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Synthesis and structural analysis of *cis*-bis(1,10-phenanthroline)dicarbonyl ruthenium(II) 1.72-trifluoromethanesulfonate 0.28-hexafluoridophosphate

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RESEARCH ARTICLE



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ABSTRACT

Ruthenium(II) complexes containing both 1,10-phenanthroline (Phen) and carbonyl (CO) ligands are important molecules for various applications including catalysis. In this work, the molecular structure of $[\text{Ru}(\text{Phen})_2(\text{CO})_2]^{2+}$ was determined via X-ray diffraction analysis for the first time. The complex exhibits substitutional disorder of one of counter-anions in the asymmetric unit, with different occupancies for CF_3SO_3^- (0.72) and PF_6^- (0.28). The ruthenium atom is coordinated in a distorted octahedral environment by two carbonyl carbon atoms and four nitrogen atoms from bis-Phen ligands. The cation displays a *cis* configuration of the carbonyl ligands. Several hydrogen bonds and π - π interactions are present in the crystal. In addition to structural characterization, IR spectral data for the complex is compared with calculated values. These results provide fundamental data for understanding various properties of related ruthenium complexes.

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1. Introduction

1,10-Phenanthroline has been used as a rigid and planar bidentate chelate ligand (Figure 1a). In particular, because of its similarities in structure and properties to 2,2'-bipyridine (Bpy; Figure 1b), numerous catalytic, redox, photochemical, and photophysical properties have been studied in metal complexes containing those ligands [1]. In the *cis*- $[\text{RuL}_2(\text{CO})_2]^{2+}$ (L = Bpy or Phen) complexes shown in Figure 1c, some ligand effects regarding electrochemical CO_2 reductions and reactivities have been compared [2,3]. Thus, the comparison of properties between Bpy-containing complexes and Phen-containing ones is an important area of research. Although the structural analysis of $[\text{Ru}(\text{Bpy})_2(\text{CO})_2]^{2+}$ was reported approximately thirty years ago [4], to the best of our knowledge, no structural determination of $[\text{Ru}(\text{Phen})_2(\text{CO})_2]^{2+}$ has been performed. Therefore, direct structural comparisons between the dyad have not been studied, despite the great interest in these comparisons.

This study reports the single crystal X-ray structural analysis of $[\text{Ru}(\text{Phen})_2(\text{CO})_2]^{2+}$. We compare not only the structural data with previously reported analyses of similar complexes but also the spectroscopic data of the title compound with calculated data derived from computational chemistry.

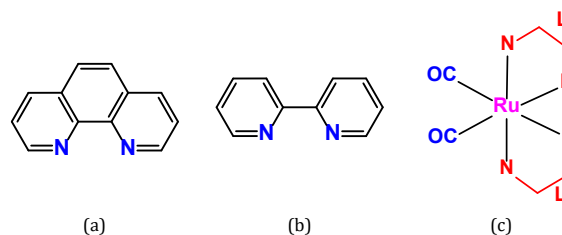


Figure 1. Chemical structures of (a) 1,10-phenanthroline (Phen), (b) 2,2'-bipyridine (Bpy), and (c) *cis*- $[\text{RuL}_2(\text{CO})_2]^{2+}$ (L = Phen or Bpy).

2. Experimental

2.1. Measurements

IR spectra were measured as KBr pellets using a JASCO FT-IR 4100 spectrometer. Electrospray ionization mass spectrometry (ESI-MS) data were obtained using a Bruker Daltonics micrOTOF spectrometer. ^1H NMR spectra were acquired using a JEOL JMN-AL300 spectrometer operating at ^1H frequency of 300 MHz. The formation of the title compound was confirmed by conducting spectroscopic measurements [2].

Table 1. Crystal data and details of the structure refinement for the complex.

Empirical formula	C _{27.72} H _{16.63} F _{6.83} N _{4.07} O _{7.17} P _{0.28} RuS _{1.72}
Formula weight	814.52
Temperature (K)	113(2)
Crystal system	Monoclinic
Space group	<i>P2₁/c</i>
<i>a</i> , (Å)	13.0106(2)
<i>b</i> , (Å)	17.5914(3)
<i>c</i> , (Å)	12.8315(2)
α (°)	90
β (°)	92.9715(7)
γ (°)	90
Volume (Å ³)	2932.85(9)
<i>Z</i>	4
ρ _{calc} (g/cm ³)	1.845
μ (mm ⁻¹)	0.772
F(000)	1620.0
Crystal size (mm ³)	0.150 × 0.150 × 0.100
Radiation	MoKα (λ = 0.71075)
2θ range for data collection (°)	6.272 to 54.968
Index ranges	-16 ≤ <i>h</i> ≤ 16, -22 ≤ <i>k</i> ≤ 22, -16 ≤ <i>l</i> ≤ 16
Reflections collected	30123
Independent reflections	6728 [R _{int} = 0.0181, R _{sigma} = 0.0138]
Data/restraints/parameters	6728/0/471
Goodness-of-fit on F ²	0.997
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0268, wR ₂ = 0.0693
Final R indexes [all data]	R ₁ = 0.0299, wR ₂ = 0.0711
Largest diff. peak/hole (e.Å ⁻³)	0.39/-0.44

Density functional theory (DFT) calculations were performed using the quantum chemical program, Gaussian 16 [5]. The geometries of the complex were fully optimized using restricted DFT methods employing the B3LYP function [6,7], with a 6-31G(d) basis set for the light elements [8,9] and a LanL2DZ basis set [10] for the Ru atom. Vibrational analyses were performed at the same calculation level employed for geometry optimization.

2.2. Synthesis of the complex

All solvents for the synthesis were anhydrous and used without further purification. Ruthenium trichloride was purchased from Furuya Metal Co. Inc. [Ru(CO)₂Cl₂]_{*n*} and *cis*-[Ru(Phen)(CO)₂(OH)₂]₂(CF₃SO₃)₂ were prepared according to previously reported procedures [11,12]. [Ru(Phen)(CO)₂(OH)₂]₂(CF₃SO₃)₂ (39 mg, 0.10 mmol) and Phen (21 mg, 0.10 mmol) were added to ethanol (20 mL). The mixture was refluxed with stirring for 1.5 h. The reaction vessel was cooled to room temperature. The reaction mixture was condensed to 3 mL under reduced pressure and was then cooled to 4 °C and allowed to stand overnight. The addition of diethyl ether (20 mL) to the solution resulted in the formation of a precipitate. The product was collected via filtration, washed with cold water and diethyl ether, and dried in vacuo to produce 41 mg of [Ru(Phen)₂(CO)₂](CF₃SO₃)₂ (50% yield). ESI-MS (CH₃CN, *m/z*): 259.0 ([M]²⁺). ¹H NMR (300 MHz, Acetone-*d*₆, δ, ppm): 10.04 (dd, *J* = 5.1, 1.2 Hz, 2H, Ar-H), 9.31 (dd, *J* = 8.4, 1.2 Hz, 2H, Ar-H), 8.93 (dd, *J* = 8.4, 1.5 Hz, 2H, Ar-H), 8.56-8.49 (m, 4H, Ar-H), 8.43 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.13 (dd, *J* = 5.7, 1.2 Hz, 2H, Ar-H), 7.81 (dd, *J* = 8.1, 5.4 Hz, 2H, Ar-H).

2.3. Crystallography

Single crystals suitable for X-ray diffraction analysis were obtained via vapor diffusion of diethyl ether into an acetone solution of the complex and a small amount of methanolic solution of NH₄PF₆ over the course of a few days. A single crystal of the title compound was analyzed using a Rigaku Saturn70 CCD diffractometer. The crystal was kept at 113 K during the data collection. All calculations were performed using Crystal Structure [13] except for the refinement, which was performed using SHELXL2018/3 [14]. The non-hydrogen atoms, with the exception of PF₆⁻, were anisotropically refined. All hydrogen

atoms bonded to carbon atoms were positioned geometrically and refined as a riding model. The counter-anion sites were refined as being substitutionally disordered between trifluoromethanesulfonate and hexafluoridophosphate, with an occupancy of 0.723(3) for CF₃SO₃⁻ and 0.277(3) for PF₆⁻. Crystallographic data are summarized in Table 1.

3. Results and discussion

3.1. Crystallization and structure

Initially, we prepared the title compound as a hexafluorido phosphate (PF₆) salt, as per a previously reported procedure [2]. Although we tried, we could not obtain any single crystals of the compound suitable for X-ray diffraction experiments. Therefore, we developed the title compound via another route, which involved the reaction of the mono-Phen precursor, *cis*-(OH)₂-[Ru(Phen)(CO)₂(OH)₂](OTf)₂ (OTf = Trifluoromethanesulfonate) [11], with Phen and subsequent isolation as a triflate salt. Various spectroscopic data suggested that the obtained complex is identical to the reported one [2].

Figure 2 shows the molecular structure of the title compound. The Ru(II) ion is six-coordinated by four nitrogen donors of two Phen molecules and two carbon atoms of two CO ligands. As expected, two CO ligands lie in the *cis* position. In the crystal, one of the two triflate ions (OTf⁻) is partially replaced by a PF₆⁻ anion, which is added to promote crystallization. Hence, the total ratio of counterions was confirmed to be OTf⁻:PF₆⁻ = 7:1 in the unit cell. Bond parameters of the primary coordination sphere in this complex cation agree with those of the related [Ru(Bpy)₂(CO)₂]²⁺ and [Ru(Phen)₂(CH₃CN)₂]²⁺ complexes (CSD refcodes: SUKCEG and MUGREL, respectively) [4,15]. Two Ru–CO bond lengths have the same values (1.905(2) and 1.902(2) Å), whereas Ru–N bond lengths *trans* to CO ligands (2.1100(16) and 2.1135(16) Å) are longer than those *trans* to Phen-nitrogens (2.0780(16) and 2.0864(16) Å), because of the *trans* influence of the CO ligands (Table 2). The C–O bond lengths appear to be the same (1.127(2) and 1.126(2) Å), being typical C≡O triple bonds. It is noted that these CO bond lengths are distinctly shorter than those of the isostructural rhenium(I) complex (CSD refcode: RECFAH) [16]. The N1–Ru1–N2 and N3–Ru1–N4 bond angles formed by Phen are less than 90° (79.46(6) and 79.49(6)°), as required by the bite angle of the chelating ligand, Phen.

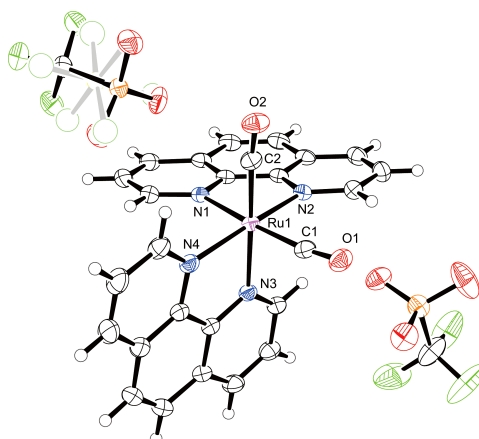
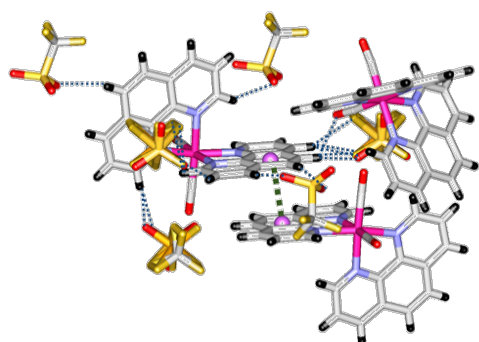
Table 2. Selected experimental and optimized bond parameters (\AA , $^\circ$) of the title complex cation.

Bond lengths	Experimental	Calculated	Bond angles	Experimental	Calculated
Ru1-N1	2.1100(16)	2.158	N1-Ru1-C1	173.82(7)	175.11
Ru1-N2	2.0780(16)	2.135	N3-Ru1-C2	177.16(7)	175.12
Ru1-N3	2.1135(16)	2.158	N2-Ru1-N4	167.98(6)	169.24
Ru1-N4	2.0864(16)	2.135	Ru1-C1-O1	173.36(18)	179.21
Ru1-C1	1.905(2)	1.930	Ru1-C2-O2	174.25(18)	179.24
Ru1-C2	1.902(2)	1.930	C1-Ru1-C2	85.69(8)	91.88
C1-O1	1.127(2)	1.144	N1-Ru1-N2	79.46(6)	78.35
C2-O2	1.126(2)	1.144	N3-Ru1-N4	79.49(6)	78.35

Table 3. Hydrogen-bond geometry (\AA , $^\circ$).

D-H...A	D-H	H...A	D...A	D-H...A
C3-H1...F5 ⁱ	0.95	2.36	3.112(3)	136
C3-H1...F8 ⁱ	0.95	2.46	3.096(6)	124
C4-H2...O8 ⁱ	0.95	2.34	3.188(8)	148
C5-H3...O3 ⁱⁱ	0.95	2.45	3.400(3)	174
C8-H4...O5 ⁱⁱ	0.95	2.51	3.421(3)	161
C9-H5...O1 ⁱⁱ	0.95	2.54	3.014(3)	111
C9-H5...O7 ⁱⁱⁱ	0.95	2.39	3.247(8)	150
C9-H5...F11 ⁱⁱⁱ	0.95	2.40	3.23(2)	145
C12-H6...O7 ⁱⁱⁱ	0.95	2.57	3.373(9)	142
C12-H6...F9 ⁱⁱⁱ	0.95	2.54	3.407(7)	152
C12-H6...F11 ⁱⁱⁱ	0.95	2.38	3.21(2)	145
C15-H9...O8	0.95	2.50	3.114(8)	122
C15-H9...F12	0.95	2.50	3.148(18)	126
C20-H12...O3 ^{iv}	0.95	2.57	3.479(3)	161
C24-H14...F9 ^v	0.95	2.50	3.416(7)	161
C26-H16...O4	0.95	2.50	3.310(3)	143

(i) 1-x, y, 1-z. (ii) -x, -y, 1-z. (iii) -x, y, 1-z. (iv) x, y, -1+z. (v) 1+x, y, z.

**Figure 2.** The structures of the molecular components in the title salt $[\text{Ru}(\text{Phen})_2(\text{CO})_2][\text{CF}_3\text{SO}_3]_{1.72}(\text{PF}_6)_{0.28}$, with atom labels and displacement ellipsoids for non-H atoms drawn at the 50% probability level. Minor components (PF_6^-) are shown as light-colored plots.**Figure 3.** Intermolecular hydrogen bonds (blue) and π - π interactions (green), shown as dashed lines in the crystal packing of the title compound. Ring centroids are shown as colored spheres.

The axial groupings are less than 180° , ranging from $167.98(6)$ to $177.16(7)^\circ$. These bond parameters support a distorted octahedral geometry. The Ru-C-O bond angles are also distorted from a linear system ($173.36(18)$ and $174.25(18)^\circ$). Additionally, the dihedral angle between the COs are lower than 90° ($85.69(8)^\circ$), which is consistent with those

in $[\text{Ru}(\text{Bpy})_2(\text{CO})_2]^{2+}$ ($88.8(4)^\circ$) and $[\text{Re}(\text{Phen})_2(\text{CO})_2]^+$ ($86.9(6)^\circ$) [4,16].

Intermolecular interactions of the title compound are shown in **Figure 3**. Several complicated hydrogen bonds are present between the hydrogen atoms of Phen in the complex cation and the adjacent counterions (**Table 3**).

Table 4. Comparison between the experimental and the DFT-calculated IR peaks for vCO.

Parameters	Experimental ^a	Calculated
$\nu_{\text{as}}(\text{C}\equiv\text{O})$ (cm ⁻¹)	2033	2113
$\nu_{\text{s}}(\text{C}\equiv\text{O})$ (cm ⁻¹)	2093	2164
$I_{\text{s}}/I_{\text{as}}$ ^b	1.08	1.01
θ (°) ^c	87.8	89.8

^a KBr method.^b Relative absorption intensity.^c The value derived from Equation (1).

In addition, π - π stacking (3.512(1) Å) is present between adjacent phenyl rings of Phen. These interactions stabilize the crystal packing.

3.2. Comparison of experimental and calculated data

The optimized structure of the complex cation was calculated using DFT. Table 2 summarizes the selected bond parameters of both the optimized and the observed structures. The calculated and the experimental values are consistent with each other, and the simulation data also suggest the existence of the *trans* influence on the carbonyl group.

Table 4 shows the result of the vibrational analyses for the CO stretching vibration and the observed IR spectral data. Both data indicate two peaks because of the CO stretching mode in cases of *cis* configuration. In mononuclear metal complexes having two CO ligands, the bond angle (θ) between the CO ligands can be calculated from the relative intensity ($I_{\text{s}}/I_{\text{as}}$) of the two IR absorptions using Equation 1 [17]:

$$I_{\text{s}}/I_{\text{as}} = \cotan^2(\theta/2) \quad (1)$$

The calculated bond angle is 87.8° when the intensity ratio of 1.08 is used from the IR spectrum. This value agrees well with the observed data (85.69(8)°) in Table 2. The intensity ratio (1.01) obtained from computational chemistry also contributed to a similar bond angle (89.8°). Both results support the fact that the two CO ligands are coordinated to the ruthenium(II) ion in the *cis* configuration.

4. Conclusion

In summary, this study demonstrated comparison of the spectroscopic data for [Ru(Phen)₂(CO)₂]²⁺ to the values calculated using DFT, as well as the structural characterization of the title compound. Because structural and spectroscopic measurements of the complex provide fundamental data for understanding various properties, this work could contribute to further research in this area. For example, the isostructural Re(I) complex ([Re(Phen)₂(CO)₂]⁺) has been studied for practical use as photosensitizers [16]. This suggests that similar applications are available for the present Ru(II) complex.

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Supporting information

CCDC-2073803 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.

Ethical approval: All ethical guidelines have been adhered.

Sample availability: Samples of the compounds are available from the author.

CRedit authorship contribution statement

Conceptualization: Dai Oyama; Methodology: Tsugiko Takase, Dai Oyama; Validation: Dai Oyama; Formal Analysis: Tsugiko Takase; Investigation: Tsugiko Takase; Data Curation: Dai Oyama; Writing - Original Draft: Tsugiko Takase, Dai Oyama; Writing - Review and Editing: Dai Oyama; Visualization: Tsugiko Takase; Funding acquisition: Dai Oyama; Supervision: Dai Oyama; Project Administration: Dai Oyama.

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