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Novel $[Ru(polypyridine)(CO)_2Cl_2]$ and $[Ru(polypyridine)_2(CO)Cl]^+$-type complexes: Characterizing the effects of introducing azopyridyl ligands by electrochemical, spectroscopic and crystallographic measurements

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ABSTRACT

The reaction of ruthenium carbonyl polymer ($[Ru(CO)_2Cl_2]_n$) with azopyridyl compounds (2,2′-azobispyridine; apy or 2-phenylazopyridine; pap) generated new complexes, $[Ru(azo)(CO)_2Cl_2]$ (azo = apy, pap). $[Ru(apy)(CO)_2Cl_2]$ underwent photodecarbonylation to give a chloro-bridged dimer complex, whereas the corresponding pap complex ($[Ru(pap)(CO)_2Cl_2]$) was not converted to a dimer. The reactions of the chloro-bridged dimer containing the bpy ligand (bpy = 2,2′-bipyridine) with either apy or pap resulted in the formation of mixed polypyridyl complexes, $[Ru(azo)(bpy)(CO)Cl]^+$. The novel complexes containing azo ligands were characterized by various spectroscopic measurements including the determination of X-ray crystallographic structures. Both $[Ru(azo)(CO)_2Cl_2]$ complexes have two CO groups in a *cis* position to each other and two chlorides in a *trans* position. The azo groups are situated *cis* to the CO ligand in $[Ru(azo)(bpy)(CO)Cl]^+$. All complexes have azo N–N bond lengths of 1.26–1.29 Å. The complexes exhibited azo-based two-electron reduction processes in electrochemical measurements. The effects of introducing azopyridyl ligands to the ruthenium carbonyl complexes were examined by ligand-based redox potentials, stretching frequencies and force constants of CO groups and bond parameters around Ru–CO moieties.

1. Introduction

Ruthenium(II) carbonyl complexes with bidentate pyridyl ligands are attractive catalysts for the water–gas shift reaction and for carbon dioxide reduction [1]. Additionally, ruthenium carbonyl complexes incorporating bidentate pyridyl ligands have been investigated as precursors to heteroleptic tris polypyridyl ruthenium complexes of the type $[Ru(L_1)(L_2)(L_3)]^{2+}$ [2]. Currently, 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) and their derivatives have been predominantly used as polypyridyl ligands in this research field. While polypyridyl-based redox reactions play a significant role as electron reservoirs in photo- and electrochemical reductions of carbon dioxide [3,4], it should be possible to use other polypyridyl ligands which possess non-innocent properties. The characteristics of these new potential complexes should be explored. A candidate for the new complex is the azopyridyl derivatives. Azopyridyl compounds are photochemically active [5]. In addition, azopyridyl compounds can undergo one or two-electron transfer reactions because these compounds have a low-lying azo-centered π^* MO [6]. Therefore, the construction of complex systems containing azopyridyl derivatives as ancillary ligands should be very interesting from the viewpoint of redox and structural chemistries. A variety of metal complexes including azopyridyl ligands have been reported [6,7]. We have recently reported specific properties of azopyridyl moieties in ruthenium carbonyl complexes [8,9]. In these reports, we have demonstrated that azopyridyl ligands can control the redox behavior or steric configurations of the complexes. Although metal complexes containing azopyridyl ligands demonstrate a variety of interesting properties compared with typical polypyridines such as bpy or phen, there have been no systematic reports on the effects of introduction of azopyridyl ligands to the ruthenium carbonyl complexes. In this paper, we report the preparation and characterization of mono-bidentate pyridyl complexes ($[Ru(apy)(CO)_2Cl_2]$ and $[Ru(pap)(CO)_2Cl_2]$; apy = 2,2′-azobispyridine, pap = 2-phenylazopyridine) and bis-bidentate pyridyl complexes ($[Ru(apy)(bpy)(CO)Cl]^+$ and $[Ru(pap)(bpy)(CO)Cl]^+$), both containing one azopyridyl ligand. Comparisons with other analogous polypyridyl-containing ruthenium complexes based on electrochemical, spectroscopic and crystallographic measurements are also described.

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2. Experimental

2.1. Physical measurements

Elemental analyses were carried out at the Research Center for Molecular-Scale Nanoscience, Institute for Molecular Science. IR spectra were obtained on KBr pellets with a JASCO FT-IR 4100 spectrometer. Mass spectra were obtained with a Bruker Daltonics microTOF mass spectrometer equipped with an electrospray ionization (ESI) interface. UV–Vis spectra were obtained with a JASCO V-570 UV/Vis/NIR spectrophotometer. NMR spectra were recorded on a JEOL JMN-AL300 spectrometer operating at ^{1}H and ^{13}C frequencies of 300 and 75.5 MHz, respectively. Chemical shifts were calibrated against tetramethylsilane (TMS). Cyclic voltammograms were obtained in a one-compartment cell consisting of a platinum working electrode, a platinum counterelectrode and an Ag/AgNO$_3$ (0.01 M) reference electrode in CH$_3$CN containing tetra-*n*-butylammonium perchlorate (0.1 M) as a supporting electrolyte and the complex (1 mM). The data were collected with an ALS/Chi model 620A electrochemical analyzer. All potentials are reported in volts versus ferrocene/ferrocenium couple (Fc$^+$/Fc) at 25 °C under N$_2$.

2.2. Preparation of compounds

All solvents were dehydrated solvents for organic synthesis and used without further purification. CH$_3$CN for electrochemical experiments was distilled over CaH$_2$ under N$_2$ just prior to use. 2-phenylazopyridine (pap), 2,2′-azobispyridine (apy), [Ru(CO)$_2$Cl$_2$]$_n$, and [Ru(bpy)(CO)$_2$Cl$_2$] were prepared according to procedures outlined elsewhere [10,11].

2.2.1. [Ru(apy)(CO)$_2$Cl$_2$]

A methanolic solution (10 mL) containing [Ru(CO)$_2$Cl$_2$]$_n$ (200 mg, 0.88 mmol) and apy (200 mg, 0.92 mmol) was refluxed for 1 h. The black precipitate was collected by filtration and washed with methanol and diethyl ether, and then dried in vacuo. The yield was 200 mg (55%). *Anal.* Calc. for C$_{12}$H$_8$N$_4$O$_2$Cl$_2$Ru: C, 34.96; H, 1.96; N, 13.60. Found: C, 34.83; H, 2.00; N, 13.58%. IR (KBr): 2074, 2004 cm^{-1} (νC≡O). ^{1}H NMR (CD$_2$Cl$_2$): δ 9.23 (d, 1H), 8.92 (d, 1H), 8.72 (t, 1H), 8.38–8.28 (m, 2H) and 8.05–7.71 (m, 3H) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ 196.53, 194.53 (each CO), 163.43, 152.09, 149.27, 141.96, 139.51, 131.27, 130.29, 129.56, 116.89 and 114.90 ppm.

2.2.2. [Ru(pap)(CO)$_2$Cl$_2$]

A similar reaction between [Ru(CO)$_2$Cl$_2$]$_n$ and pap under the same conditions described above gave rise to [Ru(pap)(CO)$_2$Cl$_2$] with a 39% (140 mg) yield. *Anal.* Calc. for C$_{13}$H$_9$N$_3$O$_2$Cl$_2$Ru: C, 37.97; H, 2.21; N, 10.22. Found: C, 37.82; H, 2.25; N, 10.23%. IR (KBr): 2074, 2010 cm^{-1} (νC≡O). ^{1}H NMR (CD$_2$Cl$_2$): δ 9.13 (d, 1H), 8.65 (d, 1H), 8.35 (t, 1H), 8.11–8.08 (m, 2H) and 7.83–7.60 (m, 4H) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ 195.54, 194.57 (each CO), 163.32, 155.47, 151.50, 142.32, 134.14, 130.33, 130.01, 129.88, 123.97 and 123.66 ppm.

2.2.3. [Ru(apy)(CO)Cl$_2$]$_2$

The dimer complex was prepared according to the method in the literature [12]. [Ru(apy)(CO)$_2$Cl$_2$] (60 mg, 0.14 mmol) was dissolved in dichloromethane (60 mL) and filtered. The filtrate was placed in a quartz flask with a stopper and irradiated with a 100 W mercury lamp for 15 h, after which time a dark green precipitate had formed. The precipitate was collected by filtration, washed with diethyl ether and dried in vacuo. The yield was 50 mg (45%). *Anal.* Calc. for C$_{22}$H$_{16}$N$_8$O$_2$Cl$_4$Ru$_2$ · 3CH$_2$Cl$_2$: C, 29.35; H, 2.17; N, 10.95. Found: C, 29.42; H, 2.15; N, 10.75%. IR (KBr): 1991 cm^{-1} (νC≡O).

2.2.4. [Ru(apy)(bpy)(CO)Cl]PF$_6$

The complex was prepared by modification of a previously reported method [13]. A mixture of [Ru(bpy)(CO)Cl$_2$]$_2$ (140 mg, 0.39 mmol) and apy (108 mg, 0.58 mmol) was heated under reflux in 2-methoxyethanol (10 mL) for 2 h. The mixture was evaporated to dryness under reduced pressure and the remaining solid was dissolved in water (24 mL). The solution was filtered and added to an excess of KPF$_6$. The precipitate was collected by filtration and washed with water and diethyl ether. The product was then dried in vacuo. The crude product was purified by column chromatography using Al$_2$O$_3$ (eluent: CH$_3$CN). The volume of the solution was reduced to ca. 5 mL using a rotary evaporator. The black crystals were precipitated by the addition of diethyl ether, collected, washed with diethyl ether and finally dried in vacuo. The yield was 80 mg (31%). *Anal.* Calc. for C$_{21}$H$_{16}$N$_6$OClPF$_6$Ru: C, 38.86; H, 2.68; N, 12.78. Found: C, 38.81; H, 2.48; N, 12.93%. ESI-MS (CH$_3$CN): $m/z = 505$ (M$^+$), 477 (M−CO$^+$). IR (KBr): 2002 cm^{-1} (νC≡O). ^{1}H NMR (CD$_3$CN): δ 9.50 (d, 1H), 8.83 (bs, 1H), 8.57 (d, 1H), 8.42–8.20 (m, 6H), 8.07–7.89 (m, 5H), 7.52 (bs, 1H) and 7.29 (t, 1H) ppm. ^{13}C NMR (CD$_3$CN): δ 196.48 (CO), 156.81–156.43 (multiple signals), 155.10, 152.78, 141.51, 140.70, 129.61, 128.91, 128.62 and 125.43–125.28 (multiple signals) ppm.

2.2.5. [Ru(pap)(bpy)(CO)Cl]PF$_6$

The complex was prepared in a similar manner as outlined in Section 2.2.4 [9]. Recrystallization of the crude product from acetonitrile/diethyl ether gave single crystals of [Ru(pap)(bpy)(CO)Cl] PF$_6$. The yield was 54 mg (21%). *Anal.* Calc. for C$_{22}$H$_{17}$N$_5$OClPF$_6$Ru: C, 40.72; H, 2.64; N, 10.79. Found: C, 40.71; H, 2.83; N, 10.89%. ESI-MS (CH$_3$CN): $m/z = 504$ (M$^+$), 476 (M−CO$^+$). IR (KBr): 2001 cm^{-1} (νC≡O). ^{1}H NMR (CD$_3$CN): δ 9.53 (d, 1H), 8.54 (d, 1H), 8.41–8.29 (m, 5H), 8.09–7.60 (m, 8H), 7.50 (bs, 1H) and 7.40 (t, 1H) ppm. ^{13}C NMR (CD$_3$CN): δ 194.96 (CO), 156.62–156.25 (multiple signals), 154.00, 152.64, 141.50, 140.80, 129.01, 128.85 and 125.33–125.26 (multiple signals) ppm.

2.3. X-ray crystallography

2.3.1. [Ru(apy)(CO)$_2$Cl$_2$] · CH$_2$Cl$_2$ and [Ru(pap)(CO)$_2$Cl$_2$]

The single crystals of the complexes were obtained from dichloromethane/methanol mixtures. A black crystal of [Ru(apy)(CO)$_2$Cl$_2$] · CH$_2$Cl$_2$ with the dimensions 0.2 × 0.2 × 0.2 mm was mounted on a glass fiber. A dark red crystal of [Ru(pap)(CO)$_2$Cl$_2$] with the dimensions 0.2 × 0.2 × 0.2 mm was mounted on a glass fiber. All data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) at −100(1) °C. Data were collected to a maximum 2θ value of 55.0°. All calculations were carried out using the TEXSAN crystallographic software package [14]. The structures were solved either by the heavy-atom Patterson method [15] for [Ru(apy)(CO)$_2$Cl$_2$] · CH$_2$Cl$_2$ or by a direct method [16] for [Ru(pap)(CO)$_2$Cl$_2$], and were expanded using Fourier techniques. Empirical absorption corrections were applied using Lorentz polarization (Lp) and absorption. Structures were refined using full-matrix least-square techniques. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were built in using standard geometry. The final cycle of full-matrix least-squares refinements was based on 3860 observations (all data) and 217 variable parameters for [Ru(apy)(CO)$_2$Cl$_2$] · CH$_2$Cl$_2$, whereas 3109 observations (all data) and 190 variable parameters were used for [Ru(pap)(CO)$_2$Cl$_2$]. Crystallographic parameters are summarized in Table 1 and selected bond lengths and angles are listed in Table 3.

2.3.2. [Ru(apy)(bpy)(CO)Cl]PF$_6$

Crystals suitable for X-ray crystallography were prepared by a week-long diffusion of diethyl ether into an acetonitrile solution

Table 1
Crystallographic data for $[Ru(apy)(CO)_2Cl_2] \cdot CH_2Cl_2$, $[Ru(pap)(CO)_2Cl_2]$ and $[Ru(apy)(bpy)(CO)Cl]PF_6$.

Chemical formula	$C_{13}H_{10}N_4O_2Cl_4Ru$	$C_{13}H_9N_3O_2Cl_2Ru$	$C_{21}H_{16}N_6OF_6ClPRu$
Formula weight	497.13	411.21	649.88
Temperature (K)	173(1)	173(1)	173(1)
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Unit cell parameters			
a (Å)	7.905(3)	7.1251(1)	9.1342(2)
b (Å)	9.038(3)	8.9479(2)	12.9869(3)
c (Å)	13.604(6)	12.3328(5)	20.5545(6)
α (°)	83.05(1)	86.41(1)	
β (°)	87.81(1)	80.39(1)	100.3311(9)
γ (°)	66.382(8)	70.441(9)	
V (Å^3)	884.0(6)	730.48(6)	2398.75(10)
Z	2	2	4
μ (Mo Kα) (cm^{-1})	15.04	14.44	9.069
Number of reflections measured	3860	3109	5493
Number of observations	3860 (all)	3109 (all)	4589 ($I > 2\sigma(I)$)
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F
Parameters	217	190	350
R[a]	0.0296	0.0282	0.0415
R_w	0.0701[b] (all data)	0.0906[b] (all data)	0.0652[c] ($I > 2\sigma(I)$)
S	1.523	1.529	1.003

[a] $R = \sum ||F_o| - |F_c|| / \Sigma |F_o|$.
[b] $R_w = \{\sum_w (F_o^2 - F_c^2)^2 / \sum_w (F_o^2)^2\}^{1/2}$.
[c] $R_w = \{\sum_w (|F_o| - |F_c|)^2 / \sum_w F_o^2\}^{1/2}$.

Table 2
Electrochemical and UV–Vis spectral data for the prepared complexes.

	Complexes			
	$[Ru(apy)(CO)_2Cl_2]$	$[Ru(pap)(CO)_2Cl_2]$	$[Ru(apy)(bpy)(CO)Cl]^+$	$[Ru(pap)(bpy)(CO)Cl]^+$
$E_{1/2}$/V[a] (azo/azo$^-$)	−0.56	−0.68	−0.70	−0.81
(azo$^-$/azo^{2-})[b]	−1.33	−1.57	−1.46	−1.52
(bpy/bpy$^-$)			−1.93	−1.94
λ_{max}/nm[c] (ε/M^{-1} cm^{-1})	513 (1590)	484 (1670)	525 (3910)	502 (4820)
	358 (14 700)	354 (13 200)	343 (12 000)	348 (14 000)
			314 (17 900)	315 (21 200)
			303 (16 900)	305 (19 400)
			268 (18 100)	262 (sh)
			237 (19 300)	236 (sh)

[a] In CH_3CN, vs. Fc^+/Fc.
[b] E_{pc} values.
[c] In CH_3CN.

Table 3
Selected bond lengths (Å) and angles (°) for $[Ru(apy)(CO)_2Cl_2] \cdot CH_2Cl_2$, $[Ru(pap)(CO)_2Cl_2]$ and $[Ru(apy)(bpy)(CO)Cl]PF_6$.

	$[Ru(apy)(CO)_2Cl_2] \cdot CH_2Cl_2$		$[Ru(pap)(CO)_2Cl_2]$		$[Ru(apy)(bpy)(CO)Cl]^+$	
Bond lengths	Ru1–Cl1	2.389(1)	Ru1–Cl1	2.3828(6)	Ru1–Cl1	2.3859(8)
	Ru1–Cl2	2.394(1)	Ru1–Cl2	2.4008(5)	Ru1–C1	1.889(3)
	Ru1–C1	1.895(2)	Ru1–C1	1.896(3)	Ru1–N1	2.114(2)
	Ru1–C2	1.905(3)	Ru1–C2	1.909(2)	Ru1–N3	1.998(2)
	Ru1–N1	2.108(2)	Ru1–N1	2.099(2)	Ru1–N5	2.096(3)
	Ru1–N3	2.107(2)	Ru1–N3	2.119(2)	Ru1–N6	2.069(2)
	C1–O1	1.136(3)	C1–O1	1.134(3)	C1–O1	1.116(4)
	C2–O2	1.097(3)	C2–O2	1.098(3)	N2–N3	1.291(4)
	N2–N3	1.265(3)	N2–N3	1.264(3)		
Bond angles	Ru1–C1–O1	174.7(2)	Ru1–C1–O1	176.2(2)	Ru1–C1–O1	173.0(3)
	Ru1–C2–O2	177.7(2)	Ru1–C2–O2	175.5(2)	N1–Ru1–N3	75.89(11)
	N1–Ru1–N3	74.79(7)	N1–Ru1–N3	75.01(7)	N5–Ru1–N6	78.53(10)

of the complex. A black crystal of $[Ru(apy)(bpy)(CO)Cl]PF_6$ with the dimensions 0.4 × 0.3 × 0.1 mm was mounted on a glass fiber. All data were collected on a Rigaku RAXIS-RAPID diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71075 Å) at −100(1) °C. Data were collected to a maximum 2θ value of 55.0°. All calculations were carried out using the CrystalStructure crystallographic software package [17]. The structure was solved by a direct method [16], and was expanded using Fourier techniques. A multi-scan absorption correction was applied [18]. The structure was refined using full-matrix least-square techniques. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were built in using standard geometry. The final cycle of full-matrix least-squares refinements was based on 4589 observations ($I > 2\sigma(I)$) and 350 variable parameters. Crystallographic parameters are summarized in Table 1 and selected bond lengths and angles are listed in Table 3.

3. Results and discussion

3.1. Synthesis and characterization of carbonyl complexes with azopyridyl ligands

Synthetic routes and some characterization data for the present complexes are summarized in Scheme 1 and Table 2, respectively. When a methanolic solution containing $[Ru(CO)_2Cl_2]_n$ and one equivalent of azopyridyl ligands was refluxed for 1 h, the reaction proceeded to form $[Ru(azo)(CO)_2Cl_2]$ (azo = apy, pap). The complexes imparted an intense purple color (Fig. 1), whereas the complexes ($[Ru(polypyridine)(CO)_2Cl_2]$) exhibited lighter yellow to orange colors. The very low energy of the π^* azopyridyl MO is responsible for the observed long-wavelength metal-to-ligand charge transfer (MLCT) transitions in $[Ru(azo)(CO)_2Cl_2]$ [19]. In addition, the intensities of these MLCT ($d\pi \rightarrow \pi^*$) transitions are typically high because of the large LUMO coefficients at the coordinating nitrogen centers [19]. In the IR measurements, two stretching bands of the terminal CO ligands were observed. This implied that two CO groups existed at *cis* positions relative to each other. Both complexes displayed two carbonyl carbon signals in $^{13}C\{^1H\}$ NMR spectra, indicating that the two CO groups exist in magnetically inequivalent environments.

Photoirradiation of ruthenium(II) carbonyl complexes with UV or visible light has been known to result in decarbonylation [20]. For example, irradiation of $[Ru(polypyridine)(CO)_2Cl_2]$ complexes (polypyridine = bpy, phen, etc.) in poorly coordinating solvents in a pyrex flask resulted in mono-decarbonylation and the subsequent formation of a chloro-bridged dimer within a few hours [12]. Photodecarbonylation of $[Ru(apy)(CO)_2Cl_2]$, however, did not proceed under the same condition. Irradiation of $[Ru(apy)(CO)_2Cl_2]$ using a quartz flask led to the solution gradually changing from a purple to a greenish color. After several hours, a small amount of dark green powder had precipitated from the solution. The $[Ru(polypyridine)(CO)Cl_2]_2$ dimers have two different structural isomers [12]: in $[Ru(phen)(CO)Cl_2]_2$, the carbonyls are *trans* to the bridging Cl and the terminal Cl *trans* to the pyridyl nitrogens ("phen-type" in Scheme 2), whereas in $[Ru(dpk)(CO)Cl_2]_2$ (dpk = di(2-pyridyl) ketone), the terminal and bridging Cl are mutually *trans*, and the carbonyls are *trans* to the pyridyl nitrogens ("dpk-type" in Scheme 2). As a result, structural differences in $[Ru(polypyridine)(CO)Cl_2]_2$ led to the observed variance in νCO frequencies. The lower νCO frequencies (around 1945 cm^{-1}) indicated $[Ru(phen)(CO)Cl_2]_2$-type configurations, whereas the higher νCO (around 1985 cm^{-1}) frequencies indicated $[Ru(dpk)(CO)Cl_2]_2$-types. Based on the IR data, the present dimer ($[Ru(apy)(CO)Cl_2]_2$), therefore, is expected to have the latter structure. By contrast, the photochemical reaction of $[Ru(pap)(CO)_2Cl_2]$ did not produce the corresponding dimer. We may need to reinvestigate some reaction conditions such as solvents, temperature or the wavelength of irradiation to ascertain whether conditions need to be changed so as to obtain the dimer.

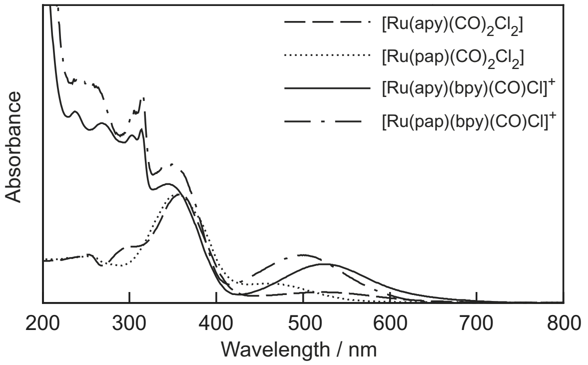
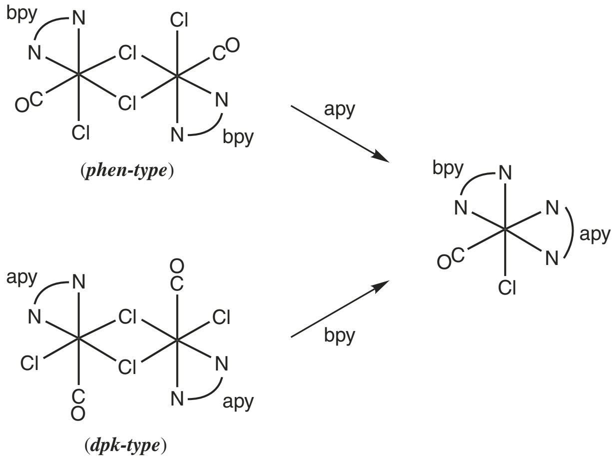
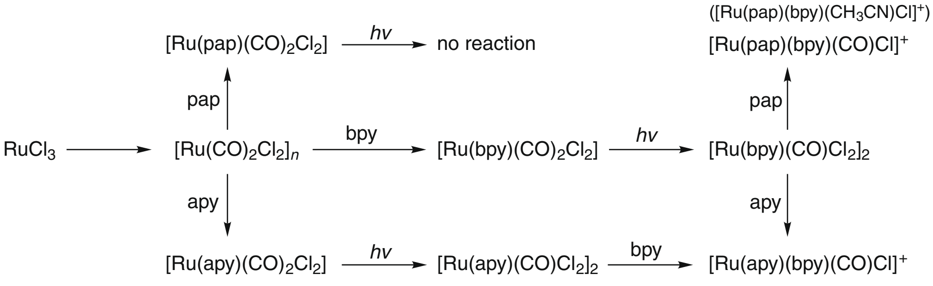


Fig. 1. UV–Vis spectra of the prepared complexes ($c = 1.0 \times 10^{-4}$ M in CH_3CN).



Scheme 2. Formation of the $[Ru(apy)(bpy)(CO)Cl]^+$ complex via different precursors.

The $[Ru(azo)(bpy)(CO)Cl]^+$ complexes (azo = apy, pap) were prepared by reacting $[Ru(bpy)(CO)Cl_2]_2$ with the corresponding azopyridyl ligand in 2-methoxyethanol (Scheme 1). The asymmetrical nature of the azopyridyl units led to the possible formation of several isomers of $[Ru(azo)(bpy)(CO)Cl]^+$. IR spectra of the $[Ru(azo)(bpy)(CO)Cl]^+$ complexes showed single strong νCO bands, indicating that only one isomer formed in both complexes. Although partial decarbonylation occurs during the reaction of

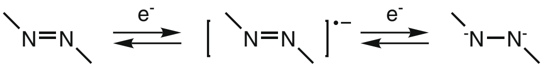


Scheme 1. Synthetic routes for the prepared complexes.

the $[Ru(bpy)(CO)Cl_2]_2$ dimer with pap ($[Ru(pap)(bpy)(CH_3CN)Cl]^+$ in Scheme 1) [9], such decarbonylation behavior was not observed for the apy ligand introduced in the reaction. The distinctions between the two reactions may result in the pendant moiety of the azo ligands. Here the non-coordinating pyridyl nitrogen atom in the apy ligand prevents or reduces decarbonylation of the adjacent CO ligand by strong donor–acceptor interaction after coordination to the ruthenium center (see the next section).

Reaction of the apy-dimer ($[Ru(apy)(CO)Cl_2]_2$) with bpy should give a different isomer to $[Ru(apy)(bpy)(CO)Cl]^+$ because the order of the addition of the ligands confers geometric specificity [13]. Nevertheless, the molecular structure obtained by the reaction of the apy-dimer with bpy clearly indicates that the reaction of $[Ru(apy)(CO)Cl_2]_2$ with bpy and the inverse reaction yield identical structures (Scheme 2). This result supports the concept that the structures of dimers ($[Ru(bpy)(CO)Cl_2]_2$ and $[Ru(apy)(CO)Cl_2]_2$) are different as mentioned above. UV–Vis spectra of $[Ru(azo)(bpy)(CO)Cl]^+$ indicated strong MLCT transitions in the visible region which were similar to that observed for $[Ru(azo)(CO)_2Cl_2]$ (Fig. 1 and Table 2). Since general carbonyl ruthenium complexes with polypyridyl ligands are poor absorbers of visible light, the presence of azopyridyl ligands in $[Ru(azo)(bpy)(CO)Cl]^+$ caused a lowering of the π^* azopyridyl MO which contributed to a shift in the MLCT transition into the visible region.

Cyclic voltammograms (CV) of the present complexes exhibited the successive two-electron reductions based on the low lying LUMO of the azo moieties in Eq. (1) and Fig. 2 [6]. As shown in Table 2, the apy-complexes ($[Ru(apy)(CO)_2Cl_2]$ and $[Ru(apy)(bpy)(CO)Cl]^+$) undergo reductions at a more positive region (ca. 0.1 V) than the corresponding pap-copmlexes ($[Ru(pap)(CO)_2Cl_2]$ and $[Ru(pap)(bpy)(CO)Cl]^+$). These observations suggest that the apy ligand is better π-acceptor than the pap ligand. The irreversible behavior of the second step indicated the dissociation of a chloro or a carbonyl ligand accompanied by two-electron reductions [21,22]. In addition to these reductions, $[Ru(azo)(bpy)(CO)Cl]^+$ showed another quasi-reversible reduction wave at a more negative region (Table 2). This redox wave is assigned to the bpy-based reduction [23]. In comparison to $[Ru(bpy)_2(CO)L]^+$ (L = anionic ligands) [3c,24,25], the reduction potentials show that the replacement of the bpy ligand with an azopyridyl ligand caused a shift to more positive potentials by 0.8–1.2 V. No oxidation wave caused by $Ru^{3+/2+}$ was observed within the potential window of the present complexes.



(1)

3.2. Single crystal X-ray analysis

We carried out X-ray analyses to obtain detailed structural information of the complexes. The molecular structures of the $[Ru(azo)(CO)_2Cl_2]$ complexes are shown in Figs. 3 and 4. Both complexes have two CO groups in a *cis* position to each other and two chlorides in a *trans* position. The azopyridyl ligands are bound to the ruthenium ion with the pyridine nitrogen and the azo nitrogen possessing a bite angle of 74.79(7)° in $[Ru(apy)(CO)_2Cl_2]$ and 75.01(7)° in $[Ru(pap)(CO)_2Cl_2]$. As shown in Table 3, the shorter C–O lengths at *trans* position of the azo nitrogen (1.097(3) Å in $[Ru(apy)(CO)_2Cl_2]$ and 1.098(3) Å in $[Ru(pap)(CO)_2Cl_2]$) compared with C–O lengths at *trans* of the pyridyl nitrogen (1.136(3) and 1.134(3) Å) are due to strong $(d\pi)Ru^{II} \rightarrow \pi^*(azo)$ backbonding [26]. Noteworthy is that the dihedral angle between the two aromatic rings in $[Ru(apy)(CO)_2Cl_2]$ (7.99°) is approximately parallel and this contrasts that observed for $[Ru(pap)(CO)_2Cl_2]$ (35.29°). As a result, the distance between the non-coordinating nitrogen atom (N4) and the CO carbon (C1) in $[Ru(apy)(CO)_2Cl_2]$ is very short (2.682(3) Å) and this suggests that a significant interaction may exist between the non-coordinating pyridine and the adjacent carbonyl group.

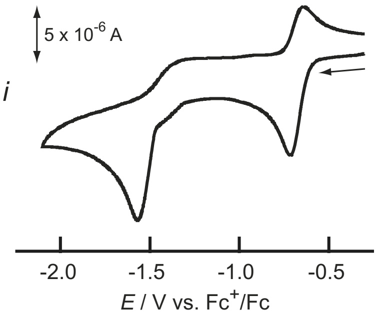


Fig. 2. Cyclic voltammogram of $[Ru(pap)(CO)_2Cl_2]$ (scan rate = 0.1 V s^{-1}).

The molecular structure of $[Ru(apy)(bpy)(CO)Cl]^+$ is shown in Fig. 5. The azo group of the apy ligand is situated *cis* to the CO ligand. The Ru1–C1, C1–O1 and Ru1–Cl1 bond lengths, and the Ru1–C1–O1 bond angle are 1.889(3), 1.116(4), 2.3859(8) Å and 173.0(3)°, respectively (Table 3). These parameters are consistent

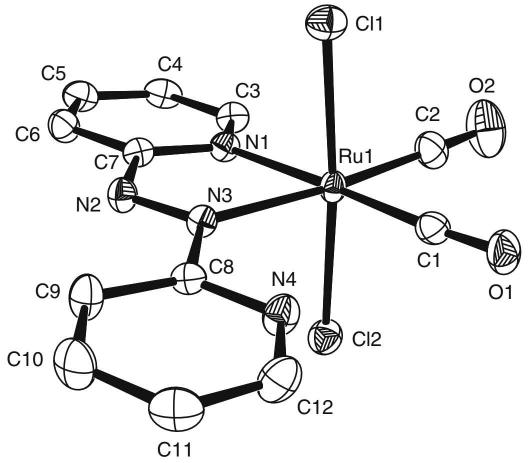


Fig. 3. ORTEP drawing of $[Ru(apy)(CO)_2Cl_2]$ with the atom numbering scheme. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level.

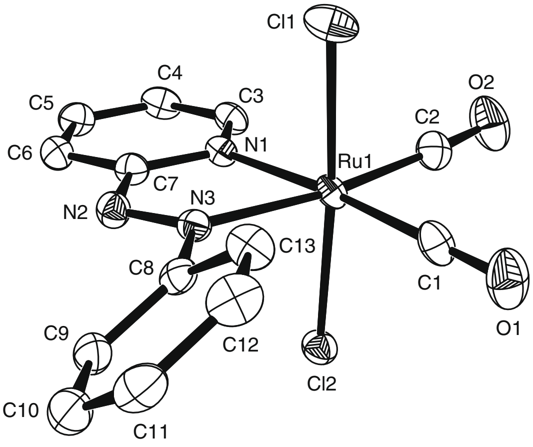


Fig. 4. ORTEP drawing of $[Ru(pap)(CO)_2Cl_2]$ with the atom numbering scheme. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level.

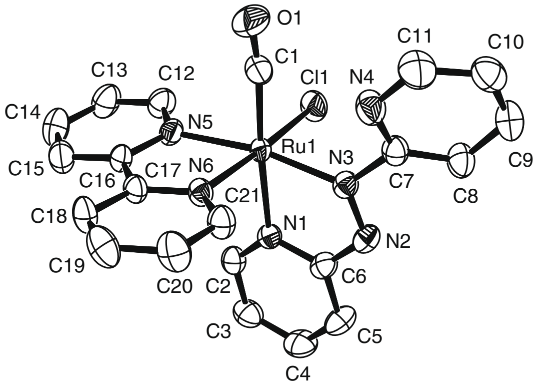


Fig. 5. ORTEP drawing of $[\mathrm{Ru(apy)(bpy)(CO)Cl}]^+$ with the atom numbering scheme. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level.

with those observed in $[\mathrm{Ru(pap)(bpy)(CO)Cl}]^+$ [9]. The ruthenium–azo nitrogen bond length (Ru1–N3) is shorter than the ruthenium–pyridine nitrogen in the apy ligand of the complex. This agrees with the corresponding pap complex [9], and can be explained by the stronger π-backbonding effect [27]. The short interatomic distance between the non-coordinating nitrogen atom (N4) and the CO carbon (C1) of 2.711(5) Å implies a donor–acceptor interaction between these atoms as mentioned above.

The N–N distance in an azo moiety is an excellent indicator of the charge on an azo group [6]. The values for unreduced azo N–N bonds are 1.25–1.30 Å in metal complexes (ca. 1.24 Å for free ligands). The one-electron reduced (anion radical) ligands have a bond lengths of about 1.35 Å, whereas the two-electron reduced (hydrazido) forms have single bonds with >1.40 Å lengths. All molecules in this study have N–N bond distances of 1.26–1.29 Å. This clearly suggests the presence of the unreduced forms of the azopyridyl ligands. The same results were obtained for other azopyridyl ruthenium(II) complexes [28].

3.3. Comparison with analogous complexes using spectroscopic and crystallographic data

Some physical data of terminal carbonyl groups are generally useful indicators for electronic states around metal centers in metal complexes. In particular, bond lengths and vibrational spectra are considered important [29]. In addition to these data, we calculated the stretching force constants of the CO group using IR spectral data. This was used to distinguish between the electronic states of the azo and other polypyridyl ligands in the complex systems [30,31]. The stretching force constants of the CO group in the present and analogous complexes are summarized in Tables 4 and 5 together with the values of νCO, d(Ru–C) and d(C–O). As shown in Table 4, Fig. 6a and b, the electron density in the ruthenium center did not significantly change when the bidentate pyridyl ligand was exchanged in the mono-pyridyl systems. At least two points should be considered: (1) the average values of the parameters in the two CO groups were used, and (2) an equatorial plane of octahedral configuration has been constituted by the two nitrogen atoms of the bidentate pyridyl ligands and the two carbonyl carbons including the ruthenium atom. Synergistic effects of both (1) and (2) might reduce the differences of the parameters in the mono-pyri-

Table 4

Stretching frequencies, force constants, and bond lengths of the CO groups in *cis*(CO),*trans*(Cl)-$[\mathrm{Ru(polypiridine)(CO)_2Cl_2}]$.

Polypyridine[a]	νCO (cm^{-1})	k (N cm^{-1})	d(Ru–C) (Å)	d(C–O) (Å)	Ref.
moppt	2077, 2020	16.96	1.876(3), 1.888(3)	1.127(4), 1.125(3)	[33]
4,4′-dnbpy	2074, 2018	16.92	1.877(4), 1.890(4)	1.118(4), 1.122(4)	[34]
mppt	2074, 2012	16.87	1.862(3), 1.871(3)	1.126(4), 1.135(4)	[33]
pap	2074, 2010	16.85	1.896(3), 1.909(2)	1.134(3), 1.098(3)	this work
4,4′-dpbpy	2073, 2011	16.85	1.893(9), 1.864(1)	1.132(1), 1.148(1)	[34]
tpyr	2072, 2011	16.84	1.875(4), 1.882(4)	1.140(5), 1.130(5)	[33]
apy	2074, 2004	16.80	1.895(2), 1.905(3)	1.136(3), 1.097(3)	this work
apt	2073, 2005	16.80	1.851(6), 1.881(6)	1.135(8), 1.131(8)	[35]
pynp	2064, 2012	16.78	1.901(7), 1.880(6)	1.126(9), 1.129(7)	[36]
bpy	2067, 2003	16.74	1.835(17), 1.817(8)	1.133(22), 1.159(11)	[1 h]
4,4′-dbbpy	2066, 2000	16.70	1.878(4), 1.878(4)	1.137(5), 1.137(5)	[34]
4,4′-dmbpy	2063, 2001	16.69	1.879(10), 1.866(12)	1.117(11), 1.129(11)	[37]
mopip	2066, 1999	16.69	1.886(3), 1.873(3)	1.132(3), 1.122(3)	[33]
6,6′-dmbpy	2063, 1999	16.67	1.873(6), 1.872(5)	1.131(7), 1.138(6)	[38]

[a] moppt = 3-(4-methoxyphenyl)-pyridin-2-yl-1,2,4-triazole; 4,4′-dnbpy = 4,4′-dinitro-2,2′-bipyridine; mppt = 3-(4-methylphenyl)-pyridin-2-yl-1,2,4-triazole; 4,4′-dpbpy= 4,4′-diphosphonic acid-2,2′-bipyridine; tpyr = 2-(4H-[1,2,4]triazol-3′-yl)-pyrazine; apt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole; pynp = 2-(2-pyridyl)-1,8-naphthyridine; 4,4′-dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine; 4,4′-dmbpy = 4,4′-dimethyl-2,2′-bipyridine; mopip = 3,6-bis[(4-methoxyphenyl)iminomethyl]pyridazine.

Table 5

Stretching frequencies, force constants, and bond lengths of the CO groups in *cis*-$[\mathrm{Ru(polypiridine)_2(CO)Cl}]^+$.

Polypyridines[a]	νCO (cm^{-1})	k (N cm^{-1})	d(Ru–C) (Å)	d(C–O) (Å)	Ref.
apy/bpy	2002	16.20	1.889(3)	1.116(4)	this work
pap/bpy	2001	16.18	1.891(2)	1.122(3)	[9]
4,4′-Me$_2$bpy/5,6′-Me$_2$phen	1978	15.81	1.867(5)	1.112(7)	[13]
4,7′-Me$_2$phen/dpk	1976	15.80	1.820(11)	1.146(13)	[13]
5,5′-Me$_2$bpy/dpa	1972	15.72	1.917(4)	1.026(6)	[13]
bpy/dpk	1970	15.68	1.880(5)	1.119(7)	[13]
4,4′-Me$_2$bpy/4,7′-Me$_2$phen	1967	15.64	1.95(2)	1.05(2)	[13]
bpy/dpa	1967	15.64	1.883(16)	1.08(2)	[13]
bpy/phen	1966	15.62	1.857(4)	1.126(6)	[13]
bpy/bpy	1966	15.62	1.861(29)	1.122(32)	[39]
biq/biq	1964	15.59	1.91(2)	1.01(2)	[40]

[a] 4,4′-Me$_2$bpy = 4.4′-dimethyl-2,2′-bipyridine; 5,6′-Me$_2$phen = 5,6′-dimethyl-1,10-phenanthroline; dpa = di(2-pyridyl)amine; biq = 2,2′-biquinoline.

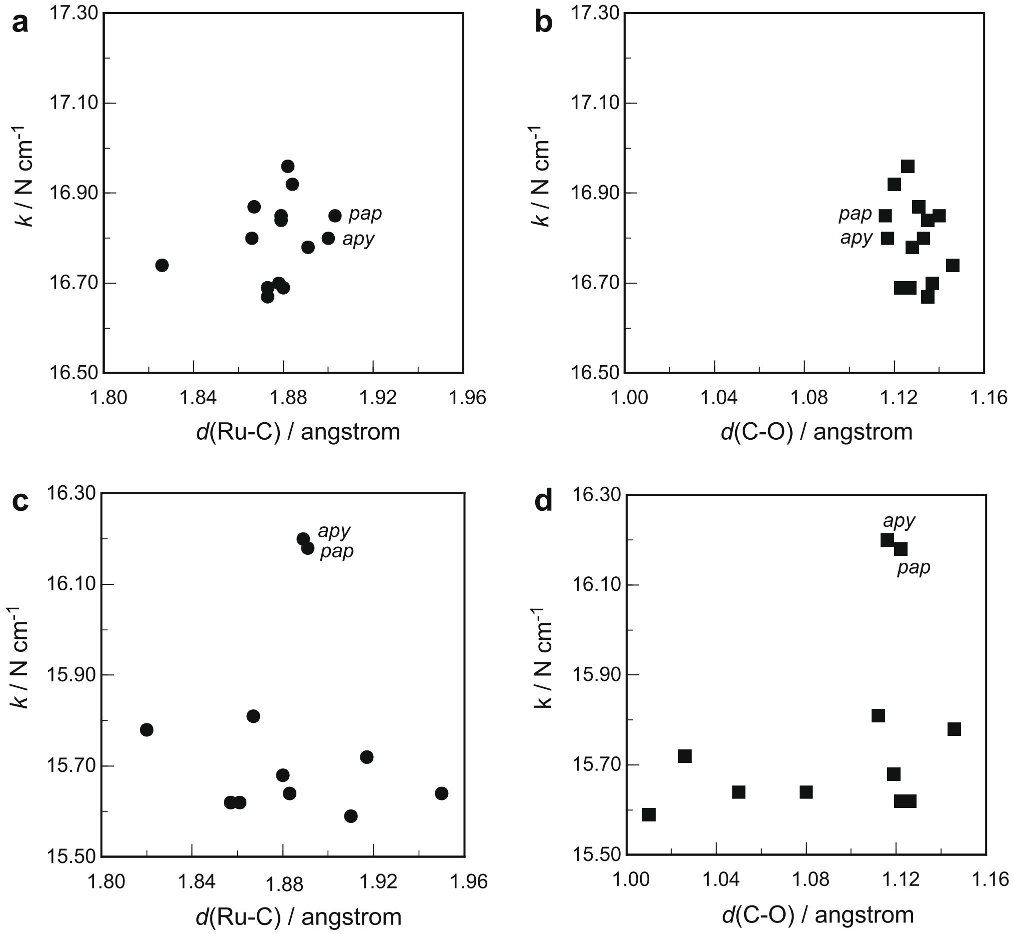


Fig. 6. Relationship between the force constants (k) and bond lengths (d) in [Ru(polypyridine)$(CO)_2Cl_2$] (a and b) and [Ru(polypyridine)$_2$(CO)Cl]$^+$ (c and d). The values of the bond lengths in a and b are derived from the mean values of two CO groups.

dyl systems. Conversely, while obvious characteristics about the bond lengths (Ru–C and C–O) are not shown in the bis-pyridyl complexes, the force constant (k) and the stretching frequencies of CO groups can be classified into two groups (Table 5, Fig. 6c and d): the k values of the azo-containing complexes were higher ca. 0.4–0.6 N cm^{-1} than of the values for the bis-pyridyl complexes without azopyridines. As the decrease of the k value of [Ru(bpy)$_2$(CO)(quinoline)]$^{2+}$ caused by quinoline-based one-electron reduction is 0.56 N cm^{-1} [32], it is presumed that the electron density of the ruthenium center considerably decreases when an azo group (which has greater π-acidity) coordinates to the ruthenium atom. Accordingly, it can be concluded that complex formation of the bis-pyridyl compound with azopyridyl ligands induced relatively high k values. This observation can be ascribed to the decrease of the π back-donation from the ruthenium center to the CO group.

4. Conclusion

We have demonstrated the synthesis and characterization of ruthenium(II) carbonyl complexes bearing the azopyridyl ligands. The molecular structures in mono-azopyridyl complexes, [Ru(azo)$(CO)_2Cl_2$], revealed *cis*-CO and *trans*-Cl coordinations. The azo groups were found to be situated *cis* to the CO ligand in [Ru(azo)(bpy)(CO)Cl]$^+$. The N–N bond length data indicated that the present complexes have the unreduced azo moieties. All the complexes showed the azo-localized reduction at more positive regions. This suggests that the azo ligands serve as prominent electron reservoirs compared with other polypyridyl ligands such as bpy and phen. Since azopyridine-coordinated complexes show some interesting properties, we are currently extending the investigation to other systems containing Ru–CO moieties.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.11.023.

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