highly polarizing Co^{2+} cations play a crucial rôle. The water excess of the present case prevents the interaction of Co^{2+} and $[Co(CO)_4]^-$ to form tight HNIPs, which are intermediates in equilibrium 1 in the presence of CO and in the formation of **2** on CO removal. Only water molecules are in the first coordination sphere of Co^{2+} cations. The poorer Lewis base $[Co(CO)_4]^-$ is presumably able to replace a THF or Et_2O molecule in the second coordination sphere of Co^{2+} giving a H_2O separated ion pair[11] $[(H_2O)_nCo\text{-}O(H)\text{-}H\cdots(OC)_3CoCO]^+$. Hydrolysis can then occur with formation of $HCo(CO)_4$ and $[(H_2O)_nCoOH]^+$. $HCo(CO)_4$ decomposes to H_2 and **1**, the latter one being disproportionated by H_2O, and the sequence continues until the formation of insoluble **3**.

The here reported water reduction promoted by Co^{2+} and $[Co(CO)_4]^-$ formally resembles that performed by $Zn[Co(CO)_4]_2$ in toluene, with the $H_2O/Zn[Co(CO)_4]_2$ molar ratio being 1.[12] In this latter case, the reaction presumably occurs through an intramolecular proton transfer from Zn-coordinated water to the Zn-bonded $Co(CO)_4$ unit in the $H_2OZn[Co(CO)_4]_2$ intermediate.

The achievement of water reductions using **1** instead of $Zn[Co(CO)_4]_2$ has the important consequence that the hydroxocobalt **3** can be reduced by CO. In anhydrous THF, **3** remains unchanged under 80 atm of CO and 150 °C. In the presence of added water, however, reaction 3 is observed. No H_2 is produced

$$\underset{\mathbf{3}}{2Co_4(OH)_7Co(CO)_4} + 39CO \xrightarrow[80\ \text{atm},\ 100\ ^\circ C]{0.5\%\ H_2O,\ THF} \underset{\mathbf{1}}{5Co_2(CO)_8} + 7H_2O + 7CO_2 \quad (3)$$

during reaction 3. The water reduction described above and reaction 3 constitute a stepwise WGSR where no promoters are required and H_2 and CO_2 are formed in two separate steps.

Finally, we examined the behavior of a 0.03 M solution of **1** in 5% H_2O/THF. During 20 h of reflux at 65 °C no gas was evolved and the 1887-cm^{-1} band of $[Co(CO)_4]^-$ remained unchanged. The lack of reaction supports our view of HNIPs as intermediates in electron-transfer reactions occurring in wet ethereal solutions of **1**: as a large excess of water prevents both the tight and water-separated Co^{2+},$[Co(CO)_4]^-$ HNIP, stable solutions are obtained.

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Registry No. 1, 10210-68-1; **2**, 125413-22-1; $[Co(CO)_4]^-$, 14971-27-8; $Co_6(CO)_{16}$, 12182-17-1.

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Dinuclear Ruthenium Complexes with Bridging 1,4,5,8-Tetraoxonaphthalene: Redox Properties and Mixed-Valence Interactions

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Dinuclear ruthenium complexes are the focus of active research aimed at understanding the mechanism of electron transfer between metal centers in mixed-valence states.[1-12] The studies of the intervalence transition occurring in the electronic spectra and the analysis of the spectral parameters of the band have provided considerable information about the interaction between the two metal centers.[13-17]

Recently, mononuclear ruthenium dioxolene complexes were reported showing at least five different oxidation states, which provided evidence of the noninnocent nature of the dioxolene ligands toward ruthenium.[18] Since the extent of the overlap between ruthenium(II) and ruthenium(III) in dinuclear complexes, which determines the nature of the mixed-valence species, is expected to depend on the mixing of the metal and bridging ligand orbitals, the use of noninnocent ligands may favor the formation of class III complexes. $[Ru(bpy)_2]^{n+}$ (bpy = 2,2'-bipyridine) cations appear to be particularly suitable to this purpose because of their stability toward disproportionation. Kaim et al. recently reported[19] dinuclear ruthenium complexes bridged by *o*- and *p*-quinoid molecules, in which borderline behavior between radical and metal-centered mixed-valence character was observed. This observation in fact showed that in principle it is possible to tune the metal-ligand delocalization by using appropriate quinoid molecules. With this in mind, we decided to investigate dinuclear ruthenium complexes with 1,4,5,8-tetraoxonaphthalene (tetrox), which potentially can bridge two different metal ions in five different oxidation states, as shown in Scheme I. We wish to report here the cations $[Ru_2(bpy)_4(tetrox)]^{n+}$ with n = 2-4, which we could isolate as polycrystalline solids, and show that the complex with n = 3 is a genuine example of class III ruthenium mixed-valence compounds with unprecedented spectral features.

Experimental Section

Chemicals. *cis*-$Ru(bpy)_2Cl_2$ was prepared by using a published procedure.[20] 5,8-Dihydroxy-1,4-naphthoquinone (Fluka) was used as received. All other reagents were purchased commercially and used without further purification.

$[Ru_2(bpy)_4(tetrox)](PF_6)_2\cdot 2H_2O$ (2). A 2-mmol sample of $Ru(bpy)_2Cl_2$ was suspended in 60 mL of methanol and heated for 0.5 h with stirring. Solid 5,8-dihydroxy-1,4-naphthoquinone (1 mmol) and a sodium hydroxide (2 mmol) solution in methanol were added. The reaction mixture was refluxed for 4 h, and the deep blue solution turned green. Upon the addition of 40 mL of a saturated potassium hexafluorophosphate aqueous solution, a black precipitate was formed. It was filtered out, washed several times with water, and then recrystallized from acetone/water and acetonitrile/diethyl ether mixtures. Anal. Calcd for $C_{50}H_{40}F_{12}N_8O_6P_2Ru_2$: C, 44.78; H, 2.98; N, 8.34. Found: C, 44.93; H, 2.66; N, 8.03.

$[Ru_2(bpy)_4(tetrox)](PF_6)_3$ (3). A sample of **2** (268 mg, 0.2 mmol) was dissolved in 30 mL of freshly distilled acetonitrile, and then $(NH_4)_2Ce(NO_3)_6$ (111 mg, 0.2 mmol) in 20 mL of water was added. The blue solution turned green. Upon addition of a saturated aqueous solution of

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Scheme I

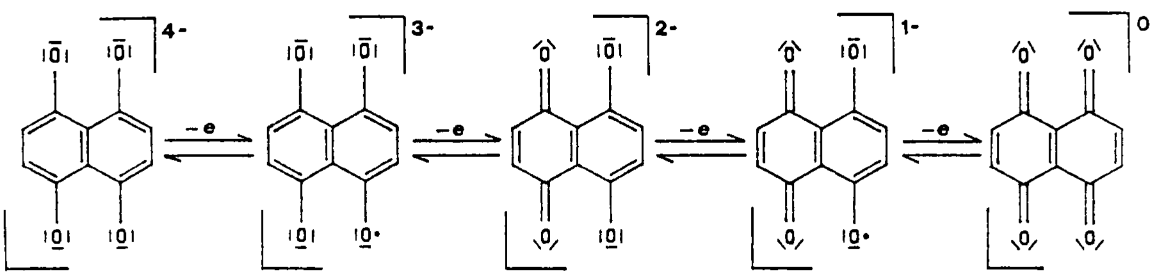

Table I. Electronic Data for $[Ru_2(bpy)_4(tetrox)]^{n+}$ Complexes (n = 2–4) in Acetonitrile Solution

complexes	abs max[a,b]
$tetrox^{2-}$[b]	15 350 (3.86), 16 300 sh, 31 000 sh, 32 500 (3.75)
$[Ru_2(bpy)_4(tetrox)]^{2+}$	12 900 sh, 15 400 (4.39),[d] 16 600 (4.35),[d] 19 400 sh, 22 200 (4.00), 23 400 (3.98), 27 400 (4.12), 30 000 sh,[d] 34 200 (4.90)
$[Ru_2(bpy)_4(tetrox)]^{3+}$	4800 (3.96),[e] 10 500 sh, 14 800 (4.48),[d] 21 900 (4.21), 22 500 sh, 28 000 sh, 34 800 (4.90)
$[Ru_2(bpy)_4(tetrox)]^{4+}$	8700 (3.94), 9800 (3.75), 17 300 (4.41),[f] 18 400 sh, 19 400 sh, 23 400 sh, 26 000 (4.32), 35 500 (4.93)

[a] In cm^{-1}; log ϵ in parentheses. [b] sh = shoulder. [c] Prepared from 5,8-dihydroxy-1,4-naphthoquinone and tetrabutylammonium hydroxide. [d] Internal $tetrox^{2-}$ transitions. [e] Proposed assignment: intervalence transition. [f] Proposed assignment: internal tetrox transition.

potassium hexafluorophosphate, a deep green precipitate was obtained. It was filtered out, washed several times with water, and then recrystallized from acetonitrile/water mixtures. Anal. Calcd for $C_{50}H_{36}F_{18}N_8O_4P_3Ru_2$: C, 41.41; H, 2.49; N, 7.73. Found: C, 41.05; H, 2.63; N, 7.71.

$[Ru_2(bpy)_4(tetrox)](PF_6)_4$ (4). This complex was prepared in a fashion similar to that used for 3 by using a double stoichiometric amount of ceric salt. This compound yields a deep violet solution and can be recrystallized from acetonitrile/water mixtures. Anal. Calcd for $C_{50}H_{36}F_{24}N_8O_4P_4Ru_2$: C, 37.65; H, 2.27; N, 7.03. Found: C, 37.61; H, 2.43; N, 7.09.

Physical Measurements. Physical measurements were carried out as previously described.[21]

Results and Discussion

The reaction of $Ru(bpy)_2Cl_2$ with 5,8-dihydroxy-1,4-naphthoquinone (1) in alkaline media readily yields $[Ru_2(bpy)_4(tetrox)]^{2+}$, which can be isolated as the bis(hexafluorophosphate) salt (2) to give a diamagnetic microcrystalline compound. We formulate the cation of 2 as $[Ru^{II}_2(bpy)_4(tetrox^{2-})]^{2+}$ with the tetraoxolene ligand acting as a bis-bidentate bridging ligand in its dinegative form. Support of this hypothesis comes from the electronic spectra of this compound, which do not show any pH dependence and compare well with those of 1 in alkaline media, with a strong absorption at 15 400 cm^{-1}, which we assign to an internal transition of $tetrox^{2-}$ (Table I). According to its nature, 2 might be a mixture of meso and *dl* diastereoisomers;[12,19,22] however no evidence of such isomers was detected.

The cyclic voltammograms of deareated acetonitrile solutions of 2 show three reversible redox couples at −0.91, 0.45, and 0.76 V vs SCE. Coulometric experiments indicate that these process are monoelectronic. By comparison with the voltammograms of some 3d metal complexes of 1[23] the redox process observed at −0.91 V is associated with the ligand-centered electron transfer $tetrox^{2-}$–$tetrox^{3-}$.

The couples occurring at positive potentials involve the existence of both tripositive and tetrapositive cations, which have been isolated as hexafluorophosphate derivatives after oxidation of 2

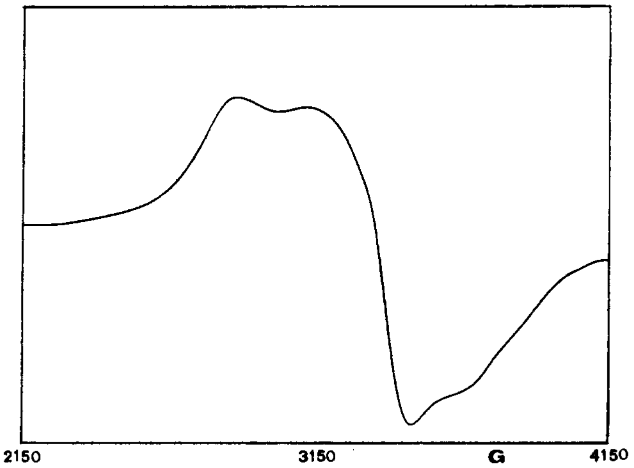

Figure 1. Polycrystalline powder ESR spectrum of $[Ru_2(bpy)_4(tetrox)](PF_6)_3$ at liquid nitrogen temperature.

with ceric salts. Indeed the difference in the redox potentials associated with the two couples points out a quite large stability of the tripositive cation toward disproportionation ($K_c = 1.8 \times 10^5$), thus justifying its isolation as solid.

$[Ru_2(bpy)_4(tetrox)](PF_6)_3$ (3) is paramagnetic with $\mu_{eff} = 1.70$ μ_B, consistent with a $S = {}^1/_2$ ground state of the dinuclear cation. Polycrystalline powders of this compound are ESR silent at room temperature but are characterized by a broad rhombic signal at liquid nitrogen temperature (Figure 1), whose spectral parameters are $g_1 = 2.33$, $g_2 = 2.01$, and $g_3 = 1.88$. No temperature dependence of the spectral parameters is observed on cooling to 4 K. The large deviations of the g values from 2 suggest that the molecular orbital containing the unpaired electron is mainly localized on the metal ion, indicating therefore that this compound must be described as a Ru^{III}–Ru^{II} derivative. However, the deviations of g values from 2 are not as high as usually observed in ruthenium(III) dioxolene derivatives. For instance, $[Ru(NH_3)_4(cat)]^+$ (cat = catecholato) is characterized by $g_\parallel = 2.72$ and $g_\perp = 1.89$.[24] Therefore the observed g values may suggest that in 3 the electron is partially delocalized also onto the bridging ligand. In fact the sum of the squares of the g values is expected to be close to 16 for d^5 ions,[25] while in the present case it is only 13. Theoretically such low values can be justified by orbital reduction factors k smaller than 1, which indicates electron delocalization toward the ligands. Therefore we explain these EPR parameters describing the ground state of 3 as $[(bpy)_2Ru^{II}(tetrox^{2-})Ru^{III}(bpy)_2]^{3+}$ with a substantial admixture of $[(bpy)_2Ru^{II}(tetrox^{3-})Ru^{II}(bpy)_2]^{3+}$.

The electronic spectrum of 3 in acetonitrile shows a band at 14 800 cm^{-1}, which we assign to an internal electron transfer of the ligand, and a very intense absorption at 4800 cm^{-1}, which is not present in the spectra of either 2 or 4 (Figure 2). We assign this band to an intervalence transition involving ruthenium(III) and ruthenium(II). The spectral parameters characterizing this absorption band are rather unusual when compared to those reported for similar related systems: indeed the energy is the

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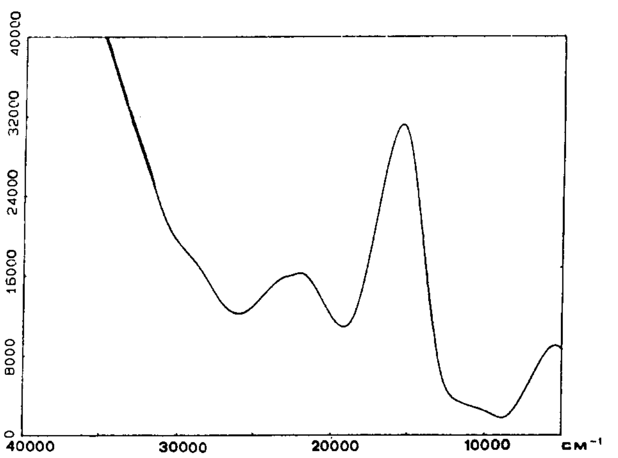

Figure 2. Electronic spectrum of $[Ru_2(bpy)_4(tetrox)](PF_6)_3$ in acetonitrile solution.

lowest so far reported for mixed-valence ruthenium complexes and the extinction coefficient (9300 $M^{-1}\ cm^{-1}$) is the highest. High intensity of the transition and low frequency are characteristic of class III mixed-valence compounds. An additional feature of the spectra of these compounds is the relative insensitivity of the frequency maxima to changes in solvent. The spectral region in which we observe the maximum absorption for the intervalence band of **3** is very difficult to investigate, due to the presence of absorption bands of the solvents and to low sensitivity of the spectrophotometers, which prevent accurate analysis. However, we observe that the absorption maximum does not shift more than 100 cm^{-1} in DMF, acetone, and DMSO, thus providing additional evidence of class III behavior. Furthermore, the experimental half-height bandwidth ($\Delta\nu_{1/2}$) is ca. 3000 cm^{-1}, lower than expected from the theory for a pure class II mixed-valence system. In fact, a value of 3330 cm^{-1} is calculated with the use of the Hush formula[13]

$$\Delta\nu_{1/2} = (2310E_{op})^{1/2}\ cm^{-1}$$

where E_{op} is the absorption maximum of the intervalence transition. The class III behavior of **3** must be associated with the extent of the electron delocalization toward the bridging ligands evidenced by the EPR spectra.

$[Ru_2(bpy)_4(tetrox)](PF_6)_4$ (**4**) is diamagnetic. Possible descriptions are either $[Ru^{III}_2(bpy)_4(tetrox^{2-})]^{4+}$ or $[Ru^{II}_2(bpy)_4(tetrox)]^{4+}$. One-electron oxidation of a Ru^{III}–Ru^{II} moiety usually yields a dinuclear ruthenium(III) derivative. Under this hypothesis the observed magnetic properties of this compound might be explained, assuming that a strong antiferromagnetic interaction between the two metal ions is operative. Although this possibility cannot be discarded, previous studies on 3d dinuclear complexes of this ligand led us to consider this hypothesis as highly unprobable.[23,26] Therefore we conclude that **4** must be described as containing two ruthenium(II) ions bridged by uncharged 1,4,5,8-naphthodiquinone. Indeed one-electron oxidation of the $[Ru_2(bpy)_4(tetrox)]^{3+}$ cation involves the reduction of the ruthenium(III) ion and the two-electron oxidation of the ligand. A similar behavior has been suggested to occur for oxidation processes involving some Ru^{III}–catecholate adducts, which yield products to be described as Ru^{II}–quinone derivatives.[24] A confirmation of this assignment comes from the electronic spectrum of **4**, which is different from those of both **2** and **3**, with a maximum at 17 300 cm^{-1}, which can be compared to the absorption at 19 500 cm^{-1} for the uncharged tetrox ligand. In this case the observed decrease in the transition energy might be consistent with π interactions involving metal and ligand orbitals.

Since the metal and ligand orbitals are of comparable energies, we conclude therefore, in agreement with Lever et al.,[18] that the nature of the frontier orbitals for the $[Ru_2(bpy)_4tetrox]^{n+}$ cations depends on the relative stabilization of the ruthenium and tetrox orbitals upon oxidation. In **2** the metal orbitals are higher in energy than the ligand orbitals. Upon one-electron oxidation, the metal orbitals are more stabilized than the tetrox orbitals and, even if the SOMO of **3** is essentially a metal orbital, a contribution from the ligand orbital must not be neglected. Further, one-electron oxidation stabilizes the metal orbitals more, to such an extent that in **4** the orbital order is reversed and the frontier orbitals have more tetrox character. Therefore **4** is a ruthenium(II)–tetrox complex.

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Adducts of π-Acceptor Ligands with Copper(I) Thiolates

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A number of recent publications from this laboratory have described the direct electrochemical synthesis of copper(I) thiolates and their adducts,[1-3] and as in related cases, the advantages of the method include simplicity and high product yield. The richness and variety of the range of molecular structures which have been identified for these copper(I) compounds is indeed remarkable,[4-6] and a recent report suggests that similar results may be expected for analogous diorganophosphido derivatives.[7] We have now extended the electrochemical studies to the synthesis of a range of copper(I)–thiolato compounds with the monodentate ligands triphenylphosphine and *tert*-butyl isocyanide, and with phenyl isothiocyanate. A number of the products were also obtained by direct reaction between the copper(I) thiolate and ligand in nonaqueous solution. As in earlier work on these systems, we find that the stoichiometry of the product depends upon the nature of the organic group attached to sulfur.

Experimental Section

General Data. Solvents were distilled from calcium hydride and stored over molecular sieves.

Copper anodes were foils, 0.25 mm thick with a total surface area of ca. 5 cm^2. The metal was treated successively with concentrated nitric acid and distilled water, dried, abraded lightly with fine sandpaper, and finally polished with tissue paper.

Thiols, triphenylphosphine, phenyl isothiocyanate (Aldrich), and *tert*-butyl isocyanide (Fluka) were used as supplied.

Copper analysis was by atomic absorption spectrophotometry, using an IL 251 instrument. Microanalysis was carried out by Guelph Chemical Laboratories Ltd. Infrared spectra were obtained with a Nicolet 5DX interferometer, and NMR spectra were recorded on Varian EM 360, Bruker 300 (^1H), and Bruker 200 (^{31}P) spectrometers. Mass spectra were run on a Varian MAT CH-5 instrument operating in the electron impact mode.

Electrochemical Procedures. The electrochemical syntheses followed the methods used previously,[1-3] with cells of the general form

$$Pt(-)/CH_3CN + RSH + L/Cu(+)$$
$$L = P(C_6H_5)_3,\ C_6H_5NCS,\ t\text{-}C_4H_9NC$$

Details of solution composition, length of experiment, etc. are given in

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