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A comparative study on structures and theoretical models of Rh azido complexes

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Abstract

The syntheses of PF_6^- salt of six-coordinate Rh(III) azido complexes containing polypyridyl ligands have been accomplished by treatment of the corresponding Rh(III) chloride with NaN_3 in $EtOH-H_2O$ followed by the addition of NH_4PF_6. The complexes have been characterized by UV–vis, FTIR, ^1H and ^{14}N-NMR spectroscopy along with elemental analysis. The X-ray crystal structures of compounds $[Rh(tpy)(phen)(N_3)](PF_6)_2$ ($\mathbf{1}\cdot(PF_6)_2$, tpy: 2,2′:6′,2″-terpyridine, phen: 1,10-phenanthroline) and $[Rh(tpy)(bpy)(N_3)](PF_6)_2$ ($\mathbf{2}\cdot(PF_6)_2$, bpy: 2,2′-bipyridine) confirm that a rhodium atom is six-coordinate and the tpy and bpy or phen ligands are orthogonal and the $Rh-N_3$ distances are 2.038(7) and 2.048(6) Å, respectively. The two N–N distances for the coordinated azide in complex $\mathbf{1}\cdot(PF_6)_2$ are identical with distances of 1.17 (1) and 1.17 (1) Å. However, the two N–N distances for the azido group in the complex **2** may or may not be inequivalent with 1.170(8) and 1.15(1) Å. The bond angles formed by the azide group, Rh, and the axially-positioned nitrogen atom are 172.1(3) and 173.5(8)°. In order to answer the question as to whether the two N–N distances in **2** would be expected to be different, calculations were carried out at HF/LANL2DZ and HF/SDD levels of theory. The results indeed predict the N–N distances in **2** to be different. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium; Azides; HF/LANL2DZ; HF/SDD calculations

1. Introduction

The coordination chemistry of complexes containing nitrogen ligands is an emerging field with the introduction of the six-electron reduction of nitrite to ammonia [1]. An extensive study of the activation of the dinitrogen molecule at metal sites has been reported [2]. In all cases, a key intermediate suggests the formation of the complex containing the nitrido ligand, which can be obtained from thermal fragmentation or photolytic cleavage of covalently bound azide complex [3].

In the preceding study [4], the synthesis and characterization of ruthenium azido and diazido complexes was presented. The objective of this report is to reveal some of the important synthetic and structural details of stable Rh(III) azido complexes, $[Rh(tpy)(phen)(N_3)](PF_6)_2$ ($\mathbf{1}\cdot(PF_6)_2$) and $[Rh(tpy)(bpy)(N_3)](PF_6)_2$ ($\mathbf{2}\cdot(PF_6)_2$) (tpy: 2,2′:6′,2″-terpyridine; phen: 1,10-phenanthroline; bpy: 2,2′-bipyridine). We also report results from quantum-chemical calculations of their theoretical models and compare the results with the experimentally obtained structures.

2. Results and discussion

The synthesis of six-coordinate rhodium complexes has been reported by many researchers [6,7]. The syntheses reported here represent an alternative procedure for obtaining similar complexes. The new rhodium azido complexes of the phosphate salts **1** and **2** were prepared by the reaction of the corresponding Rh–Cl

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complex with 2.5 molar equivalent of NaN_3 in ethanol–water solution, which resulted in the desired product with high yield (Eq. 1).

$$[Rh(tpy)(L)(Cl)](PF_6)_2 + NaN_3 \underset{reflux}{\overset{EtOH:H_2O=2:1}{\rightarrow}} [Rh(tpy)(L)(N_3)](PF_6)_2 + NaCl \quad (L = phen,\ bpy) \qquad (1)$$

The rhodium azido complexes were fully characterized using elemental analysis and spectroscopic data. The visible spectra for the complexes under investigation were measured in acetonitrile. The broad MLCT band at $\lambda_{max} = 550$ nm was observed in the UV–vis spectrum.

Transition metal azido complexes exhibit an intense infrared band around 2000 cm^{-1} corresponding to the asymmetric stretching. An intense and characteristic absorption peak for the asymmetric azide stretching mode at 2030 cm^{-1} was observed in the FTIR spectrum. The Raman spectra of the azide complexes display the characteristic symmetric azide stretching mode as a very strong peak at 1330 cm^{-1}. A moderately strong peak was observed at 3088 cm^{-1} for the aromatic C–H stretching modes for complex **1**, and at 3098 cm^{-1} for complex **2**. The signals in the region 1460–1600 cm^{-1} are assigned to the C–C stretching mode of the aromatic phenyl rings and the tpy ligand.

2.1. Crystal structures

We were able to obtain crystals of Rh–N_3 complexes suitable for X-ray diffraction and to solve the crystal structures of the phosphate salts of complexes **1** and **2**. The perspective views of each cation with the numbering scheme of the atoms are shown in Figs. 1 and 2. Details of the crystallographic data collection are given in Table 1. Selected bond lengths and angles are presented in Table 2.

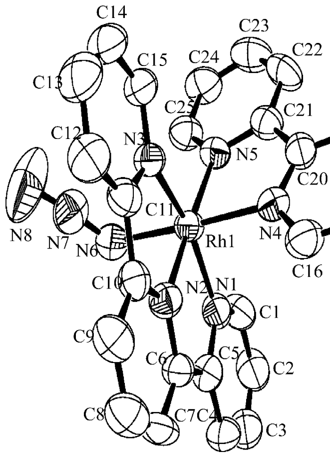

Fig. 1. The molecular structure of compound **1**. Displacement ellipsoids are shown at the 50% probability level. H atoms and PF_6^- anions have been omitted for clarity.

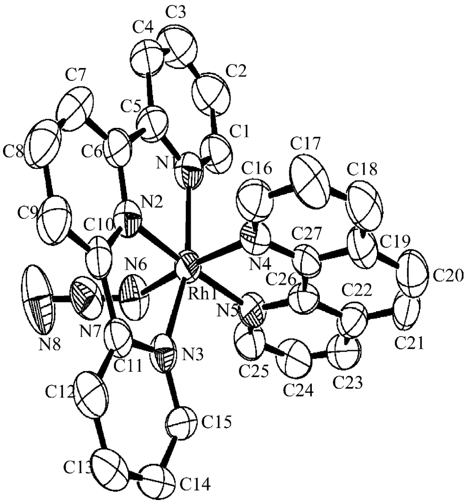

Fig. 2. The molecular structure of compound **2**. Displacement ellipsoids are shown at the 50% probability level. H atoms and PF_6^- anions have been omitted for clarity.

Crystals of complex $\mathbf{1}\cdot(PF_6)_2$ were obtained by the diffusion method using CH_3CN–ether. Complex $\mathbf{1}\cdot(PF_6)_2$ crystallizes in the space group $P2_1/n$. The rhodium atom is six-coordinate with three nitrogen atoms [N1, N2, and N3] of the tpy ligand and one nitrogen atom [N5] of the phen ligand in equatorial positions and the remaining nitrogen atom [N4] of the phen ligand and the azido group in axial positions. The bond angles about the metal center deviate somewhat from 90 and 180° largely due to the restricted bite angle of the tpy and phen ligands, resulting in a distorted octahedral environment. The crystal structure shows that the tpy and phen rings are orthogonal.

The interatomic Rh–N_3 distance in **1** is 2.038 Å and the azido group is symmetric with identical N–N distances (1.172 Å). The closely related complex $[Rh(tpy)(PPh_3)_2(N_3)]^+$ displays a Ru–N_3 bond length of 2.132(5) Å and an average N–N distance of 1.16 Å [4a], which suggests a much stronger bond for the Rh–N_3 molecule. The azido group in complex **1** is almost linear *trans* configuration with an N–N–N bond angle of 175.7(9)°. The bond angle N_3–Rh–N4 (phen) is 172.1(3)°, and the N4–Rh–N5 angle of the phen ligand is 80.8(2)°. It is also of interest that the N1–Rh–N3 angle (tpy) is ca. 14° smaller than N_3–Rh–N4 in the equatorial plane.

Complex $\mathbf{2}\cdot(PF_6)_2$ in which the phen ligand in $[Rh(tpy)(phen)(N_3)]^{2+}$ is replaced by the bpy ligand was prepared by the reaction of $[Rh(tpy)(bpy)(Cl)](PF_6)_2$ with NaN_3 in ethanol–water followed by precipitation with NH_4PF_6. The structure shown in Fig. 2 is quite similar to that of $[Rh(tpy)(phen)(N_3)]^{2+}$. Compound **2** crystallizes in the space group $P\bar{1}$ and the crystal structure shows that the tpy and bpy ligands are orthogonal. The rhodium atom of the complex is in the center of a distorted octahedron with three nitrogen

Table 1
Details of X-ray data collection and refinement for $[Rh(tpy)(L)(N_3)](PF_6)_2$

	$[Rh(tpy)(phen)(N_3)](PF_6)_2 \cdot (CH_3CN)_2$	$[Rh(tpy)(bpy)(N_3)](PF_6)_2 \cdot CH_3CN$
Chemical formula	$C_{29}H_{22}F_{12}N_9P_2Rh$	$C_{29}H_{25}F_{12}N_{10}P_2Rh$
Formula mass (amu)	889.40	906.43
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	22.212(5)	12.394(6)
b (Å)	13.528(3)	2.667(5)
c (Å)	11.265(2)	12.843(4)
α (°)	90	96.49(3)
β (°)	97.99(17)	113.67(3)
γ (°)	90	100.28(3)
V (Å^3)	3352(1)	1778(1)
Z	2	4
T (K)	130(1)	120(1)
Radiation	Graphite monochromated Mo–K$_\alpha$ ($\lambda = 0.71069$ Å)	
Linear absorption coefficient (cm^{-1})	7.10	6.72
D_{calc} (g cm^{-3})	1.762	1.693
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
Scan with (°)	$0.95 + 0.35 \tan \theta$	$1.0 + 0.35 \tan \theta$
2θ Limits (°)	$3.0 \leq 2\theta \leq 50.0°$	$3.0 \leq 2\theta \leq 48.0°$
Number of unique data ($F_o^2 > 0$)	5028	5147
Number of unique data ($F_o^2 > 2\sigma(F_o^2)$)	3757	4124
wR_2 ($F_o^2 > 0$)	0.1592	0.1250
R (on F_o for $F_o^2 > 2\sigma(F_o^2)$)	0.0642	0.0575
Goodness of fit on F^2	1.049	1.066

Table 2
Selected bond distances (Å) and angles (°) for $[Rh(tpy)(L)(N_3)](PF_6)_2$

$[Rh(tpy)(phen)(N_3)](PF_6)_2$		$[Rh(tpy)(bpy)(N_3)](PF_6)_2$	
Bond distances			
Rh–N1	2.030(6)	Rh–N1	2.031(5)
Rh–N2	1.944(6)	Rh–N2	1.949(5)
Rh–N3	2.036(6)	Rh–N3	2.037(5)
Rh–N4	2.055(6)	Rh–N4	2.043(5)
Rh–N5	2.057(6)	Rh–N5	2.042(5)
Rh–N6	2.038(7)	Rh–N6	2.048(6)
N6–N7	1.172(10)	N6–N7	1.170(8)
N7–N8	1.172(11)	N7–N8	1.146(10)
Bond angles			
N1–Rh–N2	80.7(3)	N1–Rh–N2	80.9(2)
N1–Rh–N3	161.2(2)	N1–Rh–N3	161.5(2)
N1–Rh–N4	91.2(2)	N1–Rh–N4	93.1(2)
N2–Rh–N3	80.7(2)	N1–Rh–N5	80.6(2)
N2–Rh–N4	94.7(2)	N1–Rh–N	97.4(2)
N3–Rh–N4	93.2(2)	N2–Rh–N3	90.5(2)
N1–Rh–N5	98.6(2)	N2–Rh–N4	100.1(2)
N2–Rh–N5	175.5(2)	N2–Rh–N5	176.8(2)
N3–Rh–N5	100.1(2)	N3–Rh–N5	98.5(2)
N4–Rh–N5	80.8(2)	N4–Rh–N5	79.6(2)
N1–Rh–N6	89.0(3)	N1–Rh–N6	86.0(2)
N2–Rh–N6	93.2(3)	N2–Rh–N6	88.8(2)
N3–Rh–N6	89.1(2)	N3–Rh–N6	92.4(2)
N4–Rh–N6	172.1(3)	N4–Rh–N6	173.5(8)
N5–Rh–N6	91.3(3)	N5–Rh–N6	94.2(8)
Rh–N6–N7	120.4(6)	Rh–N6–N7	116.0(5)
N6–N7–N8	175.7(9)	N6–N7–N8	174.8(9)

atoms of the tpy ligand and the nitrogen atom [N5] of the bpy ligand in the same plane. The remaining nitrogen atom [N4] of the bpy ligand and the azido ligand are positioned axially.

The $Rh–N_3$ distance is 2.048(6) Å and the bond distance between the rhodium atom and the apical nitrogen atom N4 of the bpy ligand is 2.043(5) Å, which is about 0.012 Å shorter than Rh–N4 of the phen ligand. The angle $N_3–Rh–N4$ is 173.5(8)°, and the N1–Rh–N2 angle [80.9(2)°] is similar to N2–Rh–N3 of the tpy ring [80.6(2)°] in the pyridyl rings of the tpy ligand.

The azido group in complex **2** is almost linear and has inequivalent bond lengths with δN–N varying 0.024 Å (δN–N is the difference between the N–N distances in an azido group). The longer N–N distance occurs between the central nitrogen and the nitrogen coordinated to the metal ion. This difference is not unusual and still reflects a resonance form of a covalently bound azide as expected. The structures of the azido group in the title complexes are very similar to those found for *mer*-$[Cr(py)_3(N_3)_3]$ ([7]), *mer*-[Co(3,4-dimethylpy)$_3$(N$_3$)$_3$] ([8]), *cis*- and *trans*-$[Fe(cyclam)(N_3)_2][ClO_4]$ ([3b]), and $[Cu(trpn)(N_3)][ClO_4]$ (trpn: 3,3′,3″-triaminopropylamine) [9].

2.2. Multinuclear NMR studies

The characterization of the complexes was further enhanced by the use of ^{1}H- and ^{14}N-NMR spectroscopy. There is no evidence for paramagnetic broadening in the ^{1}H-NMR spectra of the complexes prepared. In the ^{1}H-NMR spectra of the $Rh–N_3$ complexes, we observed a low-field doublet peak at 10.32 and 9.89 ppm for complexes **1** and **2**, respectively. The peaks correspond to one of the two neighboring protons such as protons 2 and 9 of the phen ligand (C25–H in Fig. 1) or protons 6 and 6′ of the bpy ligand (C25–H in Fig. 2) to the azido ligand. Since one of the two protons of the bidentate ligand positioned next to the azido group lies outside of the aromatic ring current of the polypyridyl ligands, its chemical shift moves downfield [6a,10]. The sensitivity of the chemical shift towards the nature of the different ligands X (X = Cl, N_3, DMSO, NO_2 etc.) provides a diagnostic tool for detecting ligand change in $[LM–X]^{+/2+}$ complexes (M: Ru, Os, Rh; L: py and its derivatives) complexes [6a,6b,11].

From a comparison with ^{14}N-NMR data previously reported for coordinated azides [12,13], three well resolved resonances to Na, Nb, and Nc (connectivity:

Rh–Na–Nb–Nc) in the ^{14}N-NMR spectrum of the complexes have been assigned. The resonance at −336, −134, and −250 ppm each correspond to nitrogen atom of the azide group coordinated to Ru in the complexes $[Ru(tpy)(PPh_3)_2(N_3)]^+$ and $[Ru(tpy)(PPh_3)(N_3)_2]$ ([4]). The ^{14}N-NMR spectrum (Fig. 3) shows four, well resolved resonances, which can be assigned to the three chemically inequivalent nitrogen atoms of the azide group covalently bound to the Rh metal ion, and the N atoms of the tpy and phen/bpy ligands in the complex. The nitrogen atoms in the polypyridyl ligands could be observed around $\delta = -163$ ppm as a broad peak. The N_b atom at $\delta = -131$ ppm is observed as a sharp signal, whereas N_c atom around $\delta = -215$ ppm is observed as a broad resonance, and the peak corresponding to the N_a atom is observed at around $\delta = -328$ ppm as a much broader signal. In this context it should be noted that the relative line-widths in the ^{14}N-NMR spectra are related to the local symmetry around the nitrogen atom with highly symmetric N atoms, the more symmetric N atoms, and the very asymmetric N atoms [14–16].

2.3. *Ab initio calculations*

All ab initio (HF) calculations were carried out using the program package GAUSSIAN-98 [17] with the input files (*z* matrices) being generated using the program package HYPERCHEM [18]. All structures were fully optimized without symmetry constraints and the vibrational frequencies computed on the optimized structures.

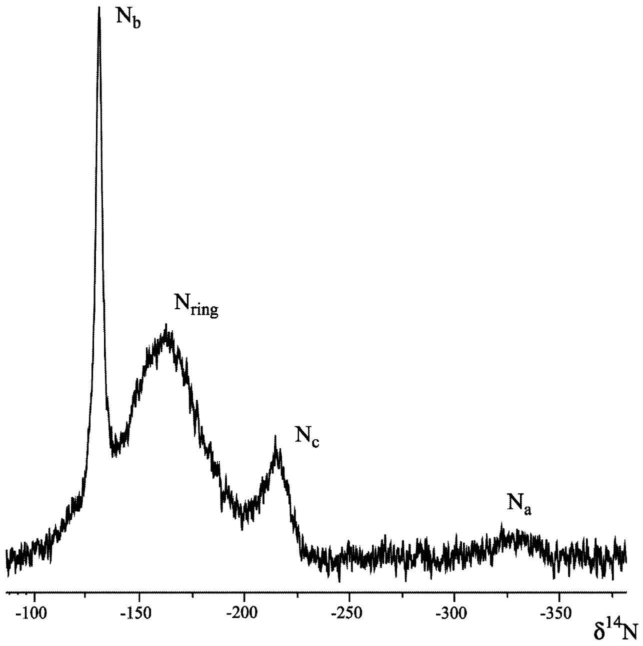

Fig. 3. ^{14}N-NMR spectrum of **1**, $[(tpy)(phen)Rh–Na–Nb–Nc]^{2+}$ ((tpy)(phen) = L) in $(CD_3)_2CO$ in the region between 0 and −500 ppm.

For hydrogen and all first row elements either (i) a standard D95 Dunning/Huzinaga full double zeta [19] basis set was applied and Rh was treated with a quasi-relativistic LANL2DZ pseudo-potential [20–22] or (ii) for hydrogen and all first row elements a standard D95V Dunning/Huzinaga valence double zeta [19] basis set was applied and Rh was treated with a quasi-relativistic Stuttgart/Dresden (SDD) pseudo-potential [23–25].

The results of the calculations are summarized in Table 3. At HF level of theory with both pseudo-potentials applied, the N–N distances in **2** are predicted to be significantly different with 1.30 and 1.16 Å (LANL2DZ) and 1.32 and 1.16 Å (SDD), respectively.

3. Experimental

3.1. *Materials*

$RhCl_3 \cdot H_2O$ was purchased from Hesung Engelhard Co. 2,2′:6′,2″-terpyridine (tpy), 2,2′-bipyridine (bpy), and NH_4PF_6 were obtained from Aldrich Chemical Co. and were used as received. 1,10-phenanthroline (phen) was purchased from Junsei Co. All solvents were purified before use [26].

3.2. *Instrumentation*

Routine UV–vis spectra were recorded on a Hewlett–Packard 8452A Diode Array spectrophotometer using HP 89532A general scanning software. FTIR spectra were obtained on a Bomen MB 100 FTIR spectrophotometer either as KBr discs or in solution cells using NaCl plates. Raman spectra were recorded on a Perkin–Elmer system R 2000 at 25 °C. All ^{1}H-NMR data were obtained on a Varian Model Gemini 200 FTNMR spectrometer using deuterated solvent. The chemical shift parameters are presented in parts per million (ppm) downfield from internal tetramethylsilane (TMS) reference. The ^{14}N-NMR spectra were recorded on a JEOL

Table 3
Structure, energy, and vibrational frequencies of $[(tpy)(bpy)Rh–N_3]^{2+}$ computed at STO-3G levels of theory

	Experimental	HF/LAN2DZ	HF/SDD
Symmetry	$P\bar{1}$	C_1	C_1
$-E$ (au)		1484.574301	1485.728399
NIMAG		0	0
zpe (kcal mol^{-1})		287.8	287.2
d(Rh–N1) (Å)	2.048(6)	1.995	1.999
d(N1–N2) (Å)	1.170(8)	1.304	1.321
d(N2–N3) (Å)	1.146(10)	1.163	1.161
∠ (Rh–N1–N2) (°)	116.0(5)	115.8	112.0
∠ (N1–N2–N3) (°)	174.8(9)	170.4	173.4
ν_1 (cm^{-1})		22.3	23.1

EX 400 Delta-NMR spectrometer referenced to nitromethane. Elemental analyses were performed by the analytical laboratory at the Basic Science Institute of Korea (BSIK) or by the Organic Chemistry Reactions Center (OCRC).

3.3. Preparation

[Rh(tpy)(phen)(Cl)]$(PF_6)_2$ and [Rh(tpy)(phen)(Cl)]$(PF_6)_2$ were prepared according to the previously reported in the literature [5].

3.3.1. Compound **1**·$(PF_6)_2$

[Rh(tpy)(phen)(Cl)]$(PF_6)_2$ (1.80 g, 2.19 mmol) and NaN_3 (0.36 g, 5.47 mmol) were dissolved in 30 ml of absolute ethanol and 15 ml of water and were heated under reflux for 2 h. To the yellow solution, an excess of a saturated NH_4PF_6 solution was added, which resulted in the formation of a pale yellow precipitate. After the solution was filtered, the solid was washed with ethyl ether three times and vacuum-dried. Yield: 81%.

Elemental analysis (Carlo Erba, EA 1180), $C_{27}H_{19}F_{12}N_8P_2Rh$, Anal. Calc.: C, 38.23; H, 2.26; N, 13.21. Found: C, 38.27; H, 2.37; N 13.22%.

^{1}H-NMR (200 MHz, $(CD_3)_2CO$, ppm): 10.32 (dd, 1H, C25–H), 9.34 (t, 2H), 9.17 (d, 1H), 8.99 (t, 3H), 8.65 (m, 2H), 8.62 (d, 1H), 8.56 (d, 2H), 8.49 (m, 3H), 8.16 (t, 1H), 8.08 (t, 2H), 7.97 (m, 2H), 7.83 (m, 1H).

^{14}N-NMR (29 MHz, $(CD_3)_2CO$, ppm): −131 (120), −167(1100), −217(430), −337(630).

FTIR (KBr, cm^{-1}): 3102 w, 2030 vs, 1605 w, 1560 w, 1522 w, 1478 w, 1452 w, 1434 w, 1316 w, 1281 w, 1031 w, 839 vs, 776 m, 717 w, 558 s.

Raman (1064 nm, 200 mW, 5000 scans, cm^{-1}): 3088 m, 2036 w, 1606 vs, 1563 s, 1501 m, 1479 m, 1458 vs, 1436 m, 1329 vs, 1271 m, 1121 w, 1059 s, 1025 m, 750 m, 681 w, 565 w.

3.3.2. Compound **2**·$(PF_6)_2$

A similar procedure was utilized as was used for the preparation of **1**. Yield: 89%.

Elemental analysis, $C_{29}H_{25}F_{12}N_{10}P_2Rh$, Anal. Calc.: C, 37.47; H, 2.56; N, 14.57. Found: C, 37.67; H, 2.52; N, 14.78%.

^{1}H-NMR (ppm): 9.89 (dd, 1H, C25–H), 8.96 (d, 1H), 8.78(m, 3H), 8.62 (t, 2H), 8.55 (d, 2H), 8.38 (m, 3H), 8.25 (t, 2H), 8.13 (t, 2H), 8.02 (t, 1H), 7.88 (d, 1H), 7.77 (t, 1H), 7.62 (t, 2H).

^{14}N-NMR (ppm): −131 (140), −158(905), −224(440), −318(1300).

FTIR (cm^{-1}): 3094 w, 2030 vs, 1607 w, 1500 w, 1478 w, 1453 w, 1402 w, 1318 w, 1269 w, 1250 w, 1170 w, 1031 w, 839 vs, 776 m, 727 w, 558 s.

Raman (cm^{-1}): 3098 m, 2037 w, 1608 vs, 1566 s, 1503 m, 1480 m, 1436 w, 1330 vs, 1275 m, 1124 w, 1058 s, 1025 m, 769 w, 741 m, 681 w.

3.4. Crystallography

The crystal structures of compounds **1**·$(PF_6)_2$ and **2**·$(PF_6)_2$ were determined by single-crystal X-ray diffraction methods. Preliminary examination and data collection were performed with Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å) on an MXC3 diffractometer (MAC Science). Cell constants and an orientation matrix were determined from the least-squares analysis, using setting angles of 31 reflections in the range of $3.0 \leq 2\theta \leq 50.0°$ for compound **1**·$(PF_6)_2$ and 18 reflections in the range of $3.0 \leq 2\theta \leq 48.0°$ for compound **2**·$(PF_6)_2$. In both compounds, the initial positions for all non-hydrogen atoms were obtained by using direct methods of the SHELXS-86 program [27]. The structures were refined using the SHELXL-97 program [28]. Positional and displacement parameters for non-hydrogen atoms were refined using a full-matrix least-squares refinement procedure. Atomic positions of hydrogen atoms were generated with the riding model technique of SHELXL-97. Crystal data and crystallographic details are presented in Table 1.

3.5. Semi-empirical calculations

All ab initio calculations were performed with the program package HYPERCHEM (version 4.0 and 5.0) at HF/LANL2DZ and HF/SDD level of theory. The model which is within the unrestricted Hartree–Fock formalism is characterized by inclusion of one-center exchange terms as well as an accurate description of integrals involving 3d atomic orbitals.

4. Supporting information available

Tables containing supplementary Figs. 1 and 2, atomic coordinates, isotropic coordinates, isotropic thermal parameters, bond distances and angles, and packing diagram are available for [Rh(tpy)(phen)-(N_3)]$(PF_6)_2$ and [Rh(tpy)(bpy)(N_3)]$(PF_6)_2$.

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