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Supplementary Material Available: Tables S1–S7, listing IR and ^1H NMR data for the compounds, carbon-13 NMR data for complexes

17–21, and anisotropic temperature factors, complete bond angles, calculated hydrogen atom positions, and crystallographic data for compound 11 (15 pages); a table of observed and calculated structure factors for 11 (18 pages). Ordering information is given on any current masthead page.

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Synthesis and Properties of Binuclear Ruthenium Complexes with 2,7-Bis(2-pyridyl)-1,8-naphthyridine (bnpn). X-ray Crystal Structure of $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$

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The compounds $[\text{Ru}_2\text{Cl}_2(\text{bpy})_2\text{bnpn}](\text{PF}_6)_2$ (**1**) and $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$ (**2**) have been prepared and characterized. Cyclic voltammetry of **1** in acetonitrile shows two successive one-electron oxidations at 0.64 and 1.34 V (vs SSCE) and two one-electron reductions at -0.76 and -1.35 V. One-electron oxidation of **1** yields the corresponding stable mixed-valence Ru(II)–Ru(III) complex, which has significant metal–metal interactions, as indicated by the electrochemical and spectroscopic data. Complex **2** crystallizes in the tetragonal system, space group $I4_1cd$, with $a = b = 28.659$ (4) Å, $c = 13.968$ (3) Å, and $Z = 16$. The final reliability index R is 0.076 for 1909 reflections. The Ru–Ru distance is 2.28 (2) Å. The complex is paramagnetic with a μ_{eff} of 2.76 μ_B at 295 K, corresponding to two unpaired spins. The metal–metal bond order is 2. Cyclic voltammetry of **2** also displays multiple reversible one-electron redox processes at 0.72, -0.62 , and -1.37 V.

Introduction

Current developments in the area of binuclear ruthenium chemistry have resulted from extensive studies of two important classes of compounds, namely, mixed-valence diruthenium complexes of the Creutz–Taube type¹ and the metal–metal-bonded diruthenium tetracarboxylates and their derivatives.^{2,3} In the course of our investigations of the coordination properties of the tetradentate ligand 2,7-bis(2-pyridyl)-1,8-naphthyridine (bnpn), we have found this remarkable ligand forms stable diruthenium complexes that belong to these two distinct classes. The ability of bnpn to support both a multiple metal–metal-bonded and a mixed-valence system is unique with ruthenium; this has not been previously demonstrated in its complexes with copper,⁴ rhodium,^{5,6} and rhodium.⁷ In this article we report the syntheses and characterizations of $[\text{Ru}_2\text{Cl}_2(\text{bpy})_2\text{bnpn}](\text{PF}_6)_2$ (**1**) (bpy = 2,2'-bipyridine) and $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$ (**2**). One-electron oxidation of **1** yields the corresponding mixed-valence complex, the solution properties of which we also describe. Compound **2** is the most stable complex containing the Ru_2^{4+} core reported to date; its structure has been determined by X-ray crystallography.

Experimental Section

Materials. Reagent grade chemicals were used without further purification unless otherwise noted. Ruthenium trichloride trihydrate was purchased from Aldrich Chemical Co. The ligand bnpn and $\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}$ were prepared according to the literature.^{8,9} 2,2'-Bipyridine was recrystallized from ethanol prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized from ethyl acetate and then dried in a vacuum desiccator over P_2O_5 . Sephadex LH-20 was

used as received from Pharmacia Fine Chemicals and regenerated according to standard procedures. Spectrophotometric grade acetonitrile (CH_3CN), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) utilized in the electrochemical experiments were previously dried over 4-Å molecular sieves. Mallinckrodt spectrAR grade solvents were used for the spectroscopic and conductivity measurements.

Physical Measurements. Elemental analyses were performed by Alfred Bernhardt Analytisches Laboratorien. Infrared spectra of samples as KBr pellets were recorded on a Perkin-Elmer 283 or 683 spectrophotometer. Electronic absorption spectra were obtained on Cary 14, 15, and 118 spectrophotometers with 1-cm quartz cells at room temperature.

Molar conductivities, Λ_m , were determined for 1 mM solutions of the complexes in the appropriate solvent by using a Type CDM 2e No. 191500 conductivity meter (The London Co.). Magnetic susceptibility measurements were made by following two procedures: the Evans NMR method¹⁰ and the Faraday method using a Cahn-Ventron Faraday magnetic susceptibility apparatus.

Cyclic voltammetry and controlled-potential electrolysis were performed with an IBM EC/225 voltammetric analyzer. A conventional three-compartment cell was employed with a platinum-ball working electrode, a Pt-wire auxiliary electrode, and an aqueous saturated sodium chloride calomel (SSCE) as reference. A large-area platinum-wire gauze was used in the electrosynthesis experiments. The sample solution was at least 0.5 mM ruthenium complex in CH_3CN containing 0.1 M TBAP and was deaerated with argon prior to each run. $\Delta E_{1/2}$ values were taken as the average of the anodic and cathodic peak potentials. Electrochemical reversibility was judged on the basis of the following criteria:¹¹ (i) the separation between the anodic and cathodic peak potentials (ΔE_p) is $59/n$ mV, where n is the number of electrons involved in the redox reaction; (ii) the ratio of the anodic and cathodic peak currents (i_{pa}/i_{pc}) is unity. $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ was used as the standard in the electrochemical reversibility experiments. Redox n values were calculated by using Faraday's law from thin-layer potential-step coulometric data, as described elsewhere.¹²

Synthesis of Binuclear Complexes. All reactions were carried out under a nitrogen or argon atmosphere unless indicated otherwise; products were isolated and purified in air.

$[\text{Ru}_2\text{Cl}_2\text{bnpn}]$. (1) To 10 mL of absolute ethanol were added 19.7 mg (75 μmol) of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and 10 mg (35 μmol) of bnpn. The reaction was instantaneous with immediate formation of a heavy, dark brown

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precipitate. The mixture was refluxed for 24 h while vigorous magnetic stirring was maintained. A fine black solid was separated from the orange mother liquor by vacuum filtration and washed with copious amounts of ethanol and ether. A yield of 22.4 mg (91%) of product was obtained. The product yield was maximized when 1-butanol was used as the solvent instead of absolute ethanol. Anal. Calcd for $[\text{Ru}_2\text{C}_{18}\text{H}_{12}\text{N}_4\text{Cl}_6]$: C, 30.92; H, 1.73; N, 8.02; Cl, 30.42. Found: C, 30.98; H, 1.98; N, 7.92; Cl, 30.12. IR (KBr pellet): 3460 (br, s), 3070 (w), 1603 (s), 1525 (w), 1468 (s), 1430 (m), 1380 (m), 1332 (w), 1268 (m), 1152 (m), 1030 (w), 965 (w), 855 (m), 770 (s), 658 (w), 432 (w), 330 (br, m) cm^{-1} . $\Lambda_m(\text{DMF}) = 9 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$.

(2) Three to four drops of concentrated hydrochloric acid was added to 40 mg (50 μmol) of the diruthenium complex $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$ (**2**) in 25 mL of 1-butanol. The mixture was refluxed for 1 h, after which the initially faint blue solution turned dark blue, indicating complete dissolution of the diruthenium complex. Oxygen was then bubbled through the refluxing solution for 6 h. The black precipitate that had formed was collected on a glass frit, washed with 1-butanol and absolute ethanol, and then dried in a vacuum desiccator overnight. The black powder isolated (33 mg; 96% yield) displayed a metallic sheen. Anal. Calcd for $[\text{Ru}_2\text{C}_{18}\text{H}_{12}\text{N}_4\text{Cl}_6]$: C, 30.92; H, 1.73; N, 8.02. Found: C, 30.84; H, 2.02; N, 7.80.

$[\text{Ru}_2\text{Cl}_2(\text{bpy})_2\text{bnpn}](\text{PF}_6)_2$ (**1**). A mixture of $[\text{Ru}_2\text{Cl}_6\text{bnpn}]$ (40 mg, 57 μmol) and bpy (20 mg, 130 μmol) in 16 mL of deaerated aqueous (30%) ethanol was refluxed for 24 h. Addition of a saturated aqueous solution of ammonium hexafluorophosphate to the brownish black mixture precipitated a black solid, which was filtered out, washed with water, and then air-dried. The yield was 60 mg (90%). The crude product was redissolved in a minimum volume of absolute methanol, and the solution was filtered and chromatographed on a 1.2-m Sephadex LH-20 column. Elution with methanol gave a purple band as the major component preceded by a small brown band and followed by a very faint green band. The purple fraction was concentrated by rotary evaporation. Anhydrous ether was then added to precipitate the purple product. Anal. Calcd for $[\text{Ru}_2\text{C}_{38}\text{H}_{28}\text{N}_8\text{Cl}_2](\text{PF}_6)_2$: C, 39.35; H, 2.43; N, 9.66; Cl, 6.11. Found: C, 39.01; H, 2.37; N, 9.41; Cl, 6.88. IR (KBr pellet): 3440 (br, s), 3080 (vw), 1625 (vw), 1600 (m), 1520 (w), 1460 (m), 1440 (m), 1420 (m), 1315 (br, w), 1258 (m), 1235 (m), 1095 (s), 1020 (w), 895 (s), 840 (br, s), 760 (s), 720 (w), 652 (w), 625 (w), 550 (s) cm^{-1} . $\Lambda_m(\text{acetone}) = 284 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$.

The mixed-valence one-electron oxidation product of **1** was generated in acetonitrile solution by using Ce(IV). The red complex can likewise be prepared and isolated, though as yet not in pure form, as a fine red powder from the chemical reaction of **1** with liquid bromine in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ solution.

$[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$ (**2**). To bnpn (90 mg, 317 μmol) and $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}]$ (150 mg, 317 μmol) was added 30 mL of deaerated absolute methanol. The blue solution that formed immediately was magnetically stirred for 24 h, after which a previously deaerated aqueous solution of ammonium hexafluorophosphate was added to precipitate the blue product. After filtration, the crude product was reprecipitated from acetone-ether solution to give pure material. The yield was 200 mg (78%). Anal. Calcd for $[\text{Ru}_2\text{C}_{24}\text{H}_{21}\text{N}_4\text{O}_6]\text{PF}_6$: C, 35.65; H, 2.62; N, 6.93. Found: C, 35.31; H, 2.71; N, 6.72. IR (KBr disk): 3440 (br, s), 3080 (br, w), 2920 (br, w), 1630 (br, w), 1590 (m), 1540 (br, m), 1460 (m), 1440 (br, s), 1380 (w), 1350 (w), 1335 (w), 1270 (m), 840 (vs), 770 (m), 680 (m), 550 (m), 375 (w), 320 (w) cm^{-1} . $\Lambda_m(\text{acetone}) = 168 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; $\Lambda_m(\text{nitromethane}) = 88 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. The molar conductivities of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$, a 1:2 electrolyte, were measured to be 270 and 190 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in acetone and nitromethane, respectively.

Electrochemical Oxidations. The proper voltage settings for electrochemical oxidation of the complexes were determined from prior-survey current-potential (voltammetric) curves.

$[\text{Ru}_2\text{Cl}_2(\text{bpy})_2\text{bnpn}](\text{PF}_6)_2$. To a standard two-frit, three compartment electrochemical cell was added 10 mL of 0.6 mM ruthenium complex in acetonitrile containing 0.1 M TBAP as supporting electrolyte. Utilizing a Pt wire gauze as the working electrode and a Pt wire as the auxiliary electrode, controlled-potential electrochemical oxidation was carried out at 1.1 V (vs SSCE) to generate the mixed-valence [II,III] ion. Electrolysis was continued until the anodic or oxidative current decayed to less than 3% of its original value (after about 35 min). The initially purple solution turned burgundy red. Reverse (reductive) electrolysis was performed at 0.5 V for 20 min to regenerate the starting material; the cyclic voltammogram of this regenerated [II,III] complex was identical with that of freshly prepared starting material. For electrogeneration of the [III,III] species, the same solution was electrolyzed at 1.65 V until the anodic current had decreased to 0.5% of its original value (after about 40 min). The solution turned red initially but became greenish yellow after completion of the electrolysis reaction. The [III,III] complex was reduced at 0.5 V to regenerate the purple [II,II] complex.

Table I. Crystallographic Data^a for $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$

formula	$\text{Ru}_2\text{C}_{24}\text{H}_{21}\text{N}_4\text{O}_6\text{PF}_6$	Z	16
mol wt	808.56	ρ (calcd), g cm^{-3}	1.872
space	$I4_1cd$	μ , cm^{-1}	11.76
group		radiation; λ , \AA	Mo K α ; 0.710 69
$a = b$, \AA	28.659 (4)	temp, K	117
c , \AA	13.968 (3)	R^b	0.076
V , \AA^3	11472 (4)	R_w^c	0.101

^aNumbers in parentheses following certain data are estimated standard deviations in the least significant digit. ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

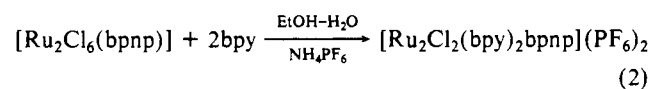
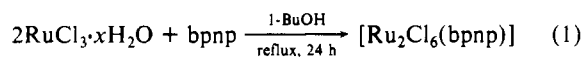
$[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$. Ten milliliters of a 1 mM solution of the diruthenium complex in acetonitrile containing 0.1 M TBAP- CH_3CN was electrolyzed as described in the preceding section. Upon oxidation at 1.2 V for 60 min, the color of the solution turned sequentially from blue to lavender, purple, gray, and, finally, green. On reduction at 0.0 V, a reverse-order color change was noted, except that the original blue color of the starting material was not obtained; this indicated that the oxidized complex had (slowly) undergone chemical side reactions. Cyclic voltammetry of this solution showed multiple irreversible redox peaks quite distinct from those of the parent complex and provided direct evidence that the starting material was indeed not generated.

X-ray Structure Determination. Dark blue crystals of $\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$ were grown by slow evaporation from a solution of the compound in methanol. Diffraction data were collected on a Picker automated diffractometer equipped with a variable-temperature device. Pertinent crystal data and data collection parameters are given in Table I. Three standard reflections measured every 97 reflections showed no appreciable decay. Observed intensities were corrected for Lorentz and polarization effects and for absorption of X-rays. All computations were done on a DEC VAX 11/780 computer at the University of California, Los Angeles. Scattering factors and corrections for anomalous dispersion were taken from ref 13.

The structure was solved by a combination of direct and heavy-atom methods. The positional coordinates of the ruthenium atoms were obtained with MULTAN. A difference Fourier map phased on the refined coordinates of the ruthenium atoms revealed the positions of all the non-hydrogen atoms in the asymmetric unit. The hexafluorophosphate ion was severely disordered; two orientations of the anion with 56% and 44% occupancies were resolved, and this model was refined as a rigid group with a P-F distance of 1.53 \AA .¹⁴ The positions of the ring hydrogen atoms were calculated by assuming idealized geometries; these atoms were assigned an isotropic thermal parameter of 2.07 \AA^2 . No attempt was made to locate the acetate hydrogens. Full-matrix least-squares refinement with anisotropic thermal parameters for the two ruthenium and the six acetate oxygen atoms and isotropic thermal parameters for the rest of the non-hydrogen atoms (the hydrogen atom parameters were kept fixed) converged at $R = 0.076$ and $R_w = 0.101$. The largest peak in the final difference map, 1.1 $e/\text{\AA}^3$, is in the vicinity of the PF_6^- ion and probably arises due to the inadequacy of the model to account for the electron density in that region. Selected molecular dimensions are listed in Table II. Tables of positional and thermal parameters, observed and calculated structure factors, and all other bond lengths and angles have been deposited as supplementary material.

Results and Discussion

$[\text{Ru}_2\text{Cl}_2(\text{bpy})_2\text{bnpn}](\text{PF}_6)_2$ (**1**). The purple complex **1** was prepared from a two-step reaction of commercial ruthenium trichloride with bnpn to form an extremely insoluble diruthenium(III) intermediate, $[\text{Ru}_2\text{Cl}_6\text{bnpn}]$, followed by reduction of this intermediate in refluxing water-ethanol solution with a stoichiometric quantity of 2,2'-bipyridine (eqs 1 and 2).



A corresponding 1,8-naphthyridine (napy) derivative, $[\text{Ru}_2\text{Cl}_2(\text{napy})_2\text{bnpn}](\text{PF}_6)_2$, may also be prepared according to

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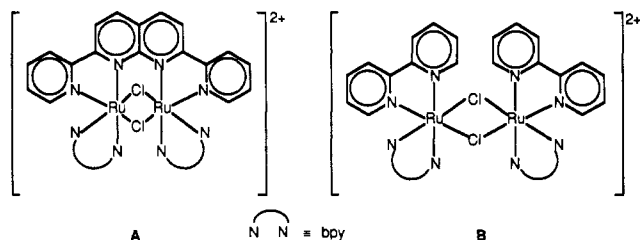
Table II. Selected Bond Distances and Angles for $[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$

Distances (Å)			
Ru(1)–Ru(2)	2.28 (2)	C(3)–O(4)	1.32 (3)
Ru(1)–N(1)	2.21 (2)	C(5)–O(5)	1.26 (3)
Ru(1)–N(2)	2.00 (2)	C(5)–O(6)	1.25 (2)
Ru(2)–N(3)	2.05 (2)	N(1)–C(7)	1.32 (3)
Ru(2)–N(4)	2.24 (2)	N(1)–C(11)	1.37 (3)
Ru(1)–O(1)	2.05 (2)	N(2)–C(12)	1.38 (3)
Ru(1)–O(3)	2.09 (2)	N(2)–C(16)	1.33 (2)
Ru(1)–O(5)	2.11 (2)	N(3)–C(16)	1.36 (3)
Ru(2)–O(2)	2.04 (2)	N(3)–C(19)	1.37 (3)
Ru(2)–O(4)	2.07 (1)	N(4)–C(20)	1.40 (3)
Ru(2)–O(6)	2.08 (1)	N(4)–C(24)	1.33 (3)
C(1)–O(1)	1.24 (3)	C(1)–C(2)	1.53 (4)
C(1)–O(2)	1.28 (3)	C(3)–C(4)	1.54 (4)
C(3)–O(3)	1.28 (3)	C(5)–C(6)	1.52 (4)

Angles (deg)			
Ru(2)–Ru(1)–N(1)	167.2 (4)	Ru(1)–Ru(2)–N(3)	91.1 (5)
Ru(2)–Ru(1)–N(2)	89.4 (5)	Ru(1)–Ru(2)–N(4)	167.7 (5)
Ru(2)–Ru(1)–O(1)	90.3 (5)	Ru(1)–Ru(2)–O(2)	88.2 (5)
Ru(2)–Ru(1)–O(3)	90.7 (5)	Ru(1)–Ru(2)–O(4)	88.9 (4)
Ru(2)–Ru(1)–O(5)	89.4 (4)	Ru(1)–Ru(2)–O(6)	88.8 (4)
N(1)–Ru(1)–N(2)	78.1 (6)	N(3)–Ru(2)–N(4)	77.1 (6)
N(1)–Ru(1)–O(1)	87.7 (8)	N(3)–Ru(2)–O(2)	93.3 (8)
N(1)–Ru(1)–O(3)	92.2 (8)	N(3)–Ru(2)–O(4)	89.5 (8)
N(1)–Ru(1)–O(5)	103.1 (6)	N(3)–Ru(2)–O(6)	179.8 (9)
N(2)–Ru(1)–O(1)	93.7 (8)	O(2)–Ru(2)–O(4)	176.0 (7)
N(2)–Ru(1)–O(3)	90.6 (8)	O(2)–Ru(2)–O(6)	86.8 (8)
N(2)–Ru(1)–O(5)	178.7 (6)	O(4)–Ru(2)–O(6)	90.3 (8)
O(1)–Ru(1)–O(3)	175.6 (7)	N(4)–Ru(2)–O(2)	95.9 (8)
O(1)–Ru(1)–O(5)	86.6 (8)	N(4)–Ru(2)–O(4)	87.5 (8)
O(3)–Ru(1)–O(5)	89.1 (7)	N(4)–Ru(2)–O(6)	103.0 (6)

eq 2; its properties¹⁵ closely parallel those of 1. However, on purification, a good fraction of it adsorbs on the chromatographic column and, during the electrochemical measurements, on the Pt electrode. The formulations of the complexes were made on the basis of their elemental analyses, molar conductivities, infrared spectra (Experimental Section), and redox chemistry. That $[\text{Ru}_2\text{Cl}_2\text{bnpn}]$ may be prepared alternatively from the reaction of 2 with HCl under oxidizing conditions further supports its formulation.

Complex 1 is air-stable both in the solid state and in solution. It is soluble in common organic solvents like methanol, acetone, and acetonitrile. Attempts to solve its structure by X-ray diffraction methods were unsuccessful due to the poor quality of the crystals obtained.¹⁵ Presumably, its structure is as shown in A.



Meyer and co-workers¹⁶ had prepared a similar complex $[\text{Ru}_2\text{Cl}_2(\text{bpy})_4]^{2+}$ (B), with two separate bipyridine ligands in place of bnpn. Surprisingly, this seemingly trivial difference leads to distinct properties for the two complexes. Thus while Meyer's dimer rapidly decomposes in acetonitrile to form mononuclear, solvated species, 1 is stable in acetonitrile for months, as evidenced by its electronic absorption spectrum. In addition, electrochemistry of the dimer is accompanied by decomposition, giving rise to only a transient mixed-valence species, while electrochemistry of 1 is clean and reversible over an even wider potential range; the

Table III. Electronic Absorption Data for the Binuclear Ruthenium Complexes and the Free Ligands in Acetonitrile^a

complex	λ_{max} , nm	ϵ_{max} , $10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$	
$[\text{Ru}_2\text{Cl}_2(\text{bpy})_2\text{bnpn}](\text{PF}_6)_2$	636 sh	5.61	
	576	9.65	
	477	7.61	
	351	46.6	
	290 sh	42.9	
	283	45.9	
	251 sh	35.5	
	246	35.9	
	$[\text{Ru}_2(\mu\text{-O}_2\text{CCH}_3)_3\text{bnpn}]\text{PF}_6$	917	1.77
		729	5.79
612		5.37	
586 sh		3.86	
520 sh		2.73	
440 sh		2.24	
351		33.4	
287		18.6	
274		24.1	
246		35.1	
$[\text{Ru}_2\text{Cl}_2(\text{bpy})_2\text{bnpn}]^{3+ b}$	770	5.51	
	556	4.78	
	477	4.17	
	366 sh		
	350	52.1	
	275	61.7	
	236	45.0	
	$[\text{Ru}_2\text{Cl}_2(\text{bpy})_2\text{bnpn}]^{4+ b}$	366	40.7
		352 sh	31.9
		300 sh	30.1
278		36.3	
bnpn ^c		355	330
		340	330
		323 sh	
bpy ^d		280	420
		250	660
		233	9.6
	281	13.4	

^a At room temperature; sh = shoulder. ^b In 0.1 M $[\text{NBu}_4][\text{ClO}_4]-\text{CH}_3\text{CN}$. The spectral region examined for these and the [II,II] complex is 220–1700 nm. ^c From ref 5. ^d From: Basu, A.; Weiner, M. A.; Strekas, T. C.; Gafney, H. D. *Inorg. Chem.* **1982**, *21*, 1085.

corresponding mixed-valence form of 1 can be prepared both electrochemically and chemically. It is obvious that the bnpn ligand imparts the stability necessary to keep the diruthenium unit intact. Consequently, the binuclear complexes in this study are resistant to bridge-cleavage reactions that are typical and facile for other bis(μ -chloro) dimers of ruthenium(II).¹⁶

The electronic absorption spectral data for the binuclear complexes and the free ligands are summarized in Table III. The spectrum of 1 is characterized by two main features, namely, intense ligand-localized or intraligand (IL) $\pi \rightarrow \pi^*(\text{bpy})$ and $\pi \rightarrow \pi^*(\text{bnpn})$ bands in the ultraviolet region and metal-to-ligand charge-transfer (MLCT) $d\pi(\text{Ru}) \rightarrow \pi^*(\text{L})$ bands in the visible region. Below 300 nm, the IL bands of both polypyridine ligands overlap, as evidenced by the width of the bands at ca. 250 and 280 nm. For complexes of the type $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^+$ (where py = pyridine)¹⁷ and $[\text{Ru}(\text{bpy})_2\text{XL}]^+$ (where X is a halide and L is an N-heterocyclic ligand), very intense UV bands characteristically occur at ca. 290 and 240 nm, which have been assigned to $\pi \rightarrow \pi^*$ transitions of the bpy ligands.^{18a} The intense band at 351 nm distinctively corresponds to a bnpn $\pi \rightarrow \pi^*$ transition. Unlike analogous $[(\text{bpy})_2\text{ClRuL}]_2$ complexes (L = pyrazine, pyrimidine, and 4,4'-bipyridine),^{18b} which display only one broad visible absorption band, 1 shows two well-resolved bands at 477 and 576 nm. These bands are tentatively assigned to $d\pi(\text{Ru}) \rightarrow$

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Table IV. Electrochemical Data for the Binuclear Ruthenium Complexes in 0.1 M TBAP-CH₃CN at 25 °C

compd	$E_{1/2}$, ^a V	i_c/i_a , ^b	ΔE_p , ^c mV
[Ru ₂ Cl ₂ (bpy) ₂ bnpn](PF ₆) ₂	0.64	1	75
	1.34	1	75
	-0.76	1	75
	-1.35	1	70
[Ru ₂ (μ-O ₂ CCH ₃) ₂ bnpn]PF ₆	0.72	1	70
	-0.62	1	70
	-1.37	0.9	75

^aHalf-wave potentials were measured versus a saturated sodium chloride calomel reference electrode (SSCE) at a scan rate of 200 mV s⁻¹. ^bRatio of anodic to cathodic peak currents. ^cDifference between cathodic and anodic peak potentials.

$\pi^*(bpy)$ and $d\pi(Ru) \rightarrow \pi^*(bnpn)$ transitions, respectively, similar to assignments made for the binuclear complex [(bpy)₂Ru(dpp)Ru(bpy)₂](ClO₄)₄, where dpp is μ -2,3-bis(2-pyridyl)pyrazine.^{19a} The bnpn-centered transition is of lower energy, consistent with the increased delocalizing ability of this ligand. MLCT transitions that terminate in two different ligands within a complex have also been observed in complexes of the type [Ru(bpy)₂L](PF₆)₂, where L is a 3,3'-polymethylene-bridged derivative of 2,2'-biquinoline and 2,2'-bi-1,8-naphthyridine.^{19b} In the latter complex, for example, the bipyridine-centered and the naphthyridine-centered absorptions occur at 436 and 574 nm, respectively. Further support for our assignments can be obtained from the spectrum of the mononuclear complex [(bpy)₂Ru(bnpn)]²⁺, which shows a broad band in the visible region at 450 nm with a distinct shoulder at 515 nm.¹⁵ Analogous to the assignments made for the mononuclear fragment of the binuclear dpp complex mentioned above,^{19a} the shoulder at 515 nm may correspond to a MLCT transition where the π -acceptor orbital is principally localized on the bnpn ligand.

The cyclic voltammogram of **1** in 0.1 M TBAP-CH₃CN is shown in Figure 1A; the redox potentials, reported here as $E_{1/2}$ values vs SSCE at 23 °C, are listed in Table IV. The peak potentials were independent of scan rate. Thin-layer coulometric measurements indicated that each oxidation and each reduction wave involved a one-electron process. Although the separations between the anodic and corresponding cathodic peaks ($\Delta E_p = 70$ –75 mV) were larger than the value (59 mV) expected for a reversible one-electron process, the observed values are comparable to those obtained for the standard [Ru(bpy)₃]²⁺ under identical experimental conditions. In the potential range -2.0 to +2.0 V, complex **1** undergoes two successive reversible one-electron oxidations and two reversible one-electron reductions. The reductions are localized on the aromatic ligands, as previously observed in dirhenium- and dirhodium-bnpn complexes.⁵⁻⁷ Typical of ruthenium complexes, the oxidations are metal-localized; specifically, the redox potentials at 0.64 and 1.34 V are for the Ru(III)/Ru(II) couple corresponding to oxidation of the [II,II] complex first to the mixed-valence [II,III] ion and subsequently to the [III,III] ion. The first reduction potential is significantly more anodic than the corresponding value of 0.3 V for the monomeric [Ru(bpy)₂Cl₂]¹⁶ due to the electrostatic effect exerted by the adjacent Ru(II) ion in the binuclear complex. However, it is less anodic compared to Meyer's dimer, which implies a higher Ru(II) t_2 orbital energy in **1**.^{19a} Hence, bnpn may not be as efficient in stabilizing the Ru(II) state as bpy. The unusually large difference of 0.70 V in the potentials between the two oxidation waves of **1** suggests significant electronic interactions between the metal centers and a stability of the mixed-valence species much greater than that observed for Meyer's complex. The comproportionation constant, K_{com} , calculated for the reaction

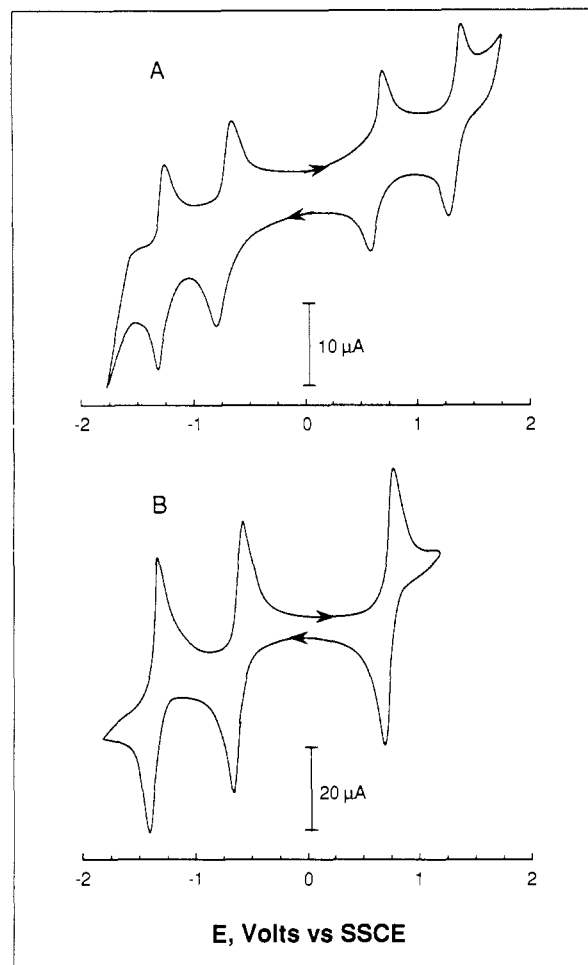
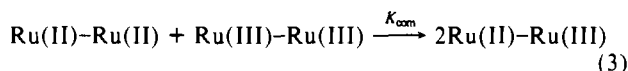


Figure 1. Cyclic voltammograms of [Ru₂Cl₂(bpy)₂bnpn](PF₆)₂ (A, 0.5 mM) and [Ru₂(μ-O₂CCH₃)₂bnpn]PF₆ (B, 1 mM) in 0.1 M [(C₄H₉)₄N][ClO₄]-CH₃CN at a scan rate of 200 mV/s.

is 7.0×10^{11} . This value is even larger than the values of ca. 10^8 for the delocalized mixed-valence complex²⁰ [Ru(NH₃)₅N₂]⁵⁺ and ca. 10^6 for the Creutz-Taube ion,²¹ [Ru(NH₃)₃]₂pyz]⁵⁺.

Controlled-potential electrolysis experiments confirmed the formation of the red mixed-valence [II,III] complex and the yellow [III,III] complex by two successive one-electron oxidations of **1** in acetonitrile. The [II,III] complex generated chemically in acetonitrile by using Ce(IV) displayed a broad ($\Delta\nu_{1/2} = 3.4 \times 10^3$ cm⁻¹) band at 770 nm ($\epsilon = 5.51 \times 10^3$ M⁻¹ cm⁻¹), which was not observed in the spectra of the [II,II] and [III,III] complexes. This band has been assigned to an intervalence transition (IT), a feature characteristic of mixed-valence complexes.²² The properties of this band deviate considerably from those predicted by Hush for a weakly interacting class II system.²³ For example, the calculated bandwidth at half-height for such a system is 5.5×10^3 cm⁻¹, which is significantly larger than the observed bandwidth, assuming the curves to be Gaussian. Furthermore, the band energy varies only very slightly with the dielectric properties of the solvent. These data as well as the relatively high intensity of the IT band suggest extensive electron delocalization in the complex, which seems reasonable in view of the short metal-metal distance (~ 3.2 Å)¹⁵ in **1** and the presence of both naphthyridine and chloride bridges. The lower oxidation potentials observed for **1** when compared to Meyer's dimer has indicated that bnpn may not be as efficient a π -back-bonding ligand as bpy. If this is indeed the case, then a large extent of the electronic

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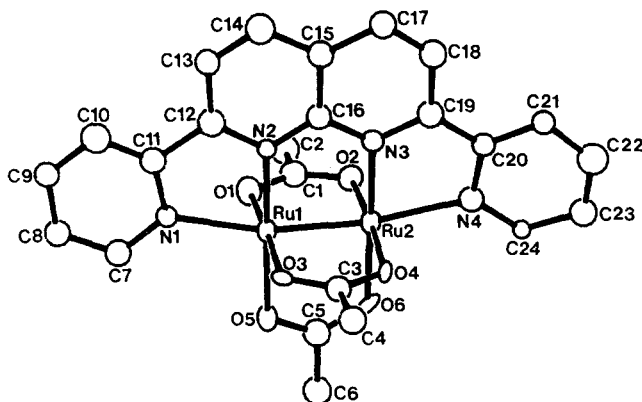


Figure 2. Structure of the tris(μ -acetato)(2,7-bis(2-pyridyl)-1,8-naphthyridine)diruthenium(II) cation. The hydrogen atoms have been omitted for clarity.

coupling occurs, not through the bnpn ligand but via enhanced chloride-bridge-mediated interactions due to a decrease in competitive back-bonding to bnpn. Such effects can be important, as suggested by the fact that, in $[(bpy)_2ClRu(py)RuCl(bpy)_2]^{3+}$, the valences are localized, while in $[(NH_3)_3Ru(py)Ru(NH_3)_2]^{5+}$, where there are no ligands competing for $d\pi$ Ru(II) electron density, enhanced Ru(II)-Ru(III) overlap apparently leads to equivalent ruthenium sites.²⁴⁻²⁶

Although the properties of the IT band imply extensive delocalization in the [II,III] complex, the UV-visible spectra of the mixed-valence ion is roughly a composite of the [II,II] and [III,III] spectra, which indicates that the complex is probably not completely delocalized. Thus, in the Robin and Day scheme,²⁷ it may well lie at the boundary of the class II and class III systems.

$[Ru_2(\mu-O_2CCH_3)_3bnpn]PF_6$ (**2**). The replacement of a bridging acetate and two chloride ligands on $[Ru_2(\mu-O_2CCH_3)_4Cl]_n$ with a molecule of bnpn to form the binuclear complex $[Ru_2(\mu-O_2CCH_3)_3bnpn]^+$ occurs under unusually mild conditions; the reaction in absolute methanol is immediate at room temperature to give product in >80% yield. A unique feature of **2** is that it is air-stable both in the solid state and in solution. Among diruthenium complexes studied to date, it has been found that most of the stable compounds have the Ru_2^{5+} core; i.e. each metal ion has a formal oxidation state of +2.5.^{32,33} Recently, a few Ru_2^{4+} ²⁹⁻³¹ and Ru_2^{6+} ^{32,33} complexes have been reported, but they are generally less stable. In fact, all the reported Ru_2^{4+} complexes with nitrogen and acetate donor ligands are extremely air-sensitive.

The X-ray structure of **2** (Figure 2) shows a pair of ruthenium(II) ions bridged by bnpn and three acetate ligands with an octahedral geometry about each metal center. The Ru(1)-Ru(2) distance of 2.28 (2) Å is within the wide range of distances (2.238-2.408 Å) observed for metal-metal-bonded diruthenium(II) complexes derived from the parent tetracarboxylates.²⁹⁻³¹ It is the shortest metal-metal distance observed in a transition-metal complex of bnpn. The average Ru-N(naphthyridine) distance

of 2.02 (2) Å is shorter than the Ru-N(pyridine) distance of 2.23 (2) Å, as is typical for mono- and binuclear bnpn complexes. However, the Ru-N(pyridine) distance is unusually long presumably due to the trans effect of the Ru-Ru multiple bond.

The effective magnetic moment of **2** as a powder is 2.79 μ_B at 295 K. This value corresponds to two unpaired electrons and is comparable to μ_{eff} values observed in other diruthenium complexes with the Ru_2^{4+} core. The two possible electronic configurations are thus $\sigma^2\pi^4\delta^2\delta^*\pi^*2$ and $\sigma^2\pi^4\delta^2\pi^*3\delta^*1$ depending on whether a $\delta^* < \pi^*$ or $\pi^* < \delta^*$ ordering exists, to give a Ru-Ru bond order of 2.

The electronic spectrum of **2** in acetonitrile shows prominent, broad absorption bands in the visible region at 612 and 729 nm ($\epsilon \sim 5000$ M⁻¹ cm⁻¹), with shoulders at 568, 520, and 440 nm, and a less intense band ($\epsilon = 1770$ M⁻¹ cm⁻¹) at 915 nm. On the basis of their energies, their rather high extinction coefficients, and the fact that they are not observed in other diruthenium carboxylate complexes, the bands at 612 and 729 nm are probably metal-to-ligand (bnpn) in nature. Similar assignments have been made in the spectrum of the dirhodium analogue⁷ of **2**. For $[Ru_2(O_2CR)_4]^+$ complexes, a band at 424 nm ($\epsilon \sim 1000$ M⁻¹ cm⁻¹) with a shoulder at 530 nm has been assigned to an allowed $O \pi \rightarrow \pi^*$ transition where the O π orbital is mainly a Ru-O bonding orbital with a significant Ru-Ru bonding contribution.³³ In $[Ru_2(\mu-O_2CCH_3)(mhp)_2]$ ²⁷ these bands are shifted to lower energies (550 nm with the shoulder at 460 nm) and increase in intensity ($\epsilon = 3370$ M⁻¹ cm⁻¹). It seems likely that these bands are also present in **2** as shoulders to the intense visible bands. For the ruthenium tetracarboxylates, the near-IR band has been assigned to a $\delta \rightarrow \delta^*$ transition. Such a transition is possible for **2** although, in the absence of corroborative data, no definite assignments can be made.

The electrochemical behavior of **2** mimics that of **1** in that it also undergoes multiple redox reactions. Cyclic voltammograms of **2** in 0.1 M TBAP-CH₃CN (Figure 1B) show a reversible one-electron, metal-centered oxidation at 0.72 V and two reversible one-electron, ligand-centered reductions at -0.62 and -1.37 V vs SSCE. Multiple reductions have not been previously observed for other Ru_2^{2+} complexes. The single oxidation observed for **2** represents the formation of a formally mixed-valence Ru_2^{5+} complex which, from controlled potential electrolysis experiments, has been demonstrated to be stable only on the cyclic voltammetry time scale. Typically, this oxidation occurs in the potential range -0.96 to +0.33 V. The dramatic positive shift in this potential for **2** indicates a stability of the Ru_2^{4+} core relative to Ru_2^{5+} that is unique to **2** and attributable to the bnpn ligand. The formation of the diosmium analogue of **2**, which, to our knowledge, is the first diosmium complex isolated with the Os_2^{4+} core, further demonstrates the great tendency of bnpn to favor the +2 oxidation state.¹⁵

In conclusion, our work establishes, for the first time, the ability of the bnpn ligand to stabilize mixed valency and multiple metal-metal bonding in its complexes with ruthenium. The compact yet flexible structure of this ligand allows it to span metal-metal distances in the range 2.28-3.20 Å. The proximity of the metal ions it encapsulates promotes significant metal-metal interactions either via other bridging ligands or through direct metal-metal bonds.

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Supplementary Material Available: For $[Ru_2(\mu-O_2CCH_3)_3]PF_6$, Tables V-IX, giving crystallographic data, positional and thermal parameters of all atoms, and other bond distances and angles (7 pages); Table X, listing observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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