

Cyclometalated rhodium(III) complex with phen-dione ligand

Ghobad Mansouri ^a, Ali R. Rezvani ^a, Hassan Hadadzadeh ^{b,*}, Hamid Reza Khavasi ^c,
Hamideh Saravani ^a

^a Department of Chemistry, University of Sistan and Baluchestan, P.O. Box 98135-674, Zahedan, Iran

^b Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

^c Department of Chemistry, Shahid Beheshti University, P.O. Box 19395, Tehran, Iran

Received 28 February 2007; received in revised form 6 May 2007; accepted 15 May 2007

Available online 3 June 2007

Abstract

The novel cyclometalated Rh(III) complex, $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^{2'})_2(\text{phen-dione})]\text{PF}_6$, where $\text{phpy-}\kappa^2\text{N,C}^{2'}$ is pyridine-2-yl-2-phenyl and phen-dione is 1,10-phenanthroline-5,6-dione has been prepared and characterized by elemental analysis, IR, ¹H NMR, and electronic absorption spectroscopies, cyclic voltammetry, and X-ray crystallography. The crystal structure of $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^{2'})_2(\text{phen-dione})]\text{PF}_6 \cdot \text{CH}_3\text{CN}$ shows that the coordination geometry around the Rh(III) is a distorted octahedron, with bite angles of 76.13°–81.09° for all three bidentate ligands.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Rh(III) complex; Cyclometalated complex; 1,10-Phenanthroline-5,6-dione; 2-Phenylpyridine; Crystal structure; Cyclic voltammetry

1. Introduction

Cyclometalated octahedral ruthenium(II), ruthenium(III), rhodium(III), and iridium(III) complexes have been widely studied with particular emphasis placed on their photoelectrochemical, photophysical, redox, and spectroscopic properties [1]. The changes in such properties observed upon the replacement of a typical N,N-donor ligand such as 2,2'-bipyridine with its carbocyclic structural analogue, 2-phenylpyridine (phpy), have been of particular interest. The strong ligand field influence of the C-donor, combined with the possibility of π -back donation into the metallocycle, yields generally high-lying d–d excited states. Charge-transfer states, particularly interesting in photochemistry, become therewith often the lowest excited states [1–5].

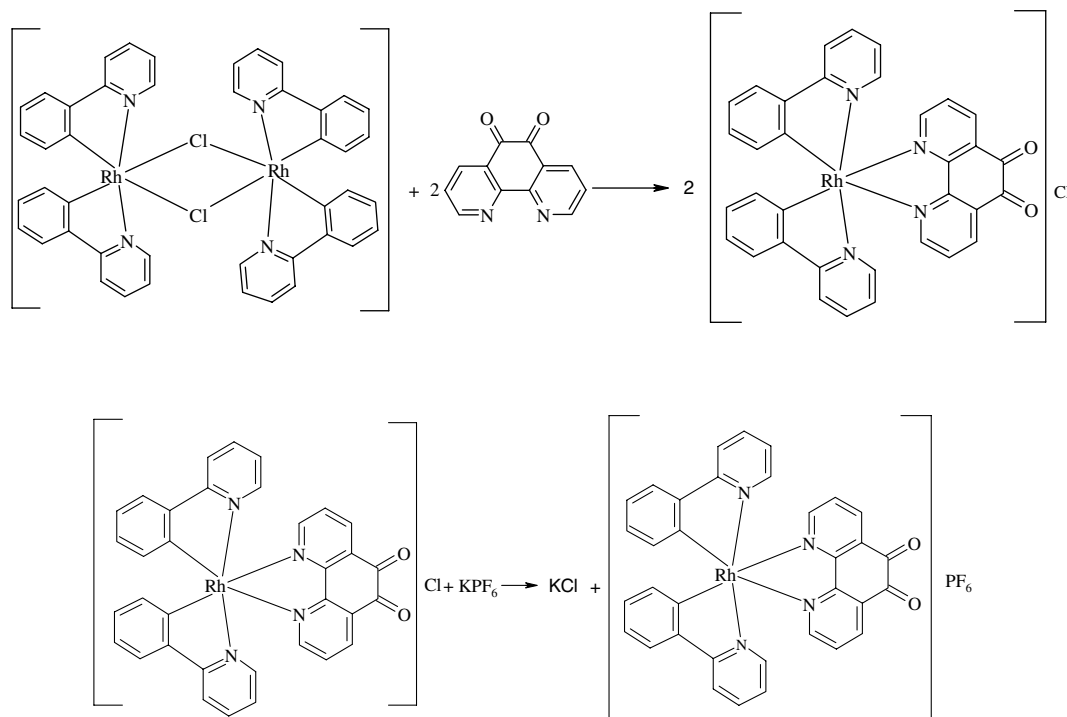
Our research into cyclometalated complexes [6] has led us to cyclometalated Rh(III) complex with 1,10-phenanthroline-5,6-dione (Scheme 1).

1,10-Phenanthroline-5,6-dione plays important roles as molecular scaffolding for supramolecular assemblies, building block for the synthesis of metallodendrimers, thin films of luminescent complexes and ligand for synthesis of ring-opening metathesis polymerization (ROMP) monomer [7]. Metal complexes of phen-dione ligand allow for the variation and control of redox properties over a wide range as well as the fine tuning of potentials through pH changes [8,9]. In this study, we report the facile synthesis of a Rh(III) cyclometalated complex, $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^{2'})_2(\text{phen-dione})]\text{PF}_6$, where $\text{phpy-}\kappa^2\text{N,C}^{2'}$ is pyridine-2-yl-2-phenyl and phen-dione is 1,10-phenanthroline-5,6-dione, and the characterization of this complex by X-ray crystallography, elemental analysis, IR, ¹H NMR, and UV–Vis spectroscopies, and cyclic voltammetry.

2. Results and discussion

The Rh(III) complex was synthesized in good yield according to the following reactions:

* Corresponding author. Tel.: +98 311 3912351; fax: +98 311 3912350.
E-mail address: hadad@cc.iut.ac.ir (H. Hadadzadeh).



Refluxing operation was thought necessary to overcome the greater inertness of Rh(III) toward substitution reaction. Due to the poor solubility of $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^{2'})_2(\text{phen-dione})]\text{Cl}$ in common organic solvents, the chloride salt of the complex was dissolved in a minimum amount of water and then excess amount of KPF_6 was added to the solution. The orange precipitate, $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^{2'})_2(\text{phen-dione})]\text{PF}_6$ was formed. $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^{2'})_2(\text{phen-dione})]\text{PF}_6$ is air-stable and can be readily recrystallized. Elemental analysis of the complex was entirely consistent with its proposed stoichiometry.

Orange crystals of $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^{2'})_2(\text{phen-dione})]\text{PF}_6 \cdot \text{CH}_3\text{CN}$ were grown by ether diffusion into an acetonitrile solution of the complex. As shown in Fig. 1, the Rh(III) center chelated to two $\text{phpy-}\kappa^2\text{N,C}^{2'}$ ligands oriented in a *cis* geometry and to a phen-dione ligand. The phen-dione ligand is coordinated to the Rh(III) through its nitrogen atoms. The σ -bonded phenyl groups of pyridine-2-yl-2-phenyl ligands are *trans* to the nitrogen atoms of the phen-dione ligand. As we know the scattering power of an atom for X-ray is proportional to its atomic number. This means that neighboring atoms in the periodic table

such as C and N atoms differ only slightly from one another. For good data sets, it is usually possible to make this distinction from X-ray data alone. The single most powerful crystallographic indicator for a wrongly chosen atom type is the refined U_{eq} value. Here, according to the crystallographic R -factors and U_{eq} values, in the structure, N atoms of two $\text{phpy-}\kappa^2\text{N,C}^{2'}$ ligands are in *trans* position to each other.

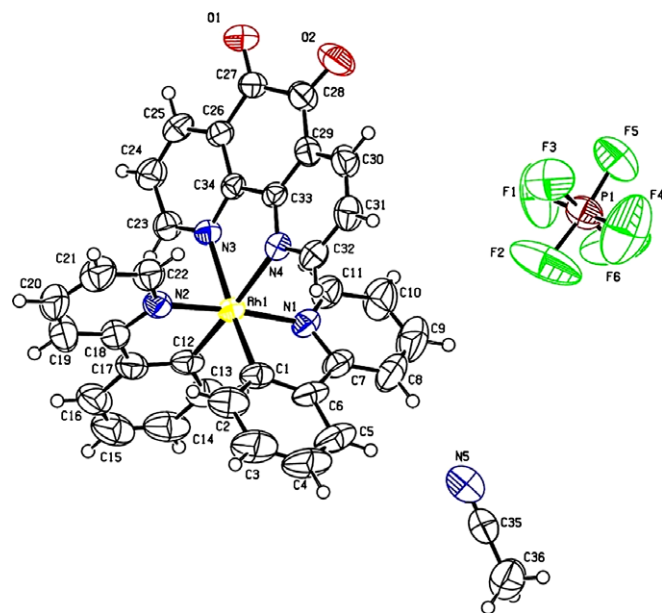
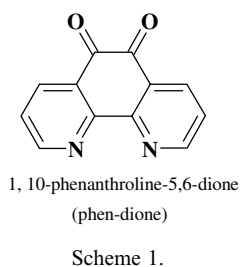


Fig. 1. ORTEP structure of $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^{2'})_2(\text{phen-dione})]\text{PF}_6 \cdot \text{CH}_3\text{CN}$.

The coordination geometry around Rh(III) is a distorted octahedron, with bite angles of 76.13–81.09° for all three bidentate ligands. The phen-dione ligand has the smallest bite angle [N(3)–Rh–N(4) = 76.13(10)°]. The average bond length between the Rh(III) and each nitrogen atom [N(1), N(2), N(3), or N(4)] is slightly larger than that formed by two carbon atoms of the pyridine-2-yl-2-phenyl ligands and Rh(III). Of the three ligands, the phen-dione is the most planar and the angle between pyridyl rings is 10.38(13)° in the lattice. The symmetry of the monocation $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^2)_2(\text{phen-dione})]^+$ is formally C_2 .

It is to be noted that fluorine atoms of PF_6^- counter ions, have a high thermal parameter due to data collection in room temperature. We tried refining these atoms in two positions with reduced occupancy but while this model converged satisfactorily, there was no decrease in R value and therefore we consider that our original refinement is the best that can be achieved and should be reported. The P–F bond lengths range from 1.549(4) to 1.603(4) Å, with an average of 1.564(4) Å.

The well-resolved ^1H NMR spectrum with sharp resonances of the cyclometalated Rh(III) complex indicates diamagnetic behavior at room temperature. The ^1H NMR spectrum of the complex shows 11 chemical shifts (see Section 3). This is consistent with its structure.

The IR spectrum of free phen-dione clearly exhibits a band at 1675 cm^{-1} that is ascribable to a stretching frequency of the C=O bonds on the ligand [8]. This band was seen to be not shifted much in the corresponding complexes, which is reasonable since the C=O moieties are far removed from the site of coordination of this ligand with the metal ion [9–11]. In the $\text{M}(\text{O,O}'\text{-phen-dione})_3$ (where $\text{M} = \text{Ti}$ and V) and $\text{M}(\text{O,O}'\text{-phen-dione})_3(\text{M}'\text{L}_n)_3$ (where $\text{M} = \text{V}$, $\text{M}'\text{L}_n = \text{TiCl}_4$; $\text{M} = \text{Ti}$, $\text{M}'\text{L}_n = \text{TiCp}_2$ and $\text{M} = \text{V}$, $\text{M}'\text{L}_n = \text{TiCp}_2$), phen-dione ligand is coordinated to metal ion as a phen-semiquinonate or phen-diolate via oxygen atoms. In these complexes, the carbon–oxygen stretching vibration was shifted about $200\text{--}300\text{ cm}^{-1}$ to the lower wave numbers [12]. The IR spectrum of the $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^2)_2(\text{phen-dione})]\text{PF}_6$ shows a strong band at 1689 cm^{-1} that is assigned to $\nu(\text{C=O})$ of the phen-dione ligand. The strong absorption band at 839 cm^{-1} is assigned to $\nu(\text{P-F})$ and demonstrates the existence of PF_6^- as counter ion [13].

Electronic spectrum of the complex was taken in acetonitrile solution (Fig. 2). The absorption bands seen in the UV region (238 nm ($\log \epsilon = 5.07$), 255 nm ($\log \epsilon = 4.89$) and 302 nm ($\log \epsilon = 2.44$)) are assigned to ligand-centered ($\pi \rightarrow \pi^*$) transitions [9,14–19]. Lower-energy absorptions (374 nm and shoulder at 485 nm) which show a solvent dependence are not present in the spectra of the ligands. Thus, they must be attributed to metal-to-ligand charge transfer (MLCT) transitions ($d\pi \rightarrow \pi^*$) involving either the phen-dione or the $\text{phpy-}\kappa^2\text{N,C}^2$ ligand. For the cyclometalated $[\text{Rh}(\hat{\text{C}}\text{N})_2(\hat{\text{N}}\text{N})]^+$ complexes, an absorption band observed around 370 nm is invariable with respect to the polypyridyl co-ligands ($\hat{\text{N}}\text{N}$) and this band is assigned to $\text{Rh} \rightarrow \text{phpy}^-$ [14,20–24]. Therefore, the

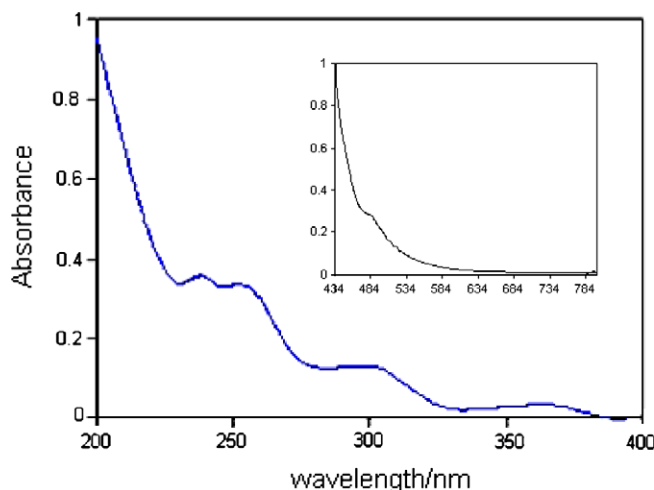
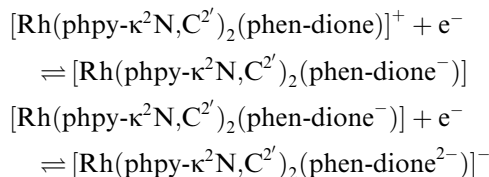


Fig. 2. Absorption spectrum of $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^2)_2(\text{phen-dione})]\text{PF}_6$ in acetonitrile.

absorption at 374 nm is most probably due to a $\text{Rh} \rightarrow \text{phpy}^-$ transition.

Cyclic voltammetry was performed on an acetonitrile solution of $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^2)_2(\text{phen-dione})]\text{PF}_6$ with 0.1 M TBAH as a supporting electrolyte (Fig. 3). The phen-dione ligand is electrochemically active due to the presence of the *o*-quinone moiety [25]. In this complex, two reversible reduction couples at -0.20 and -0.942 V are assigned to the reduction of phen-dione ligand to phen-semiquinonate and phen-diolate, respectively by analogy to other phen-dione complexes [8–10,26,27].



For the mononuclear $[\text{M}(\text{phpy-}\kappa^2\text{N,C}^2)_2(\text{N-N})]^+$ series, reduction of the anionic pyridine-2-yl-2-phenyl ligands usually takes place below -2.3 V [28]. The quasi-reversible

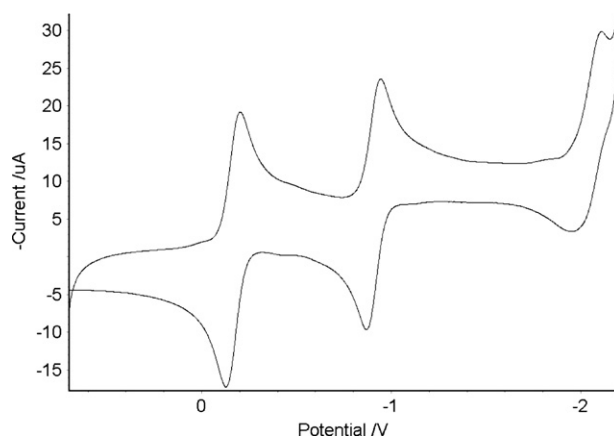


Fig. 3. Cyclic voltammogram of $[\text{Rh}(\text{phpy-}\kappa^2\text{N,C}^2)_2(\text{phen-dione})]\text{PF}_6$ in acetonitrile at a scan rate of 100 mV/s ; 0.1 M TBAH.

reduction couple at -2.195 V is assigned to the reduction of the pyridine-2-yl-2-phenyl ligands. As it was pointed out previously, the coordinating N–N ligands (phen or bpy) are much easier to reduce than the orthometalated pyridine-2-yl-2-phenyl ligand [28].

The cyclic voltammograms of Rh(III)-polypyridyl complexes exhibit a metal-based $2e^-$ reduction (Rh(III) \rightarrow Rh(I)) at the negative potentials [29]. Ronco et al. [30] reported an irreversible metal-center reduction for the reductive couple Rh(III)/Rh(II) at negative potentials in the $[\text{Rh}(\text{tpy})(\text{bpm})(4,4'\text{-bpy})]^{3+}$, $[\text{Rh}(\text{tpy})(\text{bpm})(\text{MQ})]^{4+}$, and $[\text{Rh}(\text{tpy})(\text{dpp})(\text{MQ})]^{4+}$ complexes (where tpy = 2,2':6':2''-terpyridine, bpm = 2,2'-bipyrimidine, dpp = 2,3-bis(2-pyridyl)pyrazine, and MQ^+ = monoquat). Cyclometalated Rh(III) complexes with triazole ligands showed one irreversible oxidation wave around 1.4 V, which has been assigned to a metal-centered oxidation process [24]. Complexes of Rh(III) with two chelating CN ligands and one diimine ligand exhibited at least one reversible reduction wave, attributable to ligand-centered reduction [22].

The synthesis of cyclometalated Rh(III) complexes provides a starting point for the study of a new family of metallointercalators.

3. Experimental

3.1. General

All reagents and solvents used were reagent grade. 1,10-Phenanthroline-5,6-dione was synthesized according to the literature [11]. The starting material, $[\text{Rh}(\text{phpy-}\kappa^2\text{N}, \text{C}^{2'})_2\text{Cl}]_2$ was prepared according to the literature [24]. UV–Vis spectroscopy was performed on a JASCO 7850 spectrophotometer. IR spectra were taken with a JASCO-460 FT-IR spectrophotometer (KBr disks). ^1H NMR data from acetone- d_6 solutions were obtained by using a Bruker DRX-300 MHz AVANCE spectrometer. Cyclic voltammetry was performed using a Metrohm 694 apparatus. The sample cell consisted of a double-walled glass crucible with an inner volume of ≈ 20 mL which was fitted with a Teflon lid incorporating a three-electrode system, a Pt disk working electrode (RDE), a Pt wire auxiliary electrode and SCE reference electrode. The Pt disk working electrode was manually cleaned with 1- μm diamond polish prior to each scan. Acetonitrile was dried over P_2O_5 and vacuum distilled. Tetrabutylammonium hexafluorophosphate (TBAH), purchased from Aldrich, was twice recrystallized from 1:1 ethanol/water and vacuum dried at 110 °C. Ferrocene ($E^\circ = 0.665$ V) was used as an internal reference [31].

3.2. Synthesis of $[\text{Rh}(\text{phpy-}\kappa^2\text{N}, \text{C}^{2'})_2(\text{phen-dione})]\text{PF}_6 \cdot \text{CH}_3\text{CN}$

A mixture of $[\text{Rh}(\text{phpy-}\kappa^2\text{N}, \text{C}^{2'})_2\text{Cl}]_2$ (223 mg, 0.25 mmol) and phen-dione (136 mg, 0.65 mmol) was placed in 50 mL of EtOH/ CHCl_3 (2:1 v/v) and stirred at reflux for 5 h. The light brown solution was evaporated

to dryness. The crude brown solid, $[\text{Rh}(\text{phpy-}\kappa^2\text{N}, \text{C}^{2'})_2(\text{phen-dione})]\text{Cl}$, was dissolved in 15 mL water and precipitated from solution as a hexafluorophosphate salt by the addition of KPF_6 (1 mmol, 184 mg). The product, $[\text{Rh}(\text{phpy-}\kappa^2\text{N}, \text{C}^{2'})_2(\text{phen-dione})]\text{PF}_6$, was collected by suction filtration, washed with cold water and ether, and then air dried. Diffusion of diethylether into an acetonitrile solution of the complex gave orange crystals suitable for X-ray crystallography. Yield 315 mg, 78%. Anal. Calc. for $\text{C}_{36}\text{H}_{25}\text{F}_6\text{N}_5\text{O}_2\text{P}_1\text{Rh}_1$: C, 53.54; H, 3.12; N, 8.67. Found: C, 53.21; H, 3.19; N, 8.86%. ^1H NMR: 6.39 (d, 2H); 7.02 (t, 2H); 7.14 (t, 2H); 7.22 (t, 2H); 7.87 (d, 2H); 7.98 (d, 2H); 8.00 (d, 2H); 8.07 (dd, 2H); 8.29 (d, 2H); 8.36 (d, 2H); 8.79 (dd, 2H). IR: 839 cm^{-1} (s, PF_6^-); 1689 cm^{-1} (s, C=O).

3.3. X-ray crystallographic study of $[\text{Rh}(\text{phpy-}\kappa^2\text{N}, \text{C}^{2'})_2(\text{phen-dione})]\text{PF}_6 \cdot \text{CH}_3\text{CN}$

Orange crystals of $[\text{Rh}(\text{phpy-}\kappa^2\text{N}, \text{C}^{2'})_2(\text{phen-dione})]\text{PF}_6 \cdot \text{CH}_3\text{CN}$ were grown by ether diffusion into an acetonitrile solution of the complex. Single-crystal X-ray diffraction measurement were carried out on a STOE IPDS II two-circle diffractometer using graphite-monochromated Mo $\text{K}\alpha$ ($\lambda = 0.71073$ Å) radiation at 298(2) K. Cell parameters were determined by the least-squares calculation with θ angle ranging from 2.52° to 26.81°. A numerical absorption correction was applied to the data with the help of the programs X-RED and X-SHAPE [32,33]. A total of 20801 independent reflections were collected, giving 7097 observed reflections with $I > 2\sigma(I)$. The structure was solved by direct method [34] and refined on F^2 by full-matrix least-square using the X-STEP32 program package [35] giving a final $R_1 = 0.0349$, $wR_2 = 0.0869$. The largest

Table 1
Crystallographic data and structure refinement summary for $[\text{Rh}(\text{phpy-}\kappa^2\text{N}, \text{C}^{2'})_2(\text{phen-dione})]\text{PF}_6 \cdot \text{CH}_3\text{CN}$

Empirical formula	$\text{C}_{36}\text{H}_{25}\text{F}_6\text{N}_5\text{O}_2\text{P}_1\text{Rh}_1$
Formula weight	807.49
Space group	Orthorhombic
Crystal system	$\text{Pna}21$
<i>Unit cell dimensions</i>	
a (Å)	28.3692(18)
b (Å)	8.4364(6)
c (Å)	14.0292(11)
β (°)	90
Volume (Å ³)	3357.7(4)
Z	4
D_{calc} (g/cm ³)	1.597
θ -Range for data collection (°)	2.52–26.81
Absorption coefficient (mm ⁻¹)	0.632
Crystal size (mm)	0.25 \times 0.1 \times 0.08
Range of h, k, l	–30/35, –10/10, –17/17
Reflections collected/unique	20,801/7097 [$R_{\text{int}} = 0.0265$]
Goodness-of-fit on F^2	1.063
Parameters	472
R and R_w	0.0349, 0.0869

Table 2
Selected bond lengths (Å) and bond angles (°) for
[Rh(phpy-κ²N,C^{2'})₂(phen-dione)]PF₆ · CH₃CN

Bond lengths			
Rh–N(1)	2.048(3)	Rh–N(4)	2.186(3)
Rh–N(2)	2.040(3)	Rh–C(1)	1.998(4)
Rh–N(3)	2.183(3)	Rh–C(12)	1.998(4)
Bond angles			
C(1)–Rh–N(2)	93.86(15)	N(1)–Rh–N(4)	83.51(11)
C(12)–Rh–N(2)	81.09(16)	N(3)–Rh–N(4)	76.13(10)
C(1)–Rh–N(1)	81.01(16)	C(1)–Rh–N(4)	97.73(13)
C(12)–Rh–N(1)	96.47(15)	C(12)–Rh–N(4)	174.54(12)
N(2)–Rh–N(1)	174.43(12)	C(1)–Rh–N(3)	173.74(13)
N(2)–Rh–N(3)	86.05(11)	C(12)–Rh–N(3)	98.52(12)
N(2)–Rh–N(4)	99.40(12)	C(1)–Rh–C(12)	87.64(15)
N(1)–Rh–N(3)	99.29(11)		

peak and hole on the final difference-Fourier map were 0.401 and $-0.288 \text{ e}/\text{Å}^{-3}$, respectively.

Further details of the structural analyses are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

4. Supplementary material

CCDC 632181 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgment

The authors are grateful to the Isfahan University of Technology (IUT) and USB for financial support.

References

- [1] (a) J.L. Kisko, J.K. Barton, *Inorg. Chem.* 39 (2000) 4942; (b) D. Bruce, M.M. Richter, *Anal. Chem.* 74 (2002) 1340; (c) C. Adachi, M.A. Baldo, S.R. Forrest, M.E. Thompson, *Appl. Phys. Lett.* 77 (2000) 904; (d) C.-L. Lee, K.B. Lee, J.-J. Kim, *Appl. Phys. Lett.* 77 (2000) 2280; (e) K. Dedeian, P.I. Djurovich, F.O. Garces, G. Carlson, R.J. Watts, *Inorg. Chem.* 30 (1991) 1685.
- [2] (a) M.C. DeRosa, P.J. Mosher, G.P.A. Yap, K.-S. Focsaneanu, R.J. Crutchley, C.E.B. Evans, *Inorg. Chem.* 42 (2003) 4864; (b) C.A. Craig, R.J. Watts, *Inorg. Chem.* 28 (1989) 309; (c) F.O. Garces, K.A. King, R.J. Watts, *Inorg. Chem.* 27 (1988) 3464; (d) M. Brissard, M. Gruselle, B. Malézieux, R. Thouvenot, C. Guyard-Duhayon, O. Convert, *Eur. J. Inorg. Chem.* (2001) 1745; (e) F. Barigelletti, B. Ventura, J.P. Collin, R. Kayhanian, P. Garvina, J.P. Sauvage, *Eur. J. Inorg. Chem.* (2000) 113; (f) M.A. Bennett, A.M. Clark, M. Contel, C.E.F. Rickard, W.R. Roper, L.J. Wright, *J. Organomet. Chem.* 601 (2000) 299; (g) A.M. Clark, C.E.F. Rickard, W.R. Roper, L. Wright, *J. Organomet.* 18 (1999) 2813.
- [3] (a) Y. Guari, S. Sabo-Etienne, B. Chaudret, *J. Am. Chem. Soc.* 120 (1998) 4228; (b) C. Coudret, S. Fraysse, J.-P. Launay, *Chem. Commun.* (1998) 663; (c) W.P. Mul, C.J. Elsevier, M.A. Vuurman, W.J.J. Smeets, A.L. Spek, J.L. De Boer, *J. Organomet. Chem.* 532 (1997) 89; (d) J.-P. Collin, R. Kayhanian, J.-P. Sauvage, G. Calogero, F. Barigelletti, A. DeCian, J. Fischer, *Chem. Commun.* (1997) 775; (e) H. Aneetha, C.R.K. Rao, K.M. Rao, P.S. Zacharias, X. Feng, T.C.W. Mak, B. Srinivas, M.Y. Chiang, *J. Chem. Soc., Dalton Trans.* (1997) 1697.
- [4] (a) S.A. Ionkin, W.J. Marshall, C. Roe, Y. Wang, *J. Chem. Soc., Dalton Trans.* (2006) 4942; (b) J.L. Pratihari, N. Maiti, S. Chattopadhyay, *Inorg. Chem.* 44 (2005) 6111; (c) P.J. Steel, *J. Organomet. Chem.* 408 (1991) 395; (d) L. Ghizdavu, O. Lentzen, S. Schumm, A. Brodkorb, C. Moucheron, A. Kirsch-De Mesmaeker, *Inorg. Chem.* 42 (2003) 1935; (e) S. Sprouse, K.A. King, P.J. Spellane, R.J. Watts, *J. Am. Chem. Soc.* 106 (1984) 6647; (f) Y. Ohsawa, S. Sprouse, K.A. King, M.K. DeArmond, K.W. Hanck, R.J. Watts, *J. Phys. Chem.* 91 (1987) 1047; (g) F.O. Garces, K.A. King, R.J. Watts, *Inorg. Chem.* 27 (1988) 3464; (h) C. Arz, P.S. Pregosin, C. Anklin, *Magn. Reson. Chem.* 25 (1987) 158; (i) D. Sandrini, M. Maestri, M. Ciano, U. Maeder, A. von Zelewsky, *Helv. Chim. Acta* 73 (1990) 1306.
- [5] (a) P.H. Revoco, J.H. Medley, A.R. Garber, N.S. Bhacca, J. Selbin, *Inorg. Chem.* 24 (1985) 1096; (b) E.C. Constable, J.M. Holmes, *J. Organomet. Chem.* 301 (1986) 203; (c) M.G. Colombo, H.U. Gudel, *Inorg. Chem.* 32 (1993) 3081.
- [6] H. Hadadzadeh, M.C. DeRosa, G.P.A. Yap, A.R. Rezvani, R.J. Crutchley, *Inorg. Chem.* 41 (2002) 6521.
- [7] (a) J.M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, New York, 1995; (b) V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* 96 (1996) 759; (c) J.W. Steed, J.L. Atwood, *Supramolecular Chemistry*, Wiley, Chichester, 2000; (d) A. Rezvani, H.S. Bazzi, B. Chen, F. Rakotondradany, H.F. Sleiman, *Inorg. Chem.* 43 (2004) 5112; (e) K. Larsson, L. Öhrström, *Inorg. Chim. Acta* 357 (2004) 657; (f) K. Binnemans, P. Lenaerts, K. Driesen, C. Görrler-Walrand, *J. Mater. Chem.* 14 (2004) 191; (g) P. Lenaerts, A. Storms, J. Mullens, J. D'Haen, C. Görrler-Walrand, K. Binnemans, K. Driesen, *Chem. Mater.* 17 (2005) 5194.
- [8] C.A. Goss, H.D. Abruna, *Inorg. Chem.* 24 (1985) 4263.
- [9] H. Hadadzadeh, M.M. Olmstead, A.R. Rezvani, N. Safari, H. Saravani, *Inorg. Chim. Acta* 359 (2006) 2154.
- [10] H. Saravani, A.R. Rezvani, G. Mansouri, A.R. Salehi Rad, H.R. Khavasi, H. Hadadzadeh, *Inorg. Chim. Acta* 360 (2007) 2829.
- [11] M. Yamada, Y. Tanaka, Y. Yoshimoto, *Bull. Chem. Soc. Jpn.* 65 (1992) 1006.
- [12] F. Calderazzo, G. Pampaloni, V. Passarelli, *Inorg. Chim. Acta* 330 (2002) 136.
- [13] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part II: Application in Coordination, Organometallic and Bioinorganic Chemistry*, fifth ed., Wiley-Interscience, New York, 1997.
- [14] H. Hadadzadeh, A.R. Rezvani, F. Belanger-Gariepy, *J. Mol. Struct.* 740 (2005) 165.
- [15] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, second ed., Elsevier, Amsterdam, 1984.
- [16] M.B. Gillian, J.E. Fergusson, *Aust. J. Chem.* 24 (1971) 275.
- [17] A.R. Rezvani, R.J. Crutchley, *Inorg. Chem.* 33 (1994) 170.
- [18] B.P. Sallivan, D.J. Salmon, T.J. Meyer, *Inorg. Chem.* 17 (1978) 3334.
- [19] A.R. Rezvani, H. Hadadzadeh, B. Patrick, *Inorg. Chim. Acta* 336 (2002) 125.

- [20] M.G. Colombo, T.C. Brunold, T. Riedener, H.U. Güdel, M. Fortsch, H.B. Bürgi, *Inorg. Chem.* 33 (1994) 545.
- [21] A. Zilian, U. Maeder, A. von Zelewsky, H.U. Güdel, *J. Am. Chem. Soc.* 111 (1989) 3855.
- [22] U. Mader, A. von Zelewsky, H. Stoeckli-Evans, *Helv. Chim. Acta* 75 (1992) 1320.
- [23] U. Mader, T. Jenny, A. von Zelewsky, *Helv. Chim. Acta* 69 (1986) 1085.
- [24] J.H. Van Dimen, J.G. Haasnoot, R. Hage, J. Reedijk, J.G. Vos, R. Wang, *Inorg. Chem.* 30 (1991) 4038.
- [25] K. Kano, B. Uno, *Anal. Chem.* 65 (1993) 1088.
- [26] Y. Yamada, H. Sakurai, Y. Miyashita, K. Fujisawa, K. Okamoto, *Polyhedron* 21 (2002) 2143.
- [27] S. Berger, J. Fiedler, R. Reinhardt, W. Kaim, *Inorg. Chem.* 43 (2004) 1530.
- [28] D. Sandrini, M. Maestri, V. Balezani, V. Maeder, A. von Zelewsky, *Inorg. Chem.* 27 (1988) 2640.
- [29] P. Paul, B. Tyagi, A.K. Bilakhiya, M.M. Bhadbhade, E. Suresh, G. Ramachandraiah, *Inorg. Chem.* 37 (1998) 5733.
- [30] S.E. Ronco, D.W. Thompson, S.L. Gahan, J.D. Petersen, *Inorg. Chem.* 37 (1998) 2020.
- [31] T. Gennett, D.F. Milner, M.J. Wearer, *J. Phys. Chem.* 89 (1985) 2787.
- [32] X-RED32 Version 1.28b, Program for Data Reduction and Absorption Correction, Stoe & Cie GmbH, Darmstadt, Germany, 2005.
- [33] X-SHAPE Version 2.05, Program for Crystal Optimization for Numerical, Stoe & Cie GmbH, Darmstadt, Germany, 2004.
- [34] G.M. Sheldrick, SHELXS-97 and SHELXL-97, Fortran Programs for Crystal Structure Solution and Refinement, University of Gottingen, 1997.
- [35] X-STEP32, Version 1.07b, X-ray Structure Evaluation Package, Stoe & Cie GmbH, Darmstadt, Germany, 2000.