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Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Polyaza Cavity-Shaped Molecules. 7. Dirhodium Complexes of Triaza and Tetraaza Cavities

Randolph P. Thummel,* Francois Lefoulon, Darwin Williamson, and Madhav Chavan

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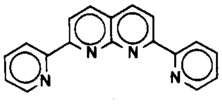
A series of cavity-shaped ligands have been prepared consisting of a 1,8-naphthyridine fragment substituted by phenyl or 2-pyridyl in the 2,7-positions, which are further bridged by two dimethylene units. The ligands containing three or four nitrogens in the cavity displace an acetate from dirhodium tetraacetate to form a complex in which the naphthryridine fragment bridges the dirhodium nucleus and the appended pyridine rings coordinate the axial metal sites. When a phenyl ring is substituted for a pyridine on the ligand, a C–H bond is constrained proximate to the dirhodium nucleus but hydride transfer or metalation is not observed. The NMR, electronic absorption, and electrochemical properties of these complexes have been examined. The system containing an annelated phenyl ring on the ligand (complex III) shows evidence for the occurrence of an irreversible chemical reaction subsequent to the loss of one electron or the gain of two electrons.

Introduction

There is much recent interest in polydentate ligands that impose certain geometric or steric constraints on their resulting transition-metal complexes. Porphyrins and their various bridged analogues, macrocyclic crown systems, and various polyaza Schiff bases fall into this category in that the properties of their coordination compounds are often dependent upon conformational requirements of the ligand. A general tactic thus involves the design of appropriately constrained ligands that might provoke unusual metal complex chemistry.

We have recently become interested in the study of polyaza cavity-shaped molecules made up of 2,2′-bonded pyridine,[1] quinoline,[2] and 1,8-naphthyridine[3] subunits whose relative orientations are controlled by 3,3′-annelating bridges. We are thus able to manipulate the relative orientations of sp^2 nitrogen lone-pair electrons on the interior of the ligand cavity. This paper presents some of our initial results in utilizing these ligands to induce unusual metal complex chemistry.

Kaska and co-workers have reported a dirhodium(II) acetate complex where 2,7-bis(2-pyridyl)-1,8-naphthyridine (**1**) has replaced a bridging acetate on dirhodium tetraacetate.[4] Thus the two rhodium atoms are bridged by three acetates and the naphthyridyl fragment of **1**. The two pyridyl rings of **1** occupy the axial sites on the complex trans to the Rh–Rh bond. A single-crystal X-ray study has shown that the incorporation of ligand **1** has only a small effect upon the bonding in the remaining tris(μ-acetato)dirhodium(II) fragment. For example, the Rh–Rh bond distance lengthens only 0.01 Å over that of the tetraacetate complex while the Rh–O bond lengths and O–Rh–O angles are essentially unchanged. The new bridging ligand **1** remains almost completely planar in the complex. The angle between the least-squares planes of the pyridine rings and the naphthyridine ring has an average value of 5.4°. The only serious distortion in the new complex is a change in the Rh–Rh–N axial bond angles from 180 to 167°.



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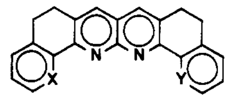
We have prepared the series of cavity-shaped ligands **2**–**4**. The tetraaza system **2** is identical with that of **1** with the addition of two dimethylene bridges at the 3,3′- and 7,3″-positions. These bridges hold the two appended pyridine rings in a geometry that is favorable for complexation. The triaza system **3** substitutes a phenyl ring for one of the two pyridines, which is equivalent to replacing a pyridine nitrogen lone pair of electrons by a C–H bond. In a dirhodium complex of **3** this C–H bond should be pointed toward a rhodium atom approximately along the axis of the metal–metal bond. The diaza system **4** substitutes phenyl rings for both pyridine rings in **2** and would thus have a C–H bond pointing at each of the two rhodium atoms from opposite directions along their internuclear axis. The intriguing possibility is presented for metal insertion into these C–H bonds to form a dirhodium metallacycle with one or two Rh–C bonds.



2: X = Y = N
3: X = N, Y = CH
4: X = Y = CH

Cotton and co-workers have reported a complex of the general formula $Rh_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2{\cdot}2L$, where L represents acetic acid or pyridine as the axial ligands.[5] In this system the dirhodium unit is bridged by two cisoid acetate ligands as well as two cisoid ortho-metalated triphenylphosphine ligands. The apparent willingness of dirhodium to metalate at an equatorial site poses the interesting question as to whether similar C–H insertion could be induced in the more labile axial sites.

Synthesis

The general strategy for the preparation of the cavity-shaped ligands **2**–**4** (Scheme I) involves two sequential Friedlander condensations of 4-aminopyrimidine-5-carboxaldehyde (**5**). When this material is allowed to react with α-tetralone (**7**), the pyrimidopyridine **9** is obtained. This material can be readily hydrolyzed in aqueous HCl to afford the α-aminopyridinecarboxaldehyde **11**. Subsequent reaction of **11** with a second 1 equiv of α-tetralone provides the diaza system **4**.[6] If **11** is instead treated with the tetrahydroquinolone **6**, the triaza system **3** may be obtained. When **5** is allowed to react with tetrahydroquinolone **6** initially, the intermediate **8** is formed, which can be hydrolyzed in a similar fashion to give the *o*-amino aldehyde **10**. Treatment of **10** with α-tetralone provided an alternate route to the triaza system **3** while the reaction of **10** with tetrahydroquinolone **6** provided the tetraaza system **2**. The singly bridged ligand **12** was prepared by the reaction of **10** with acetophenone.

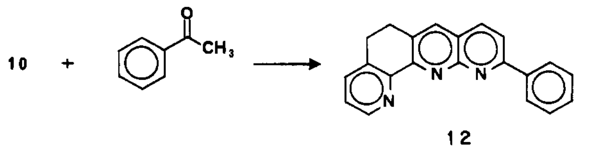


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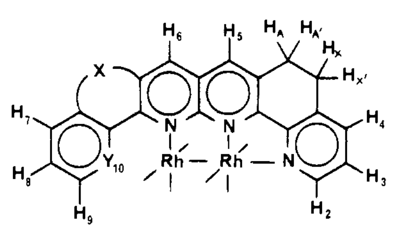
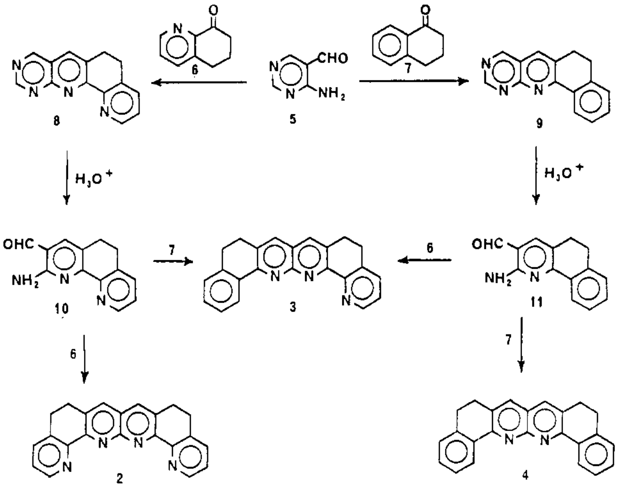
Table I. ^1H NMR Data (300 MHz, CD_3CN) for the Pyridylnaphthyridine Fragment of Dirhodium(II) Complexes[a,b]



complex	X	Y	H_2	H_3	H_4	H_5/H_6	H_{10}	$-CH_2-$
$Rh_2(OAc)_3(\mathbf{2})^+$	$-CH_2CH_2-$	N	8.24	8.10	9.56	8.31		
$Rh_2(OAc)_3(\mathbf{3})^+$	$-CH_2CH_2-$	CH	8.33	8.05	9.32	8.37[c]	11.33	3.47[c] (s, 4 H), 3.18 (t, 1 H), 3.16 (t, 1 H), 3.07 (t, 1 H), 3.04 (t, 1 H)
$Rh_2(OAc)_3(\mathbf{12})^+$	H, H	CH	8.28	8.10	9.30	8.47[c]	8.70	3.49[c] (s, 4 H)

[a] Chemical shifts given in ppm downfield from Me_4Si. [b] The proton numbering pattern is used for the sake of clarity. [c] Coincidental equivalence of H_5 and H_6 or α-methylene protons.

Scheme I



When **2** is combined with a methanol solution of $Rh_2(OAc)_4$ under neutral conditions at room temperature, the originally turquoise solution turns purple after 1 h and the addition of NH_4PF_6 precipitates a complex in 79% yield. The thermospray mass spectrum shows a peak for the singly charged ion at *m/e* 717 corresponding to the replacement of one bridging acetate by the ligand **2**. The reactions with **3** and **12** proceeded in a similar fashion to give 84% and 78% yields, respectively, of the dirhodium complexes, whose 1:1 compositions were again supported by parent ions in their thermospray mass spectra at *m/e* 716 and 692. When the reaction of the diaza cavity **4** with $Rh_2(OAc)_4$ is attempted under identical conditions, only unreacted starting materials are recovered:

$$Rh_2(OAc)_4 + \mathbf{1} \rightarrow Rh_2(OAc)_3(\mathbf{1})^+ \quad (I)$$
$$+ \mathbf{2} \rightarrow Rh_2(OAc)_3(\mathbf{2})^+ \quad (II)$$
$$+ \mathbf{3} \rightarrow Rh_2(OAc)_3(\mathbf{3})^+ \quad (III)$$
$$+ \mathbf{12} \rightarrow Rh_2(OAc)_3(\mathbf{12})^+ \quad (IV)$$
$$+ \mathbf{4} \rightarrow \text{no reaction}$$

Properties

The 300-MHz NMR spectra of complexes II–IV show three areas of interest: the acetate bridges, the aromatic protons, and the dimethylene bridges. The methyl groups of the acetate bridges occur as sharp singlets. A three-proton signal at 2.14–2.27 ppm accounts for the one trans-equatorial bridge and a six-proton signal at 1.42–1.55 ppm accounts for the two cis-equatorial bridges. These values are in good agreement with those reported by Kaska (2.21 and 1.38 ppm) for complex I.[4]

Table I records the ^1H NMR data for the pyridylnaphthyridine fragment of complexes II–IV. The symmetrical complex II shows four distinct aromatic signals as expected. These four protons are deshielded with respect to the parent ligand, and their chemical shift values appear downfield 0.38–0.82 ppm, indicating a decrease in electron density on the coordinated ligand.

The unsymmetrical complex III has nine nonequivalent aromatic protons, many of which can be assigned with reasonable certainty. The most unusual signal is H_{10}, which occurs as a doublet (J = 7.8 Hz) at 11.33 ppm, representing a downfield shift of 2.49 ppm as compared to the signal for the free ligand. This shift is in the opposite direction of what is normally observed for protons held in the vicinity of metal atoms, where the high electron density often causes substantial shielding and upfield chemical shifts. This shift is consistent, however, with the existence of ring current effects involving the equatorial ligands and the dirhodium core. These rings intersect along the dirhodium internuclear axis, and hence, any proton lying close to this axis might be substantially deshielded.

Alternatively, one might consider this deshielding effect to stem from the close alignment of H_{10} with an axial dirhodium coordination site. If this vacant orbital withdraws electron density from the $C-H_{10}$ bond, the effect is the same as intramolecular hydrogen bonding, which would cause the proton to resonate at lower field. The effect is not strong enough, however, to cause hydride transfer to rhodium or to accomplish metalation at the C_{10} position. This observation is verified by examination of the ^{13}C NMR spectrum of III, which shows nine clear signals of approximately equal intensity in the region of 120–150 ppm for the unsubstituted aromatic carbons. If any one of these carbons was directly bonded to rhodium, its resonance would be expected to shift substantially downfield as well as being split into a doublet, by the rhodium nucleus. The diminished intensities of the 10 quaternary aromatic carbons make them difficult to observe.

The possibility also existed that the deshielding of H_{10} might be due, not to the dirhodium nucleus, but instead to a molecule of acetonitrile being coordinated in the proximate axial site. This possibility was ruled out by the observation of the doublet (J = 7.5 Hz) for H_{10} at 11.36 ppm in acetone-d_6, where diminished deshielding by coordinated solvent would be expected to cause a substantial upfield shift.

A significant difference is observed in the behavior of the dimethylene bridge protons for complexes II and III. There is coincidental equivalence of the two pairs of chemically nonequivalent α-methylene protons in II. The observation of a singlet for all eight protons further indicates that both bridges in the complex are undergoing rapid inversion on the NMR time scale, causing H_A and $H_{A'}$ (also H_X and $H_{X'}$) to become equivalent. Lowering the temperature of the NMR probe to −65 °C does not cause any splitting of this signal. Complexation of **2** should enforce coplanarity of the three aromatic rings. The consequential flattening of the two dimethylene bridges should then lead to a decrease in the barrier to inversion of these bridges, thus explaining our inability to slow this process significantly on the NMR time scale.

For the triaza-bound system, III, the two bridges give rise to two distinct signals. The bridge between the pyridine and naphthyridine rings appears as a singlet at 3.47 ppm, identical with what is observed for II. The bridge between the phenyl and naphthyridine rings is more shielded and appears at higher field

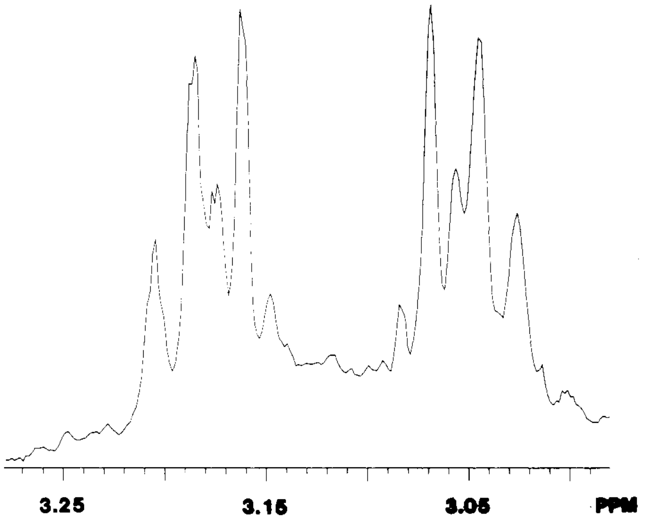


Figure 1. 300-MHz ^1H NMR spectrum of the dimethylene bridge connecting the phenyl and naphthyridyl fragments of complex III.

Table II. Electronic Absorption Data for Dirhodium Complexes (in Acetonitrile)

complex	λ_{max}, nm (log ϵ)		
II	212 (5.31)	364 (5.01)	536 (4.15)
	246 (5.27)	382 (5.24)	562 (4.22)
	288 (3.87)	420 (4.61)	
III	212 (4.07)	355 (4.80)	510 (3.92)
	234 (5.01)	392 (4.70)	
	288 (4.64)	413 (4.77)	
IV	225 (5.36)	345 (5.02)	518 (4.17)
	262 (5.24)	376 (4.88)	
		390 (4.82)	

as two distinct pairs of triplets at 3.184/3.162 and 3.068/3.044 ppm (see Figure 1). The coupling pattern appears to argue for conformational rigidity of this bridge as a result of the inability of H_{10} to pass through the dirhodium–naphthyridine equatorial plane. When this congestion is imposed on both axial sites as it would be for the complex of **4** with dirhodium, the naphthyridine ring cannot effectively coordinate and complexation does not occur.

To further examine the steric effect of phenyl ring conformation on the coordination properties of these ligands, we examined complex IV, where the phenyl ring in ligand **12** is capable of free rotation about its bond to the naphthyridine unit. The NMR signal for H_{10} is now a two-proton doublet at 8.70 ppm. This upfield shift of 2.63 ppm from the signal for III indicates that the phenyl ring is able to rotate out of the dirhodium deshielding region. The other aromatic resonances and the dimethylene bridge protons are all comparable with values observed for II and III.

Table II summarizes the electronic absorption spectra for the complexes II–IV. All three complexes show a long-wavelength absorption in the region 510–562 nm. This absorption is less intense than the shorter wavelength bands and has been attributed to a metal to ligand charge transfer (MLCT).[4b] For the more symmetrical system II there are several allowed transitions from the highest occupied orbitals of the Rh_2^{4+} core to the lowest unoccupied π orbitals of the naphthyridine chromophore, which might explain the splitting observed for this system.[4b] One other noteworthy feature is the relatively intense absorption at 382 nm that is observed for complex II.

The reduction and oxidation potentials as determined by cyclic voltammetry in acetonitrile for the naphthyridine complexes of dirhodium, I–IV, are summarized in Table III, and the scans for II–IV are illustrated in Figure 2. The half-wave potentials for the redox reactions of complex II are simply the midpoint potentials between the anodic and the cathodic peaks. The values listed for the first reduction of complexes III and IV are also the midpoint potentials. All the other reactions show chemical irreversibility, and their potentials are estimated from the relationship $E_{1/2} = E_{0.85p}$, where $E_{0.85p}$ is the potential at which the current function in a single-sweep voltammogram of a reversible electron transfer is 0.85 of its value at the peak. The potentials for the first oxidation and the first reduction of complexes I–IV are all more positive than the corresponding potentials for $Rh_2(OAc)_4$. This positive shift is expected since $Rh_2(OAc)_4$ is neutral while the complexes I–IV are 1+ charged.

Table III. Reduction and Oxidation Potentials for Naphthyridine Complexes of Dirhodium Acetate in CH_3CN (0.1 M TBAP) at 25 °C

complex	$E_{1/2}$, V (vs. SCE) oxidn	redn 1	redn 2
$Rh_2(OAc)_4$[a]	1.02	-1.08[b]	
I[a]	1.28	-0.57	-1.21
II	1.33	-0.68	-1.36
III	1.53[c]	-0.66	-1.30[c]
IV	1.44[c]	-0.64	-1.29[c]

[a] Reference 4b. [b] Irreversible. [c] Estimated from the relationship $E_{1/2} = E_{0.85p}$, where $E_{0.85p}$ is the potential at which the current function in a single-sweep voltammogram of a reversible electron transfer is 0.85 of its value at the peak for a scan rate of 500 mV/s.

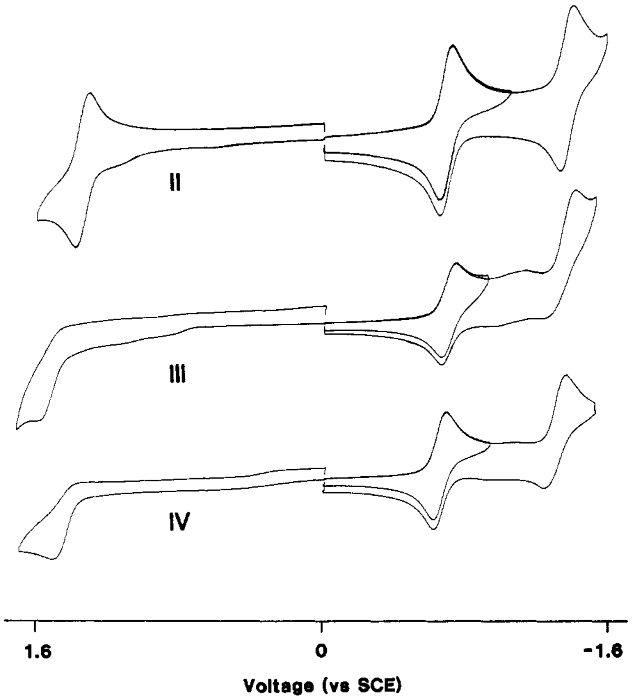


Figure 2. Cyclic voltammograms of approximately 1 mM dirhodium–naphthyridyl–triacetate complexes II–IV in acetonitrile containing 0.1 M TBAP at 25 °C with a sweep rate of 100 mV/s.

Similar to what has been reported for complex I,[4] we observe three reversible one-electron waves for complex II as characterized by a peak to peak separation (ΔE_p) of 60 mV and a ratio of anodic to cathodic peak current of 1. These three-electron-transfer reactions may be represented by the equations

$$[Rh_2(OAc)_3L]^+ \rightleftharpoons [Rh_2(OAc)_3L]^{2+} + e^- \qquad \text{(i)}$$

$$[Rh_2(OAc)_3L]^+ + e^- \rightleftharpoons [Rh_2(OAc)_3L]^0 \qquad \text{(ii)}$$

$$[Rh_2(OAc)_3L]^0 + e^- \rightleftharpoons [Rh_2(OAc)_3L]^- \qquad \text{(iii)}$$

The site of electron transfer in each of these three reactions is under investigation. However, it has been demonstrated[7] that one-electron oxidation of dirhodium complexes having mixed bridging ligands, $Rh_2(OAc)_n(HNOCCH_3)_{4-n}$, involves mainly Rh–Rh-based orbitals. Also in another study of the neutral dirhodium complex $Rh_2[(NR)_2CR]_4$ with R = phenyl, a reversible one-electron reduction was observed at −1.59 V vs. SCE and was

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found to generate a $Rh^{II}Rh^{I}$ species.[8] The same may be true for reactions i and ii for complex II.

The cyclic voltammograms of complexes III and IV, also shown in Figure 2, differ from those of complexes I and II. At a sweep rate of 100 mV/s chemically irreversible oxidations are observed in each case. However, increasing the sweep rate to 500 mV/s shows a cathodic counter peak to the anodic peak of oxidation for complex IV. This clearly indicates that a chemical reaction occurs after oxidative electron transfer, at least in the case of complex IV. A similar change was not observed in the cyclic voltammogram of complex III up to a sweep rate of 1 V/s. But these two complexes are not fundamentally different, and it is reasonable to assume that the oxidations of complexes III and IV are essentially similar, differing only in the rate of the chemical reaction following electron transfer. Further, the difference in the potential at the peak (E_p) and the potential at the half peak height ($E_{p/2}$), $E_p - E_{p/2}$, is about 60–70 mV in both cases at a sweep rate of 100 mV/s. This suggests that the electron transfer may be reversible in each case while the irreversible appearance of the cyclic voltammograms may be entirely due to an irreversible follow-up chemical reaction. In its oxidized form the dirhodium core is more electrophilic, and thus it is not unreasonable to anticipate possible hydride transfer from the aryl C–H bond of III, which is roughly aligned with the axial coordination site. In accord with this hypothesis, the irreversibility of the oxidation wave of IV is less pronounced, possibly due to the fact that the aryl C–H bond is now able to rotate away from the electrophilic metal site.

The first reduction of complexes III and IV is reversible and involves one electron as in the case of complexes I and II. In contrast, the second reduction appears irreversible at a sweep rate of 100 mV/s. As in the case of the oxidation, an increase in the scan rate to 500 mV/s results in the appearance of a counter peak to the cathodic peak of the second reduction of complex IV. A similar change of sweep rate for complex III fails to show any change in the characteristics of the voltammogram. The $E_p - E_{p/2}$ value for the second reduction peaks of both these complexes is about 60 mV at a sweep rate of 100 mV/s. Thus the second reductions of III and IV may be also characterized as a reversible electron transfer followed by an irreversible chemical reaction as in the case of oxidations.

A study of the sites of electron transfer is under way, while further studies on polyaza cavities will explore the possibility of preparing heteronuclear complexes similar to II.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Varian Associates T-60 or FT-80 spectrometer or a Nicollet NT-300 WB spectrometer with chemical shifts reported in parts per million downfield from Me_4Si. Infrared spectra were obtained on a Perkin-Elmer 1330 spectrophotometer or a Beckman IR-4250 spectrophotometer. Mass spectra were obtained on a Hewlett-Packard 5933A GC-mass spectrometer or a Biospec mass spectrometer with a thermospray ionization interface. $Rh_2(OAc)_4$ was prepared according to the method of Wilkinson et al.[9] Solvents were freshly distilled reagent grade unless otherwise noted. All melting points are uncorrected.

2-Amino-5,6-dihydro-1-phenanthridine-3-carboxaldehyde (11). A refluxing ethanol solution of 0.57 g (4.63 mmol) of 4-aminopyrimidine-5-carboxaldehyde[10] (**5**) and 0.70 g (4.78 mmol) of 1-tetralone was treated with 4 drops of 15% methanolic KOH. After 24-h reflux, a yellow precipitate formed upon cooling and was collected to afford 0.94 g (87%) of **9**, mp 222–223.5 °C (lit.[6] mp 223.5–224 °C). A solution of 1.11 g (4.76 mmol) of **9** in 100 mL of 0.01 N HCl was refluxed for 3 h, cooled, and neutralized with NH_4OH to produce a yellow precipitate which was recrystallized from EtOH to afford 0.90 g (84%) of bright yellow **11**, mp 130–132 °C (lit.[6] mp 130.5–131 °C).

2-Amino-5,6-dihydro-1,10-phenanthroline-3-carboxaldehyde (10). By the procedure described above for **11**, the reaction of 0.73 g (5.93 mmol) of 4-aminopyrimidine-5-carboxaldehyde (**5**) with 0.90 g (6.12 mmol) of 5,6,7,8-tetrahydro-8-quinolone[3] (**6**) yielded 1.14 g (82%) of **8**: mp 267–268 °C; ^1H NMR (80 MHz, $CDCl_3$) δ 9.50 (s, 1 H), 9.38 (s, 1 H), 8.83 (dd, 1 H, J = 4.6, 1.7 Hz), 8.13 (s, 1 H), 7.45 (m, 2 H), 3.32 (s, 4 H); IR (KBr) 1625, 1595, 1545, 1445, 1385, 1195, 1115, 1105, 955, 801 cm^{-1}; mass spectrum, *m/e* (rel intensity) 235 (M + 1, 18), 234 (M, 100), 233 (M − 1, 42), 206 (20), 180 (15), 179 (47). The hydrolysis of 1.14 g (4.67 mmol) of **8** in 1200 mL of 0.1 N HCl produced a precipitate, which was recrystallized from EtOH to give 0.97 g (89%) of **10** as yellow needles: mp 241–243 °C; ^1H NMR (80 MHz, $CDCl_3$) δ 9.80 (s, CHO), 8.73 (m, H_9), 7.68 (s, H_4), 7.62 (m, H_7), 7.34 (m, H_8), 6.87 (br s, NH_2), 2.90 (s, H_5 and H_6); IR (KBr) 1670, 1630, 1600, 1580, 1540, 1165, 1120, 1105, 905, 760 cm^{-1}.

5,6,9,10-Tetrahydro[1]phenanthridino[2,3-*b*][1]phenanthridine (4). A refluxing solution of 0.16 g (0.71 mmol) of **11** and 0.11 g (0.77 mmol) of 1-tetralone was treated with 2 drops of 15% methanolic KOH. After 24-h reflux, a precipitate was collected and recrystallized from EtOH to afford 0.16 g (66%) of **4** as yellow needles, mp 252–253 °C (lit.[6] mp 255–256 °C).

5,6,9,10-Tetrahydro[1]phenanthridino[2,3-*b*][1,10]phenanthroline (3). Method A. By the same procedure as described above for **4**, the reaction of 0.25 g (1.12 mmol) of **11** with 0.18 g (1.23 mmol) of 5,6,7,8-tetrahydro-8-quinolone[3] (**6**) provided 0.22 g (59%) of **3** after recrystallization from methanol: mp 248.5–249.5 °C; ^1H NMR (300 MHz, $CDCl_3$) 8.84 (dd, H_{14}, $J_{13,14}$ = 7.2 Hz, $J_{12,14}$ = 1.9 Hz), 8.82 (dd, H_2, $J_{2,3}$ = 4.7, $J_{2,4}$ = 1.7 Hz), 7.88 (s, H_7), 7.82 (s, H_8), 7.58 (dd, H_4, $J_{3,4}$ = 6.8 Hz), 7.40 (t of d, H_{13}, $J_{12,13}$ = 7.0, $J_{12,13}$ = 1.8 Hz), 7.36 (t of d, H_{12}), 7.27 (dd, H_3), 7.23 (d, H_{11}), 3.13 (m, 4 H), 3.02 (overlapping t, 4 H); IR (KBr) 1620, 1610, 1540, 1480, 1450, 1415, 1105, 925, 905, 785, 745 cm^{-1}; mass spectrum, *m/e* (rel intensity) 335 (M, 100), 332 (23), 166 (28).

Method B. By the same procedure as described above for **4**, 0.045 g (0.20 mmol) of **10** was treated with 0.038 g (0.263 mmol) of 1-tetralone. After 24 h of reflux, the solvent was evaporated and the residue was chromatographed on alumina with methanol eluant to provide 0.035 g (53%) of **3** after recrystallization from methanol: mp 246–249 °C; spectral properties identical with those described above.

5,6,9,10-Tetrahydro[1,10]phenanthrolino[2,3-*b*][1,10]phenanthroline (2). By the same procedure as described above for **4**, the reaction of 0.11 g (0.489 mmol) of **10** with 0.07 g (0.509 mmol) of 5,6,7,8-tetrahydro-8-quinolone[4] provided 0.11 g (67%) of **2** as pale yellow needles after recrystallization from methanol: mp 293–295 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.78 (dd, H_2/H_{13}, $J_{2,3}$ = 4.6 Hz, $J_{2,4}$ = 1.6 Hz), 7.93 (s, H_7/H_8), 7.60 (dd, H_4/H_{11}, $J_{3,4}$ = 7.7 Hz), 7.28 (dd, H_3/H_{12}), 3.17 (dd, $-CH_2-$), 3.06 (dd, $-CH_2-$); IR (KBr) 1620, 1580, 1540, 1455, 1435, 1420, 925, 805, 700 cm^{-1}; mass spectrum, *m/e* (rel intensity) 337 (M + 1, 26), 336 (M, 100), 335 (M − 1, 25), 333 (34), 167 (32).

5,6-Dihydro-9-phenylpyrido[2,3-*b*][1,10]phenanthroline (12). By the same procedure as described above for **4**, 0.20 g (0.889 mmol) of **10** was treated with 0.12 g (0.96 mmol) of acetophenone. After 24-h reflux, the solvent was evaporated and the residue was chromatographed on alumina with EtOAc–MeOH eluant to provide a crude product, which was dissolved in aqueous HCl and extracted with CH_2Cl_2. The aqueous phase was made basic with NaOH and the precipitate collected to afford 0.15 g (55%) of **12**: mp 112–115 °C; ^1H NMR (80 MHz, $CDCl_3$) δ 8.80 (dd, H_9, $J_{8,9}$ = 4.7 Hz, $J_{8,10}$ = 1.7 Hz), 8.31 (m, 2 H), 8.08 (m, 1 H), 7.89 (s, 1 H), 7.62–7.23 (m, 6 H); IR (KBr) 1590, 1560, 1530, 1470, 1430, 1410, 1300, 760, 690 cm^{-1}; mass spectrum, *m/e* (rel intensity) 310 (M + 1, 10), 309 (M, 11), 222 (12), 163 (13), 143 (57), 142 (100).

Preparation of Dirhodium Complexes. $Rh_2(OAc)_3(2)[PF_6]$. A mixture of 18.6 mg (55 μmol) of **2** and 24.5 mg (55 μmol) of $Rh_2(OAc)_4$ in 25 mL of methanol was stirred under N_2 at room temperature. After 1 h the turquoise solution had become deep purple, and it was allowed to stand at room temperature overnight. Aqueous NH_4PF_6 was added to precipitate the complex, which was recrystallized from acetonitrile–water to afford 38 mg (79%) of purple needles: ^1H NMR (300 MHz, CD_3CN)[11] δ 9.56 (dd, H_2/H_9, $J_{2,3}$ = 5.0 Hz, $J_{2,4}$ = 1.9 Hz), 8.31 (s, H_5/H_6), 8.24 (dd, H_4/H_7, $J_{3,4}$ = 8.0 Hz), 8.10 (dd, H_3/H_8), 3.47 (s, 8 H, $-CH_2-$), 2.27 (s, 3 H, axial OAc), 1.42 (s, 3 H, equatorial OAc) thermospray mass spectrum, *m/e* 717.

$Rh_2(OAc)_3(3)[PF_6]$. By the procedure described above, 18.6 mg (55 μmol) of **3** and 24.5 mg (55 μmol) of $Rh_2(OAc)_4$ gave a complex that was recrystallized first from acetonitrile–toluene and then from acetonitrile–water to afford 40 mg (84%) of red crystals: ^1H NMR (300 MHz, CD_3CN)[11] δ 11.33 (d, H_{10}, $J_{9,10}$ = 7.8 Hz), 9.32 (dd, H_2, $J_{2,3}$ = 5.1 Hz, $J_{2,4}$ = 1.3 Hz), 8.37 (s, H_5), 8.33 (s, H_6), 8.32 (m, H_4 and H_9), 8.05 (dd, H_3, $J_{3,4}$ = 7.9 Hz), 7.96 (t of d, H_8, $J_{7,8}$ = 6.6 Hz, $J_{8,9}$ = 5.6 Hz, $J_{8,10}$ = 1.0 Hz), 7.78 (d, H_7), 3.17–3.05 (4 t, 4 H, $-CH_2-$), 2.21 (s, 3 H, axial OAc), 1.51 (s, 6 H, equatorial OAc); ^{13}C NMR (75 MHz, CD_3CN) δ 149.5, 145.4, 141.4, 140.8, 139.0, 138.5, 137.6, 136.6, 135.7,

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135.2, 131.9, 131.8, 130.5, 127.4, 119.8, 29.8, 28.5, 26.8, 26.6; thermospray mass spectrum, *m/e* 716.

$Rh_2(OAc)_3$(12)[PF_6]. By the procedure described above, 17 mg (55 μmol) of **12** and 24.5 mg (55 μmol) of $Rh_2(OAc)_4$ gave a complex that was recrystallized from acetonitrile–water to afford 36 mg (78%) of dark red crystals: ^1H NMR (300 MHz, CD_3CN)[11] δ 9.27 (dd, H_2, $J_{2,3}$ = 5.1 Hz, $J_{2,4}$ = 2.3 Hz), 8.67 (d, H_{10} (2 H), J = 4.6 Hz), 8.54 (d, H_6, $J_{6,6a}$ = 8.4 Hz), 8.44 (s, H_5), 8.26 (d, H_4, J = 7.9 Hz), 8.12–7.96 (m, H_{6a}, H_3, H_7, H_8, H_9), 3.49 (s, $-CH_2-$), 2.14 (s, 3 H, axial OAc), 1.55 (s, 6 H, equatorial OAc); thermospray mass spectrum, *m/e* 692.

Cyclic Voltammetry. Reagent grade acetonitrile was distilled twice from P_2O_5 under nitrogen. The supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP), was recrystallized from EtOAc–hexane, dried, and stored in a desiccator.

Cyclic voltammograms were recorded with a PAR Model 174A polarographic analyzer, PAR Model 175 universal programmer, and a Houston Instruments Omnigraphic 2000 X-Y recorder. A three-electrode system was employed consisting of a platinum-button working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode. The reference electrode was separated from the bulk of the solution by a cracked-glass bridge filled with 0.1 M TBAP in acetonitrile. Deaeration of all solutions was performed by passing high-purity nitrogen through the solution for 5 min and maintaining a blanket of nitrogen over the solution while making measurements.

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Contribution from the Department of Inorganic Chemistry, The Royal Institute of Technology,
S-100 44 Stockholm 70, Sweden, and SESD, CEN-FAR, 92260 Fontenay-aux-Roses, France

Studies of Metal–Carbonate Complexes. 14. Composition and Equilibria of Trinuclear Neptunium(VI)- and Plutonium(VI)–Carbonate Complexes

Ingmar Grenthe,*† Chantal Riglet,‡ and Pierre Vitorge‡

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The chemical composition of the trinuclear complexes $(MO_2)_3(CO_3)_6^{6-}$ and the equilibrium constants for the reaction $3MO_2(CO_3)_3^{4-} \rightleftarrows (MO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$, where M = Np or Pu, have been determined by spectrophotometric and emf methods. The values of the equilibrium constants at I = 3 M ($NaClO_4$) and T = 22 ± 1 °C are $\log K_{3,6}(Np) = -10.1 \pm 0.1$ and $\log K_{3,6}(Pu) = -7.4 \pm 0.2$; the constant for U determined previously is -11.3 ± 0.1. The range of stability of the trinuclear plutonium complex is much larger than those of uranium and neptunium, a fact that might be due to a lower stability of the limiting $PuO_2(CO_3)_3^{4-}$ complex. We have demonstrated the formation of mixed complexes of the type $(MO_2)_x(M'O_2)_{3-x}(CO_3)_6^{6-}$ in the U(VI)–Np(VI)–Pu(VI)–carbonate system, formed by the isomorphic substitution of U(VI) by another actinide. Spectral characteristics and estimated stabilities are given for $(UO_2)_2(MO_2)(CO_3)_6^{6-}$ (M = Np, Pu). The equilibrium constants for the reaction $2UO_2(CO_3)_3^{4-} + MO_2(CO_3)_3^{4-} \rightleftarrows (UO_2)_2(MO_2)(CO_3)_6^{6-} + 3CO_3^{2-}$, where M = Np or Pu, are equal to $\log K(Np) = -10.0 \pm 0.1$ and $\log K(Pu) = -8.8$.

The structure and compositions of the limiting complex $UO_2(CO_3)_3^{4-}$, formed in the U(VI)–H_2O–carbonate system, have been well-known for a long time.[1,2] The corresponding Np(VI) and Pu(VI) systems have not been as extensively studied; however, several investigations indicate that the limiting complexes have the same stoichiometry as found in the uranium system. Simakin[3] and Maya[4] used solubility and emf techniques to establish this fact for the neptunium system, while Sullivan et al.[5] used a spectrophotometric technique in a study of the corresponding plutonium carbonates.

There is less agreement about the composition of the precursor to the limiting complex. We have previously established the formation of $UO_2(CO_3)_2^{2-}$ and the trimer[2,6] $(UO_2)_3(CO_3)_6^{6-}$. The trimer is strongly stabilized in solutions of high ionic strength,[2] and it is this species that accounts for the very high solubility of UO_2CO_3(s) in carbonate solutions. Gel'man et al.[7] noticed a similar high solubility of ammonium diplutonate in ammonium carbonate solutions (solubilities up to 22.7 g of Pu/L). With increasing total concentration of plutonium, the authors[5] noticed a color change from green (the color of $PuO_2(CO_3)_3^{4-}$) to red. Haag[8] made similar observations on the Np(VI)–carbonate system and suggested that the red color was due to the complex $NpO_2(CO_3)_2^{2-}$. Maya[4] made a quantitative study of the Np(VI)–carbonate system and interpreted his data in terms of the formation of $NpO_2(CO_3)_2^{2-}$, $NpO_2(CO_3)_3^{4-}$, and a mixed complex $(NpO_2)_2(OH)_3(CO_3)^-$.

From the chemical similarities generally observed in the actinide series between elements of the same oxidation state (e.g. the solubilities in actinide(VI)–carbonate systems) one expects to find chemical species of the same composition and with only minor variations in chemical properties (apart from their redox potentials). The variations of properties are of great chemical interest and can be correlated with the size of the central ion or with the f-electron configuration, as is often done when chemical variations through the lanthanide group are interpreted.

The $(MO_2)_3(CO_3)_6^{6-}$ structure[9] is extremely well adapted to the steric requirements of both the MO_2^{2+} and the CO_3^{2-} ions, and it seems very likely that one or more MO_2^{2+} ions can be replaced by another actinoid(VI) ion. One of the themes of this communication will be to demonstrate the formation of such heterometallic complexes.

We have previously described two different experimental techniques, viz. potentiometric measurements of the concentration

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† The Royal Institute of Technology.
‡ SESD, CEN-FAR.

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