.981 \AA) shorter than the Ru– N_{imzH} distance (average 2.110 \AA). The average Ru–N bond distance of 2.045 \AA is similar to that found [16] in Ru(bpy) $_3$ $^{2+}$ which is 2.066 \AA . Crystal structures of ruthenium(II) complexes[17, 18] containing terpy have also revealed that in the tridentate ligands with N_3 -donor sets, where nitrogen atoms are part of heterocyclic rings, the Ru–N distances involving the central N is always smaller than the Ru–N bonds involving terminal nitrogens, probably because of the small bite angles of the ligands. The small bite angle of the bbpH_2 ligand is also the reason behind its coordination in a distorted fashion, with the *cis*-angles being $\sim 78^\circ$, while the *trans* angle is only 157° . The two Ru–P bond lengths are also dissimilar, the average being 2.411 \AA .

In the crystal structure of the compound, pairs of lattice water molecules (atom O1 w) and uncoordinated chloride ions (atom Cl2), located near an inversion center, form a hydrogen-bonded ($\text{H}_2\text{O}\text{-Cl}^-$) $_2$ ring. Each chloride ion forms four acceptor hydrogen bonds, two with adjacent water molecules (O–H \cdots Cl, 3.179, 3.202 \AA) and one each with the N–H group of an imidazole ligand (atom N5; N–H \cdots Cl, 3.138 \AA) and a chloroform molecule (atom C56; C–H \cdots Cl 3.532 \AA). Each water molecule forms, in addition to the two O–H \cdots Cl donor hydrogen bonds in the ($\text{H}_2\text{O}\text{-Cl}^-$) $_2$ ring, an acceptor hydrogen bond with the N–H group of the other imidazole ligand (atom N3; N–H \cdots O, 2.739 \AA). These three types of hydrogen bonds connect the ruthenium complexes into an infinite double chain running parallel to the 'a' axis, as shown in Figure 2.

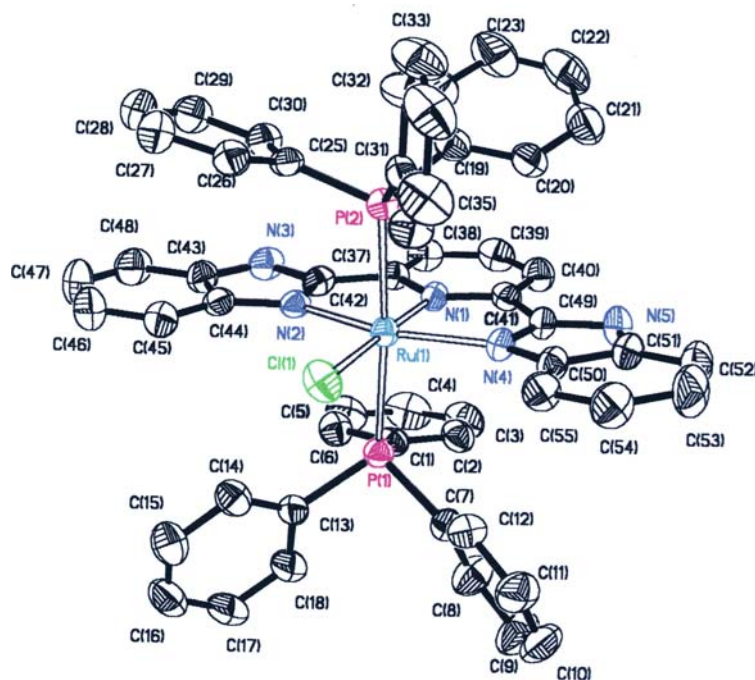


Fig. 1. ORTEP diagram and atom numbering scheme.

Electrochemistry

The Ru(III)/Ru(II) potential for (1) along with a series of related complexes are given in Table 2. From the data it is evident that the *bis* complex of bbpH_2 (2) has a very similar redox potential to that of (1). However, the corresponding terpyridyl complexes (3), (4) and (5) have somewhat higher redox potentials, indicating the higher ligand field strength of terpy, compared to bbpH_2 , resulting in greater stabilization of the d_π orbitals of ruthenium(II) in the case of terpy compared to bbpH_2 . It is well known [20] that imidazole is a better

σ -donor and much poorer π -acceptor than pyridine. Both these factors result in higher energy of the HOMO (d_π -manifold) for ruthenium(II) complexes of polyimidazole type ligands compared to similar polypyridine complexes. This is amply reflected in the redox potential data given in the Table. It is interesting to note, that on moving from compound (1) to (2), when two *trans*- PPh_3 groups and a chloride are replaced by another bbpH_2 group, the $E^\circ[\text{Ru(III)/Ru(II)}]$ remains almost constant even though the total positive charge on the complex increases. This may be contrasted with the corresponding terpy complexes, where the *bis* terpy

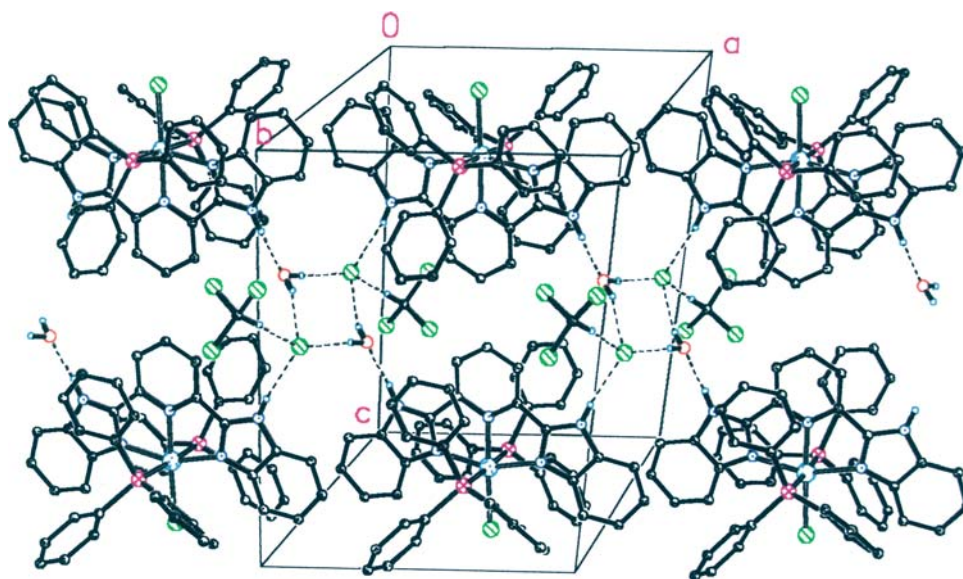


Fig. 2. Double chain running parallel to the 'a' axis, being generated by hydrogen bonds involving water molecules, chloride ions, chloroform molecules, and the N-H groups of the organic ligands. For clarity all H atoms have been omitted except those that participate in hydrogen bonding. Note that the centrosymmetric $(\text{H}_2\text{O} \cdot \text{Cl}^-)_2$ ring plays a central role in linking the complex molecules.

Table 2. $E^\circ[\text{Ru(III)/Ru(II)}$ values for (1) and some related compounds

Complex	$E^\circ[\text{Ru(III)/Ru(II)}$ (volts versus SCE)	
(1)	<i>trans</i> -[Ru(PPh ₃) ₂ (bbpH ₂)Cl] ⁺	0.78
(2)	[Ru(bbph ₂) ₂] ²⁺	0.76 ^a
(3)	<i>trans</i> -[Ru(PPh ₃) ₂ (terpy)Cl] ⁺	0.90 ^b
(4)	<i>trans</i> -[Ru(PEt ₃) ₂ (terpy)Cl] ⁺	0.73 ^b
(5)	[Ru(terpy) ₂] ²⁺	1.28 ^c
(6)	[Ru(bpy) ₃] ²⁺	1.27 ^d
(7)	[Ru(bpy) ₂ (BibzImH ₂) ₂] ²⁺	1.12 ^d
(8)	[Ru(bpy)(BibzImH ₂) ₂] ²⁺	0.91 ^d
(9)	[Ru(BibzImH ₂) ₃] ²⁺	0.80 ^d
(10)	[Ru(BilmH ₂) ₃] ²⁺	0.54 ^d
(11)	[Ru(bpy)(BilmH ₂) ₂] ²⁺	0.80 ^d
(12)	[Ru(bpy) ₂ (BilmH ₂)] ²⁺	1.04 ^d

^aref. [12].

^bref. [19].

^cref. [2].

^dref. [11].

complex (5), have much higher Ru(III)/Ru(II) potential than the mono terpy complex (4). This is probably because on going from complex (1) to (2), two PPh₃

groups of poor σ -donor and moderate π -acceptor capability are replaced by two benzimidazole moieties having strong σ as well as π donor capability, but relatively poor π -acceptor capability. This effect is more pronounced than the replacement of σ - and π -donor chloride by a σ -donor and π -acceptor pyridine.

UV-visible and luminescence spectroscopy

In the u.v.-vis spectrum of complex (1) in MeCN solution, there is a broad band with a maximum at 430 nm ($\epsilon = 3839 \text{ mol}^{-1} \text{ cm}^{-1}$), which may be assigned to a spin-allowed, metal-to-ligand charge-transfer transition to a ¹MLCT state. The other high-energy transitions, at 351 (27841), 336 (20649), 315 (16995), 300 (sh), 258 (sh), are probably intra-ligand in nature. Examination of the luminescence spectra of (1) shows that the compound is luminescent at the liquid nitrogen temperature (LNT), although at room temperature the luminescence is quite weak. Excitation at 380 nm at LNT leads to a strong emission at 587 nm with a tail extending up to 520 nm. This behavior is comparable to that of [Ru(terpy)₂]²⁺, which is weakly fluorescent at room temperature, and at LNT the fluorescence lifetime increases [2]. It may be noted that although the bbpH₂ ligand is known to be fluorescent, its bis complex [Ru(bbph₂)₂]²⁺ was found to be non-fluorescent [12]. Thus, the luminescence behavior of (1) is similar to that of [Ru(terpy)₂]²⁺, but different from that of [Ru(bbph₂)₂]²⁺.

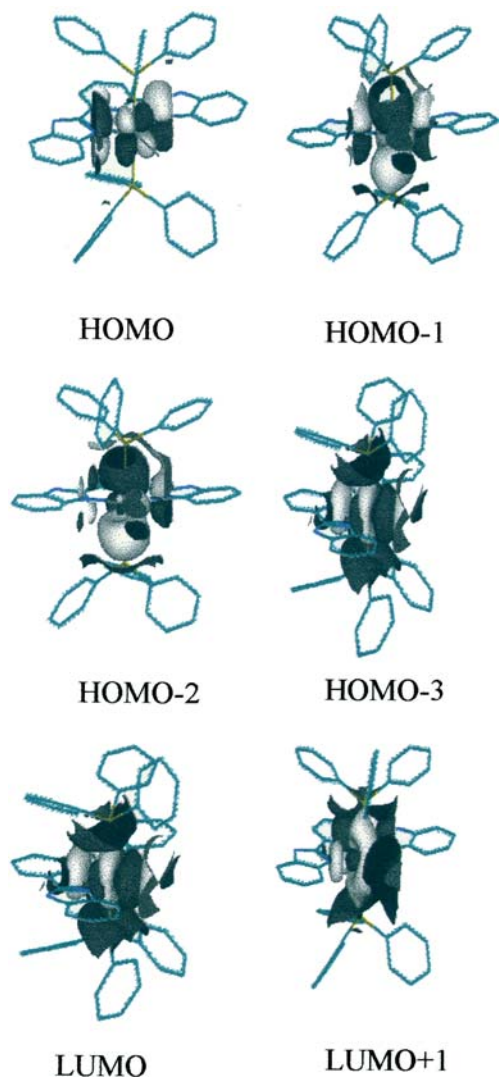


Fig. 3. Frontier molecular orbitals of *trans*-[Ru(bbph₂)(PPh₃)₂Cl]⁺.

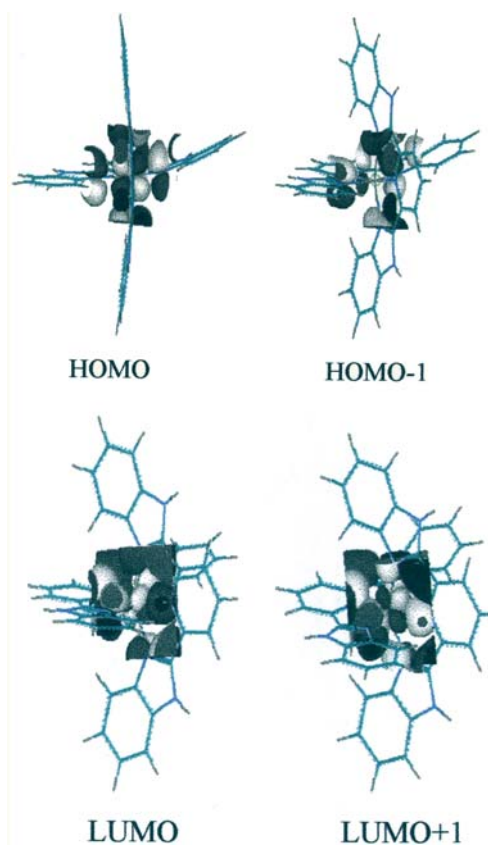


Fig. 4. Frontier molecular orbitals of [Ru(bbph₂)₂]²⁺.

Table 3. Frontier orbitals of $trans$ -[Ru(bbpH₂)(PPh₃)₂Cl]⁺ and [Ru(bbpH₂)₂]²⁺ as calculated by the EHMO method

Molecule	HOMO	HOMO-1	HOMO-2	HOMO-3	LUMO	LUMO + 1
$trans$ -[Ru(bbpH ₂)(PPh ₃) ₂ Cl] ⁺ (C ₁ point group) (geometry from crystal structure)	156A -11.96 eV	155A -12.17 eV	154A -12.36 eV	153A -12.43 eV	157A -10.06 eV	158A -9.68 eV
$trans$ -[Ru(bbpH ₂)(PPh ₃) ₂ Cl] ⁺ (C ₁ point group) (optimized geometry)	156A -11.77 eV	155A -12.05 eV	154A -12.16 eV	153A -12.27 eV	157A -9.81 eV	158A -9.50 eV
[Ru(bbpH ₂) ₂] ²⁺ (C ₁ point group) (optimized geometry)	117A -11.71 eV	116A -11.85 eV	115A -12.12 eV	114A -12.14 eV	118A -9.58 eV	119A -9.54 eV

EHMO calculations

EHMO calculations were carried out on $trans$ -[Ru(bbpH₂)(PPh₃)₂Cl]⁺ (1), using the geometry obtained from the crystal structure, as well as the MM⁺ optimized geometry, and on [Ru(bbpH₂)₂]²⁺ (2) using the MM⁺ optimized geometry. The results are given in Table 3 and some frontier orbitals are pictorially depicted in Figures 3 and 4. As the crystal structure of [Ru(bbpH₂)₂]²⁺ is not available, it is better to compare the results of EHMO calculations performed on the optimized geometry for both the molecules. It can be seen from the Table 3, that the HOMOs of the two molecules are of nearly identical energy, the energy of the bis-chelate complex (2) being slightly higher than that of the mono-chelate complex (1). This result is in good agreement with the observed E⁰[Ru(III)/Ru(II)] value for complexes, both (1) and (2) having near identical values. The HOMO and LUMO are almost orthogonal to each other in both the complexes, so the transition between them is expected to be forbidden. The absorption in the visible region is then expected to be forbidden. The absorption in the visible region is then expected to be due to HOMO → LUMO + 1, LUMO + 2, and HOMO-1 → LUMO + 1. Again these energy gaps are higher for (1) than for (2), in agreement with the observation that in the visible region λ_{max} for (2) is [12] higher than that for (1).

Acknowledgements

SC acknowledges grants from the UGC and AICTE. DM acknowledges CSIR and SN acknowledge the UGC for NET fellowships.

References

1. V. Balzani and F. Scandola, *Supramolecular Photochemistry*; Ellis Horwood, Chichester, U.K. 1991.
2. K. Kalyansundaram, *Photochemistry of Polypyridin and Porphyrin Complexes*, Academic Press, New York, 1992.
3. A.M.W. Cargill Thompson, M.C.C. Smailes, J.C. Jeffery and M.D. Ward, *J. Chem. Soc. Dalton Trans.*, 737 (1997).
4. E.C. Constable, R.W. Handel, C.E. Housecroft, A.M. Morales, L. Flamigni and F. Barigelletti, *J. Chem. Soc. Dalton Trans.*, 1220 (2003).
5. V. Aranyos, J. Hjelm, A. Hagfeldt and H. Grennberg, *J. Chem. Soc. Dalton Trans.*, 1280 (2003).
6. A. Hagfeldt and M. Gratzel, *Acc. Chem. Res.*, **33**, 269 (2000).
7. H. Durr and S. Bosmann, *Acc. Chem. Res.*, **34**, 905 (2001).
8. T.J. Meyer, *Acc. Chem. Res.*, **22**, 163 (1989).
9. M.-a. Haga, T. Takasugi, A. Tomie, M. Ishizuya, T. Yamada, M.D. Hossain and M. Inoue, *J. Chem. Soc. Dalton Trans.*, 2069 (2003).
10. S. Rau, T. Büttner, C. Temme, M. Ruben, H. Görls, D. Walther, M. Duati, S. Fanni and J.G. Vos, *Inorg. Chem.*, **39**, 1621 (2000).
11. D.P. Rillema, R. Sahai, P. Matthews, A.K. Edwards, R.J. Shaver and L. Morgan, *Inorg. Chem.*, **29**, 167, (1990).
12. X. Xiaoming, M.-a. Haga, T.M. Inoue, Y. Ru, A.W. Addison and K. Kano, *J. Chem. Soc. Dalton Trans.*, 2477 (1993).
13. M.-a. Haga, T.-a. Ano, K. Kano and S. Yamabe, *Inorg. Chem.*, **30**, 3483 (1991).
14. T.A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).
15. Hyperchem for Windows, Release 7.01, Hypercube Inc., 115NW 4th Street, Gainesville, Florida 32601.
16. D.P. Rillema and D.S. Jones, *Chem. Commun.*, 849 (1979).
17. R.P. Thummel and Y. Jahng, *Inorg. Chem.*, **25**, 2527 (1986).
18. H. Sugimoto, K. Tsuge and K. Tanaka, *J. Chem. Soc. Dalton Trans.*, 57 (2001).
19. R.A. Leising, S.A. Kubow and K.J. Tekeuchi, *Inorg. Chem.*, **29**, 4569 (1990).
20. M.G. Elliot and R.E. Shepherd, *Inorg. Chem.*, **26**, 2067 (1987).
21. T.A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).