Dalton Transactions

PAPER

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Cite this: *Dalton Trans.*, 2018, **47**, 16182

Triply bridged dinuclear ruthenium complexes bearing alkylbis(2-pyridylmethyl)amine in the mixed-valence state of Ru(n)-Ru(m)⁺

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Triply halogeno and methoxido-bridged dinuclear ruthenium complexes bearing a tridentate ancillary ligand, alkylbis(2-pyridylmethyl)amine (alkyl, ethyl and benzyl), in the Ru(II)–Ru(III) mixed-valence state were synthesized by reduction reactions of the trichloridoruthenium(III) complex, *fac*-[Ru^{III}Cl₃(ebpma)], followed by chlorido-substitution and oxidation reactions in air. The conversion of the bridging ligands of the diruthenium complexes was also made possible through reduction of the dinuclear core. The electronic structures of the mixed-valence state were investigated by electron spin resonance (ESR), X-ray crystallography, electrochemical measurements and UV-vis-near infrared (NIR) spectroscopy. The mixed-valence state of all the triply bridged complexes was stable and classified as Class III.

Received 29th August 2018, Accepted 22nd October 2018 DOI: 10.1039/c8dt03507e

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Introduction

Multi-nuclear transition metal complexes have been attracting attention in material conversion reaction fields, in which multi-electron transfer is required, such as water oxidation^{1,2} and nitrogen fixation.³⁻⁷ Many types of, in particular, dinuclear complexes of octahedral geometry having the bridging moieties such as atoms, ions or molecules in the mixedvalence state have been synthesized and investigated on their spectroscopic and electrochemical properties,⁸⁻¹¹ in connection with biological systems, for instance. The development of dinuclear frameworks (Chart 1) and the control of the mixedvalence state are important for application in molecular electronics, devices, and quantum computing owing to the inert properties and various oxidation states of these complexes. While triply or doubly bridged diruthenium complexes having only one kind of bridging ligand X (X = Cl, Br, I, OH, OR and SR) with the $\{Ru_2(\mu-X)_2\}^{n+}$ or $\{Ru_2(\mu-X)_3\}^{n+}$ core have been previously reported,^{12–22} there are still only a few diruthenium complexes having two (or more) different kinds of bridging ligands, such as $[{RuCl(p-cymene)}_2(\mu-H)(\mu-Cl)]$ (p-cymene; 1-methyl-4-(propan-2-yl)benzene)²³ or $[{Ru(Me_3tacn)}_2(\mu-O)]$ $(\mu - P_2 O_7)^{\dagger}$ (Me₃tacn; trimethyltriazacyclononane).²⁴ Thus, systematic investigations on the electronic structures and reactiv-

Department of Materials and Life Sciences, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo 102-8554, Japan. E-mail: h-nagao@sophia.ac.jp ities of a series of diruthenium complexes, which are composed of different kinds of bridging moieties, are required.

In this study, the syntheses, structures, and electrochemical and spectroscopic properties of triply bridged mixed-valence diruthenium complexes (Chart 1, C type) having two kinds of bridging ligands, Cl⁻, Br⁻, and CH₃O⁻, were investigated using tridentate alkylbis(2-pyridylmethyl)amine (Rbpma; alkyl = ethyl, benzyl, Chart 2)²⁵⁻³⁰ as a supporting ligand. The synthetic strategy for the change of bridging ligands was established as well, by reduction of the diruthenium core. Benzylbis (2-pyridylmethyl)amine (bbpma) was newly introduced to improve the solubility toward various organic solvents. Our previous work about the ethylbis(2-pyridylmethyl)amine



Chart 1 Dinuclear frameworks having bridging ligand(s).



Chart 2 Alkylbis(2-pyridylmethyl)amine (Rbpma; R = C_2H_5 , ethyl, R = $CH_2C_6H_5$, benzyl).



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[†]Electronic supplementary information (ESI) available: ESR spectra, NMR spectra, X-ray structural analysis, electrochemical and spectroscopic data, UV-vis-NIR spectra, and DFT calculations. CCDC 1861325, 1861084 and 1861326. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c8dt03507e

(ebpma) ligand system has revealed that Rbpma coordinates to the metal center in either facial or meridional fashion and the geometry of ruthenium complexes bearing ebpma is controlled by the combination of the co-existing ligands.³¹ The nitrosylruthenium complex containing an electron donating alkoxido ligand RO⁻, [Ru(NO)(OR)(ebpma)]²⁺, favors a meridional configuration due to the strong interactions between the π -accepting NO and RO⁻ which locates at the *trans* position to NO, through the metal center,³¹ while the trichloridoruthenium(m) complex, [Ru^{III}Cl₃(ebpma)], is more stable in the facial geometry than in the meridional form.

Reduction reactions of *fac*-[Ru^{III}Cl₃(ebpma)] afforded new complexes with the facial-type configuration accompanied by dissociation of chlorido ligands. In methanol in air, one chlorido and two methoxido ligands bridged between the two ruthenium centers, resulting in the formation of a triply bridged complex in the mixed-valence state of Ru(II)-Ru(III), $[{Ru^{II,III}(ebpma)}_{2}(\mu-Cl)(\mu-OCH_{3})_{2}]^{2+}$ ([1]²⁺), whose mixedvalency was classified as Class III according to the Robin-Day classification.³² The crystal structure of [1]²⁺ also suggested strong interactions between the two ruthenium centers.³³ Systematic investigation on such a mixed-valence complex having different kinds of bridging ligands has not achieved success so far. Herein we would like to report the investigation and comparison of the electronic structures of a series of mixed-valence diruthenium complexes of Ru(II)-Ru(III), whose ruthenium centers are bridged by halogeno (Cl⁻ and Br⁻) and methoxido ligands, bearing tridentate ebpma or bbpma.

Experimental

General procedures

Elemental analyses were performed with a PerkinElmer 2400-II instrument. FAB MS spectra and high-resolution MS spectra were recorded with a JEOL JMS-700 spectrometer with m-nitrobenzyl alcohol as the matrix. ¹H and ¹³C NMR spectra were recorded with a JEOL AL400 spectrometer. IR spectra were recorded on a Shimadzu IR Affinity-1 spectrophotometer using samples prepared as KBr disks. UV-vis-NIR spectra were recorded on a Shimadzu MultiSpec-1500 system and on a UV-3100 system using a quartz cell of 1 cm or 1 mm path length. The effective magnetic moment was measured by Gouy's method at 300 K using Hg[Co(SCN)₄] as a calibrant. X-band ESR spectra were recorded with a JEOL JESFA300 ESR spectrometer at 77 K in the form of frozen acetone or powder. Electrochemical measurements such as cyclic voltammetry (CV) and normal pulse voltammetry (NPV) were carried out in acetonitrile solutions containing 0.10 mol dm⁻³ tetraethylammonium perchlorate (TEAP) or tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte using the Pt disk working electrode (ϕ = 1.6 mm) and an Ag|0.01 mol dm⁻³ AgNO₃ (CH₃CN) reference electrode using a BAS 100B/W electrochemical analyzer at 25 °C. Hydrodynamic voltammograms (HDVs) were obtained with the rotating platinum disk working electrode (ϕ = 3.0 mm) using the BAS RDE-2 rotating electrode at 25 °C. Controlled potential electrolysis (CPE) experiments were carried out in a three-compartment cell with the platinum gauze working electrode in the first compartment, the auxiliary electrode in the second compartment, and the reference electrode in the third compartment using a Huso polarograph Model 312 and 343B digital coulometer at 25 °C. At the end of each measurement, ferrocene ($E_{1/2} = 0.074$ V) was added as an internal standard to correct redox potentials.

Syntheses of supporting ligands and ruthenium complexes

RuCl₃·*n*H₂O (content of Ru: 40.46 wt%) was purchased from Furuya Kinzoku Inc. All solvents and chemicals were purchased as dehydrated grade and reagent grade, respectively, and were used without further purification. Ethylbis(2-pyridyl-methyl)amine (ebpma) was prepared by the procedure previously reported in the literature.³¹ *fac*-[Ru^{III}Cl₃(ebpma)],³¹ *fac*-[Ru^{III}(NCCH₃)₃(ebpma)]³¹ and [1](PF₆)₂.³³ were synthesized as reported earlier.

Benzylbis(2-pyridylmethyl)amine (bbpma)

2-Picolylchloride hydrochloride (4.20 g, 25 mmol) and benzylamine (1.47 cm³, 13 mmol) were dissolved in water (30 cm³) and the solution was warmed at 60 °C for an hour. An aqueous solution of sodium hydroxide (5.0 mol dm⁻³, 10 cm³) was added dropwise within 30 min and the solution was warmed for a further 1 hour. The resultant solution was cooled down to room temperature and extracted with 40 cm³ of dichloromethane three times. The extract was dehydrated with MgSO₄. Then, the precipitated insoluble materials were filtered and the obtained reddish-orange solution was evaporated to afford a reddish-brown solution. Yield: 3.70 g (99%).

¹H NMR (400 MHz, CD₂Cl₂): δ 3.66 (s), 3.76 (s), 7.13 (m), 7.22 (m), 7.31 (t, J = 7.63), 7.42 (d, J = 7.02), 7.57 (d, J = 7.93), 7.65 (td, J = 6.87), 8.48 (d, J = 6.41). ¹³C NMR (400 MHz, CD₂Cl₂): δ 58.76, 60.23, 122.22, 123.07, 127.31, 128.56, 129.20, 136.63, 139.63, 149.23, 160.22. High-resolution MS: 290.17 (M + H⁺).

fac-[Ru^{III}Br₃(ebpma)]

fac-[Ru^{II}(NCCH₃)₃(ebpma)](PF₆)₂ (316 mg, 430 µmol) was suspended in water–ethanol (1/1, v/v, 60 cm³) and hydrobromic acid (48%, 1.0 cm³) was added. The mixture was refluxed for 1.5 hours and the obtained yellow solution was concentrated by heating until 3 cm³. The mixture was allowed to stand in a fridge. The reddish-purple precipitate was collected by filtration, washed with water, ethanol, and diethyl ether and dried *in vacuo*. Yield: 170 mg (74%).

Elemental analysis. Calcd for $C_{14}H_{17}N_3Br_3Ru$: C 29.97, H 3.05, N 7.41%. Found: C 29.60, H 3.02, N 7.40%.

fac-[Ru^{III}Cl₃(bbpma)]

This complex was synthesized in a similar manner to that of the corresponding complex bearing ebpma, *fac*- $[Ru^{III}Cl_3(ebpma)]$.³¹ RuCl₃·*n*H₂O (500 mg, 42.01 wt%) was dissolved in water–ethanol (2/3, v/v, 50 cm³) and refluxed until

the color of the solution turned dark blue ('Ru-blue' solution). To the Ru-blue solution, hydrochloric acid $(35-37\%, 4.0 \text{ cm}^3)$ and bbpma (590 mg, 2.04 mmol) were added in this order and the solution was refluxed for 10 hours. The obtained solution was concentrated to 10 cm³ by heating and allowed to stand in a fridge overnight. A red-brown precipitate was collected by filtration, washed with water, ethanol, and diethyl ether in this order and dried *in vacuo*. Yield: 751 mg (76%).

Elemental analysis. Calcd for $C_{19}H_{19}N_6Cl_3Ru$: C 45.93, H 3.85, N 8.46%. Found: C 45.74, H 3.72, N 8.46%. FAB MS: 521 (M + Na).

$[{Ru^{II,III}(ebpma)}_2(\mu-Cl)_3](PF_6)_2([2](PF_6)_2)$

(a) $[{Ru^{II,III}(ebpma)}_2(\mu-Cl)(\mu-OMe)_2](PF_6)_2$ ([1](PF₆)₂; 100 mg, 96 µmol) was dissolved in acetone (15 cm³) under an argon atmosphere and hydrochloric acid (35–37%, 0.05 cm³) was added and the mixture was stirred for 10 min at room temperature. To the green solution, 10 cm³ of water containing NH₄PF₆ (200 mg, 1.23 mmol) were added and the volume was reduced until a blue precipitate appeared. The blue precipitate was collected by filtration, washed with water, ethanol, and diethyl ether and dried *in vacuo*. Yield: 82 mg (81%).

(b) *fac*-[Ru^{III}Cl₃(ebpma)] (150 mg, 345 μ mol) and zinc (250 mg, 3.82 mmol) were suspended in acetone (15 cm³). To the suspension, hydrochloric acid (35–37%, 0.5 cm³) was added and the mixture was stirred for 6 hours at room temperature to obtain a reddish-brown solution. After the remaining zinc was removed, the solution was allowed to stand for two hours in air to obtain a green solution. To the green solution, 20 cm³ of water and NH₄PF₆ (300 mg, 1.84 mmol) were added and the solution was evaporated until a blue precipitate was obtained. The blue precipitate was collected by filtration, washed with water, ethanol, and diethylether and dried *in vacuo*. Yield: 155 mg (85%).

Elemental analysis. Calcd for $C_{28}H_{34}N_6Cl_3Ru_2P_2F_{12}$: C 31.94, H 3.25, N 7.98%. Found: C 32.17, H 3.39, N 7.63%. FAB MS: 765 (M – 2PF₆). The effective magnetic moment (μ_{eff}) of the blue complex, [2](PF₆)₂, at 25 °C; 1.94 μ_B .

[{Ru^{II,III}(ebpma)}₂(µ-Cl)(µ-Br)₂](PF₆)₂ ([3](PF₆)₂)

 $[{Ru^{II,III}(ebpma)}_{2}(\mu-Cl)(\mu-OMe)_{2}](PF_{6})_{2}([1](PF_{6})_{2}; 100 mg, 96 \mu mol)$ was dissolved in acetone (15 cm³) under an argon atmosphere and hydrobromic acid (48%, 0.05 cm³) was added. The solution was stirred for 10 min at room temperature. To the obtained green solution, NH₄PF₆ (200 mg, 1.23 mmol) and 20 cm³ of water were added and the volume of the solution was reduced until a green precipitate was obtained. The green solid was collected by filtration and washed with water, ethanol, and diethyl ether and dried in vacuo. The green solid was purified by precipitating in acetone (10 cm³) to remove the red-purple solid, fac-[Ru^{III}Br₃(ebpma)], by filtration. To the obtained green filtrate, 5 cm³ of water was added and the green solution was condensed until a green precipitate appeared. The green solid was collected by filtration and washed with water, ethanol, and diethyl ether in this order and dried in vacuo. Yield: 30 mg (27%).

Elemental analysis. Calcd for $C_{28}H_{34}N_6ClBr_2Ru_2P_2F_{12}$: C 30.26, H 3.18, N 7.18%. Found: C 30.53, H 3.24, N 6.93%. FAB MS: 904 (M–PF₆), 759 (M–2PF₆).

[{Ru^{II,III}(ebpma)}₂(µ-Br)(µ-OCH₃)₂](PF₆)₂ ([4](PF₆)₂)

fac-[Ru^{III}Br₃(ebpma)] (150 mg, 264 µmol) and zinc (100 mg, 1.53 mmol) were suspended in methanol (15 cm³) and stirred for 2 days at room temperature. To the suspension, 10 cm³ of water was added to dissolve the precipitated green solid and the remaining zinc was removed by filtration. NH_4PF_6 (150 mg, 920 µmol) was dissolved in the obtained green solution and the volume of the solution was reduced by using a rotary evaporator until a green precipitate appeared. The precipitate was collected by filtration, washed with water, ethanol, and diethyl ether and dried *in vacuo*. Yield: 125 mg (87%).

Elemental analysis. Calcd for $C_{30}H_{40}N_6O_2BrRu_2P_2F_{12}$: C 33.10, H 3.70, N 7.72%. Found: C 33.06, H 3.72, N 7.67%. FAB MS: 853 (M–2PF₆).

[{Ru^{II,III}(ebpma)}₂(µ-Cl)₂(µ-OCH₃)](PF₆)₂ ([5](PF₆)₂)

[{Ru^{II,III}(ebpma)}₂(μ -Cl)₃](PF₆)₂ ([2](PF₆)₂; 50 mg, 47 μ mol) was dissolved in acetone–methanol (2/1, v/v, 15 cm³) and zinc (50 mg, 0.76 mmol) was added, and then the mixture was stirred for 5 min at room temperature. After the remaining zinc was filtered, the reddish-brown solution was oxidized in air until it turned green. After NH₄PF₆ (50 mg, 310 μ mol) and water (10 cm³) were added, the volume of the solution was reduced until a blue precipitate appeared by using a rotary evaporator. The obtained blue solid was collected by filtration and washed with water, ethanol, and diethylether and dried *in vacuo*. Yield: 29 mg (58%).

Elemental analysis. Calcd for $C_{29}H_{37}N_6O_1Cl_2Ru_2P_2F_{12}$: C 33.22, H 3.56, N 8.01%. Found: C 33.12, H 3.57, N 7.90%. FAB MS: 904 (M–PF₆), 759 (M–2PF₆⁻).

[{Ru^{II,III}(bbpma)}(µ-Cl)(µ-OCH₃)₂](PF₆)₂·2H₂O ([6](PF₆)₂·2H₂O)

fac-[Ru^{III}Cl₃(bbpma)] (100 mg, 200 µmol) and zinc were suspended in methanol (50 cm³) and stirred for 72 hours at room temperature. The remaining zinc was removed and a green solution was obtained. To the solution, 10 cm³ of ethanol containing NH₄PF₆ (200 mg, 1.30 mmol) was added and the solution was slowly concentrated in air. The precipitated green solid was collected by filtration and washed with water. For purification, the solid was dissolved in acetonitrile and an insoluble matter was removed. The obtained filtrate was dried to obtain a black powder. Yield: 75 mg (64%).

Elemental analysis. Calcd for $C_{40}H_{48}N_6O_4ClRu_2P_2F_{12}$: C 39.89, H 4.02, N 6.98%. Found: C 39.97, H 4.00, N 6.94%. FAB MS: 1024 (M–PF₆), 879 (M–2PF₆), 439 {(M–2PF₆)/2}.

X-ray crystallography

Single crystals of three diruthenium complexes, [{Ru^{II,III} (ebpma)}₂(μ -Cl)₃](PF₆)₂·(CH₃)₂CO ([2](PF₆)₂·(CH₃)₂CO; CCDC 1861325†), [{Ru^{II,III}(ebpma)}₂(μ -Cl)(μ -Br)₂](PF₆)₂·0.5H₂O·(CH₃)₂CO ([3](PF₆)₂·0.5H₂O·(CH₃)₂CO; CCDC 1861084†), and [{Ru^{II,III} (ebpma)}₂(μ -Br)(μ -OCH₃)₂](PF₆)₂·H₂O ([4](PF₆)₂·H₂O; CCDC

1861326†), were obtained by diffusion of diethyl ether into the acetone solutions at room temperature. Each single crystal was platelet shaped and the size was $0.200 \times 0.160 \times 0.030$ mm for [2](PF₆)₂·(CH₃)₂CO, $0.07 \times 0.07 \times 0.03$ mm for [3](PF₆)₂·0.5H₂O·(CH₃)₂CO and $0.160 \times 0.100 \times 0.030$ mm for [4](PF₆)₂·H₂O, respectively. The colour was blue for [2](PF₆)₂·(CH₃)₂CO and green for [3](PF₆)₂·0.5H₂O·(CH₃)₂CO and [4](PF₆)₂·H₂O. The intensity data were collected on a Rigaku Mercury CCD diffractometer, using graphic monochromatized MoK α radiation (0.71069 Å). All the calculations were carried out using the Crystal Structure software package (Version 4.3, Single Crystal Structure Analysis Software). Structures were solved by direct methods, expanded using Fourier techniques and refined using full-matrix least-squares techniques.

Density functional theory (DFT) calculations

All the calculations were performed with the Gaussian09 program.³⁴ The geometry was optimized at the B3LYP level of density functional theory with the SDD (Ru)-6-31++G(d,p)(C,H, O,N) basis sets.

Results and discussion

Synthesis and characterization of dinuclear ruthenium complexes

Reduction of fac-[Ru^{III}Cl₃(ebpma)] at the Ru(III) center in methanol induced dissociation of chlorido ligands to give a dinuclear complex with the triply bridged framework, in which one chlorido and two methoxido ligands bridged between the ruthenium centers, [1](PF₆)₂.³³ Conversion reactions among the dinuclear ruthenium complexes in the mixed-valence state of Ru(II)–Ru(III) are shown in Scheme 1. A triply chloridobridged diruthenium complex, [2](PF₆)₂, was obtained in acetone containing hydrochloric acid, instead of methanol.³⁵ The composition of the bridging ligands could be controlled by the solvent and co-existing species in the solution. In a methanol-containing acetone solution, a two chlorido- and



Scheme 1 Conversion scheme of triply bridged complexes.

one methoxido-bridged complex, $[5](PF_6)_2$, was formed through a reduction reaction of $[2](PF_6)_2$. A reaction of $[1](PF_6)_2$ with hydrobromic acid in acetone afforded a corresponding one chlorido- and two bromido-bridged complex, $[3](PF_6)_2$. In methanol, through reduction reactions of *fac*-[Ru^{III}Br₃(ebpma)] or *fac*-[Ru^{III}Cl₃(bbpma)], one halogeno and two methoxidobridged complexes, $[4](PF_6)_2$ or $[6](PF_6)_2$, respectively, were obtained. One-electron reduction of the Ru(m) center induces wakening of the bridging ligands, resulting in substitution to another ligand in the reaction system, followed by oxidation to stabilize the dinuclear structure.

The electronic structures of the series of triply bridged complexes were found to be in the Ru(II)–Ru(III) state and the electronic spin was delocalized over the {Ru₂(μ -X)(μ -Y)(μ -Z)} core by magnetic susceptibility measurements, ESR spectra, NIR spectra and cyclic voltammetry, which will be discussed in detail in later sections.

Structural comparison of diruthenium complexes

The structures of the diruthenium cations showed a distorted octahedral geometry around the ruthenium centers, as shown in Fig. 1–3. The crystallographic data are summarized in Table S2† and the selected structural parameters are listed in Tables 1 and S3.† Each ruthenium center was coordinated by one amine and two pyridines of the ebpma ligand in the *fac*-manner and by three bridging ligands. For the triply chlorido-bridged complex, $[2]^{2+}$, two of the three bridging Cl⁻ ligands were located at the *trans* position to the amine group on one ruthenium center (Ru1) and pyridyl on the other ruthenium center (Ru2), while for $[3]^{2+}$ and $[4]^{2+}$, one halogeno ligand,



Fig. 1 Structure of [2]²⁺ with thermal ellipsoids at 50% probability.



Fig. 2 Structure of [3]²⁺ with thermal ellipsoids at 50% probability.



Fig. 3 Structure of [4]²⁺ with thermal ellipsoids at 50% probability.

 Table 1
 Structural parameters of triply bridged diruthenium complexes

	$[2]^{2^+}$	$[3]^{2+}$	$[4]^{2+}$	$[1]^{2+}$ (ref. 33)
X	Cl	Br	OCH ₃	OCH ₃
Y	Cl	Br	OCH ₃	OCH_3
Z	Cl	Cl	Br	Cl
Bond length	ns/Å			
Ru…Ru	2.875(2)	2.8959(8)	2.7072(4)	2.6898(3)
Ru–X	2.408(2)	2.5216(5)	2.068(2)	2.071(2)
Ru–Y	2.4016(19)	2.5217(3)	2.069(3)	2.071(2)
Ru–Z	2.417(3)	2.4121(11)	2.5427(6)	2.4200(9)
Bond angles	5/°			
Ru–X–Ru	73.12(4)	70.09(2)	81.75(9)	80.96(7)
Ru–Y–Ru	73.44(5)	70.09(2)	81.75(9)	80.96(7)
Ru–Z–Ru	73.03(5)	73.78(4)	64.329(16)	67.53(2)

Cl⁻ or Br⁻, was at the *trans* position to the amine on both Ru1 and Ru2 and two Br⁻ or CH₃O⁻ were *trans* to pyridine, respectively. Because of the order of σ -donating nature, CH₃O⁻ > Br⁻ > Cl⁻, the location of these bridging ligands is determined in relation to the position of σ -donating amines and two π -accepting pyridines in the ebpma ligand.

The structural parameters of the ebpma ligand were almost identical to those of the *fac*-form ebpma complexes as compared in Table S3,+^{31,33} The Ru…Ru distances of the triply bridged complexes of Ru(π)–Ru(π) in this work, [1]²⁺–[4]²⁺ (2.6898(3)–2.8959(8) Å), were within the range of the triply bridged mixed-valence complexes of Ru(π)–Ru(π), in which strong interactions between the Ru centers exist (2.753–3.325 Å),^{14,17–19} and were slightly longer than those of the isovalent doubly alkoxido-bridged complexes of Ru(π)– Ru(III) (2.606–2.6515 Å).^{17,38} The bridging Ru–Cl distances (2.3936(19)-2.4108(18)) were similar to those of mixed-valence complexes containing the triply chlorido-bridged framework, $\{Ru_2(\mu-Cl)_3\}$ (2.3511–2.5268 Å).^{17,19–21,38} The Ru–O(alkoxido) lengths, 2.068(3)-2.07072(4) Å, were longer than those in the doubly alkoxido-bridged unit of Ru(m)-Ru(m), $\{Ru_2(\mu-OR)_2\}$ (R; CH₃, C₂H₅, 2.022–2.042 Å),^{15,36,37} and shorter than those in the corresponding doubly alkoxido-bridged moiety of Ru(II)-Ru(II) (2.065-2.114 Å).^{39,40} The Ru-Cl-Ru angles (70.09(2)-73.44(5)°) were larger than those of the previously reported one chlorido- and two methoxido-bridged complex, $[1]^{2+}$, (67.51(3)°),³³ and smaller than those of the doubly chloridobridged complex of Ru(II)-Ru(II) (98.70-99.70°) and almost consistent with those of the triply chlorido-bridged complexes of Ru(II)-Ru(III) (70.2-87.16°).^{17,19-21,42,43} The structural comparisons indicated that the vacant d orbitals of the halogeno ligand had an influence on these structural features, in particular, the Ru-L-Ru (L; bridging ligand) angles, and stabilization of the mixed-valency of Ru(II)-Ru(III). The Ru-O(alkoxido)-Ru angles in the one bromido- and two methoxidobridged complex, $[4]^{2+}$, were 81.75(9)° and larger than those of the three chlorido-bridged one, $[2]^{2+}$. The angles were smaller than those of the doubly alkoxido-bridged complexes of Ru(II)-Ru(II) $(91.5-104.6^{\circ})^{39-41}$ and Ru(II)-Ru(III) $(100.13^{\circ})^{22}$ and closer to those of the corresponding Ru(III)-Ru(III) complexes (79.6-81.86°).^{15,36,37} These structural parameters of the present triply bridged diruthenium complexes indicated the strong interactions between the two ruthenium centres.

Mixed-valency of diruthenium complexes

The Ru(π)–Ru(π) mixed-valence electronic structure was evaluated by magnetic susceptibility measurements at 298 K, electron spin resonance (ESR) spectroscopy at 77 K in frozen acetone, electrochemical measurements and UV-vis-NIR spectroscopy in CH₃CN. The spectroscopic and electrochemical properties are summarized in Table 2.

The effective magnetic moments μ_{eff} were $1.79\mu_B$ for $[1](PF_6)_2$ and $1.94\mu_B$ for $[2](PF_6)_2$ at 300 K and the ESR spectra at 77 K indicated that an unpaired electronic spin was delocalized on the $\{Ru_2(\mu-X)(\mu-Y)(\mu-Z)\}$ core (Fig. S1 and Table S1[†]).

Cyclic voltammograms of the diruthenium complexes in $\rm CH_3CN$ showed two reversible one-electron reduction and oxidation waves at 25 °C in the potential window (Table 2 and

Table 2 Electrochemical and spectroscopic properties of triply bridged Ru(II)-Ru(III) complexes

	ebpma					
Ancillary ligand	$[2](PF_6)_2$	$[3](PF_6)_2$	$[4](PF_6)_2$	$[5](PF_6)_2$	$[1](PF_6)_2^{33}$	bbpma $[6](PF_6)_2$
$\lambda_{\max}(\epsilon)/nm (mol^{-1} dm^3 cm^{-1})$	328 (7150) 709 (6500)	328 (10 200) 732 (7540)	370 (12 000) 757 (8280)	351 (7890) 693 (7000)	370 (10 400) 734 (7870)	365 (9910) 728 (8210)
$\Delta \tilde{\nu}$ (found, calcd)/cm ⁻¹	1500 (500) 4170, 2000	1590 (300) 3920, 1700	1590 (300) 3900, 1300	1590 (200) 3960, 800	1520 (300) 4000, 1500	
$E_{1/2}$ /V at 298 K	5710, 3900 0.84	5620, 3800 0.78	5520, 3800 0.23	5770, 3800 0.50	5610, 3900 0.22	0.26
$K_{\rm c}$ (×10 ¹⁴)	-0.14 380	-0.10 7.8	-0.64 5.2	-0.41 24	-0.65 5.2	-0.61 5.1



Fig. 4 Cyclic voltammograms in CH_3CN at room temperature (a) [4](PF₆)₂, (b) [1](PF₆)₂, (c) [5](PF₆)₂, (d) [2](PF₆)₂, (e) [3](PF₆)₂ and (f) [6](PF₆)₂.

Fig. 4). These waves were assigned to one-electron oxidation and reduction processes from the Ru(II)-Ru(III) state, respectively, by the wave analyses of hydrodynamic voltammetry or normal pulse voltammetry (Fig. S4-S7, Tables S4 and S5†). The differences in redox potentials, as summarized in Table 2, were due to the electrostatic nature of the bridging halogeno (Cl⁻, Br⁻) and methoxido ligands, since the methoxido ligand shows more σ -electron donating nature than the chlorido ligand. Accompanied by substitution of the one bridging halogeno to the methoxido ligand, the redox potential shifts by ca. 0.3 V (e.g. $[1]^{2^+}$ and $[5]^{2^+}$), while only a slight change was shown by the difference between the Cl^{-} and Br^{-} ligand $([2]^{2+}$ and $[3]^{2+}$; *ca.* 50 mV), or between the ebpma and bbpma ligand $([\mathbf{1}]^{2+} \text{ and } [\mathbf{6}]^{2+}; 30 \text{ mV})$. In the K_c value, which reveals the stability of the mixed-valence state, no clear relationship with the kind of bridging ligand or un-bridging Rbpma ligand was shown.

For the triply chlorido-bridged complex, $[2]^{2^+}$, which shows a one-electron redox couple of Ru(II)–Ru(III)/Ru(II)–Ru(II) at -0.14 V (ν s. Ag|0.01 mol dm⁻³ AgNO₃), a corresponding Ru(II)– Ru(II) species was isolated through a reduction reaction with zinc in acetone.³⁵ An attempt to isolate the corresponding Ru(III)–Ru(III) species of $[1]^{2^+}$, which shows a lower one-electron oxidation potential of Ru(III)–Ru(III)/Ru(II)–Ru(III) at +0.22 V, has also been successful and a study describing this is in progress.

The diruthenium complexes showed characteristic absorption bands in the UV-vis region and very weak absorption bands around 1500 nm in the NIR region in CH₃CN (Table 2) and in CH₂Cl₂ (Fig. S8 and Table S6†). The weak absorption bands in the NIR region were also found in triply bridged mixed-valence complexes having the $\{Ru^{II}(\mu-X)_3Ru^{III}\}$ (X = Cl, Br)^{12,13} and $\{Ru^{II}(\mu-OH)_3Ru^{III}\}^{13}$ core, in which both the electronic transitions were attributed to intervalence-type exci-

tation on the delocalized dinuclear core.8,9 The band maximum in the visible region was independent of the polarity of the solvent: CH₂Cl₂, (CH₃)₂CO, CH₃CN or CH₃OH, as indicated in Tables S6 and S7.† The maximum absorption band λ_{max} and the MLCT band were exhibited in a shorter wavelength for those containing three bridging halogeno ligands, 328 nm for $[2]^{2+}$ and $[3]^{2+}$, compared to those containing one or two halogeno ligands, 351 nm for $[5]^{2+}$ and 365–370 nm for $[1]^{2^+},\,[4]^{2^+}$ and $[6]^{2^+},$ indicating that the $d\pi(\text{Ru})$ orbital is relatively more stabilized for $[2]^{2+}$ and $[3]^{2+}$ compared to the others. The other two bands shown in the NIR region suggested no explicit dependency of both λ_{max} and molar absorption coefficient ε on the combination of bridging ligands. To put the discussion one step forward, the isolation and investigation of the corresponding triply bridged Ru(II)-Ru(m) complexes without the bridging halogeno ligand, which has vacant d orbitals for an electron to pass through, seem to be important.

Spectroelectrochemical experiments for $[2]^{2+}$ and $[3]^{2+}$ using an Optically Transparent Thin-Layer Electrode (OTTLE) cell at room temperature showed spectral changes as shown in Fig. S9.[†] One-electron reduction reactions from the Ru(II)–Ru(III) state in acetone containing 0.1 mol dm⁻³ TEAP as an electrolyte afforded isovalent Ru(II)-Ru(II) species, showing isosbestic points, with a gradual decrease of the weak band around 700-730 nm and an increase of a new intense MLCT band around 410-440 nm, which was attributed to the electronic transitions from $d\pi(Ru)$ to $\pi^*(py)$. These isovalent species were reversibly changed to the original Ru(II)-Ru(III) state accompanied by spectroelectrochemical re-oxidation. The stability of the one-electron oxidized and reduced species of the Ru(II)-Ru(III) complexes was suggested by the reversibility of the one-electron reduction and oxidation waves in the CV measurement and the reversible spectral changes during redox reactions. The comproportionation constants K_c were estimated by the difference in potentials between two reversible redox couples of Ru(III)-Ru(III)/Ru(III)-Ru(II) and Ru(III)-Ru(II)/ $Ru(\pi)-Ru(\pi)$.¹⁰ The values were in the order of $10^{14}-10^{16}$. The analyses of the half width at the half maximum (HWHM) of the IVCT band of $[2]^{2+}$, $[3]^{2+}$ and $[4]^{2+}$ also supported the Class III state, according to Hush's theory,⁴⁴ in which $\tilde{\nu}_{1/2}$ (found) was smaller than $\tilde{\nu}_{1/2}$ (calcd). These results revealed that all the complexes were categorized into Class III along with the analyses of the IVCT bands observed in the NIR region in electronic transition spectra, according to the Robin-Day classification.32

The electronic structures of $[2]^{2^+} [3]^{2^+}$ and $[4]^{2^+}$ were theoretically studied by DFT calculations and the optimized structures of frontier orbitals with MOs are shown in Fig. S10–S14.† The contributions by the ruthenium centers, halogeno ligand(s) and methoxido ligands to each MO are listed in Table S8.† For the SOMO of these three mixed-valence complexes, contributions from the $\{Ru_2(\mu-X)(\mu-Y)(\mu-Z)\}$ core, which consists of the Ru centers and the three bridging ligands, were large, supporting that the one-electron oxidation and reduction reactions occur at the dinuclear core.

Conclusions

New mixed-valence diruthenium complexes, whose metal centers were triply bridged by halogeno and methoxido ligands bearing a tridentate ligand, ebpma or bbpma, [{Ru^{II}, ^{III}(Rbpma)}₂(μ -X)(μ -Y)(μ -Z)](PF₆)₂ (X, Y = Cl⁻, Br⁻ or CH₃O⁻), were synthesized through the reduction reactions of fac- $[Ru^{III}X_3(ebpma)]$ (X = Cl⁻, Br⁻) to the Ru(II) state, accompanied by the dissociation of chlorido ligand(s) under certain reaction conditions. By the synthetic strategy using reduction of the dinuclear core to control the reactivity of the bridging moiety, a wide range of diruthenium complexes having different kinds of bridging ligands could be designed and synthesized. The interconversion among the triply bridged complexes was also established by inducing dissociation of the bridging ligand(s) through reduction of the Ru(II)-Ru(III) center to Ru(II)-Ru(II) or reactions with acids. These kinds of bridging ligands could be controlled by the reaction conditions such as solvent and co-existing species in the reaction mixture. The Ru(II)-Ru(III) mixed-valence state was classified as a Class III state, according to the Robin-Day classification³² and Hush's theory,⁴⁴ for all those series of diruthenium complexes herein, which is quite a rare case. X-ray crystallography revealed that the shape of the diruthenium core structure, $\{Ru_2(\mu-X)(\mu-Y)(\mu-Z)\}$, and the position of the bridging ligand against the ebpma ligand were dependent on the kind of bridging ligand; the core structure of triply halogenoand $[3]^{2^+}$, resembled each bridged complexes, $[2]^{2^+}$ other and were relatively different from the one halogenoand two methoxido-bridged complexes, $[{Ru^{II,III}(ebpma)}]_2$ $(\mu-X)_2(\mu-OCH_3)^{2+}$ (X = Cl; $[1]^{2+}$, Br; $[4]^{2+}$). The more σ -donating methoxido ligand coordinates to the trans position toward the pyridine of ebpma. An electronic spin on the complex cation was delocalized over the $\{Ru_2(\mu-X)(\mu-Y)(\mu-Z)\}$ core to stabilize the Ru(II)-Ru(III) mixed-valence state, which was almost identical to the Ru^{2.5}-Ru^{2.5} state, regardless of the kind or combination of bridging ligand. The dinuclear core structure, $\{Ru_2(\mu-X)(\mu-Z)\}$, and the electronic properties such as redox potentials and electronic transition energy of dinuclear complexes could be controlled by the combination of bridging ligand(s).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We show our deep appreciation to Prof. Dr Shigeki Kuwata and Yoshihito Kayaki (Tokyo Institute of Technology) for the NMR measurements, Prof. Dr Ryo Miyamoto (Hirosaki University) for the comments on ESR signals and Prof. Dr Shinkoh Nanbu (Sophia University) for the DFT calculations.

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