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Contribution from the Department of Inorganic Chemistry,
Indian Association for the Cultivation of Science, Calcutta 700032, India

Chemistry of the $[Ru(RQ)(tap)_2]^z$ Family: Authentic Catecholates, Reduction Potentials, and Spectra (RQ = Quinone/Semiquinone/Catecholate; tap = 2-(*m*-Tolylazo)pyridine; *z* = 0, ±, ±2)

Nilkamal Bag, Amitava Pramanik, Goutam Kumar Lahiri, and Animesh Chakravorty*

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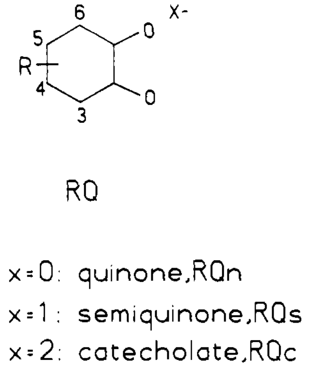
Diamagnetic complexes of type $Ru(RQc)(tap)_2$ are synthesized by reacting $[Ru(OH_2)_2(tap)_2](ClO_4)_2{\cdot}H_2O$ with catechols in the presence of base (RQc = catecholate having R = H, 4-*t*-Bu, 3,5-(*t*-Bu)$_2$ or 3,4,5,6-Cl$_4$; tap = 2-(*m*-tolylazo)pyridine). Oxidation of these by cerium(IV) affords paramagnetic ($S = {}^1/_2$) $[Ru(RQs)(tap)_2]ClO_4$ (RQs = semiquinone). The X-ray structure of $[\{Ru(RQc)(tap)_2\}_2H_2O]{\cdot}CH_2Cl_2$ (R = H) is reported: space group $P\bar{1}$, $Z = 2$, $a = 12.465$ (2) Å, $b = 14.983$ (3) Å, $c = 16.775$ (3) Å, $\alpha = 90.21$ (2)°, $\beta = 100.26$ (1)°, $\gamma = 104.86$ (2)°, and $V = 2976$ (1) Å^3. The water molecule hydrogen bridges two chelate molecules via RQc oxygen atoms to give a dimer. The average Ru–O and C–O distances are 2.022 (5) and 1.342 (9) Å, respectively. Here the interacting metal dπ and RQ pπ redox orbitals are fully occupied (eight electrons). The EPR spectrum of $[Ru^{II}(RQs)(tap)_2]^+$ in frozen (77 K) dichloromethane glass shows a small anisotropy corresponding to a minor contribution of the $Ru^{III}(RQc)$ cannonical form. The complexes display four voltammetric responses corresponding to the processes RQn/RQs, RQs/RQc, $(tap)_2/(tap^{\bullet-})(tap)$ and $(tap^{\bullet-})(tap)/(tap^{\bullet-})_2$ (RQn = quinone). The $E_{1/2}$ values in the R = H case are 0.97, 0.20, –0.68 and –1.24 V, respectively. Comparison with the bpy congeners reveals that replacement of the bpy pair by the tap pair raises the reduction potentials of both RQ and the metal by a remarkable ~800 mV. The $Ru(RQc)(tap)_2$ species, unlike the bpy analogues, are perfectly stable in air. The former complexes absorb strongly in the near-IR region (800–1300 nm) due to interligand RQc(pπ) → tap(azo pπ^*) excitation. The corresponding absorption in $[Ru(RQs)(tap)_2]^+$ occurs near 700 nm. There is also a feature near 1000 nm assignable to the MLCT excitation Ru(dπ) → RQs(pπ). The transition energies are in qualitative agreement with observed reduction potentials.

Introduction

The quinonoid triad, RQ (**1**) (skeleton only), constitutes a fascinating redox-active ligand system for transition-metal ions. The C–O length is in general an excellent index of the gross state of oxidation of coordinated RQ.[1] This work concerns RQ complexes of ruthenium and forms part of our program on phenolates of the metal.[2-4] A common feature of ruthenium–RQ chemistry is delocalization of redox electrons between the metal and the RQ ligand.[5-8] As a result of this, C–O lengths in RQ complexes of ruthenium have rarely conformed in a simple manner to any one of three specific oxidation states (**1**) of RQ.[5a,c,e]

Stable ruthenium–RQ species with localized integral oxidation states are thus of interest. Orbital considerations suggest that the $Ru^{II}(RQc)$ combination should be a good candidate for this situation. We have employed the N,N-chelating ligand 2-(*m*-tolylazo)pyridine (tap, **2**)[9-11] to confer redox stability to this combination. The family of complexes reported here is of type $[Ru(RQ)(tap)_2]^z$ (z = 0, ±, 2±). The z = 0 and + species have been isolated as air-stable solids. The others are observed electrochemically in solution. The X-ray structure of a z = 0 complex has revealed that the metal and RQ ligand are indeed bonded in the formally exact $Ru^{II}(RQc)$ configuration. The effect of the tap coligand vis-à-vis that of 2,2′-bipyridine (bpy)[6a] on reduction



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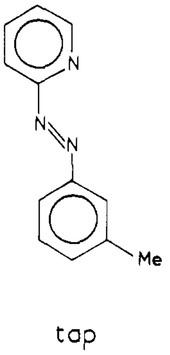

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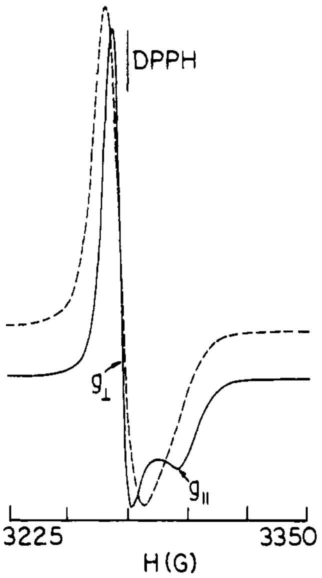

Figure 1. X-Band EPR spectra of $[Ru(Qs)(tap)_2]ClO_4$ in the microcrystalline state (---) and in a dichloromethane glass (—) at 77 K.

potentials is noted. The origin of low-energy charge-transfer transitions is briefly examined.

Results and Discussion

A. Synthesis and Characterization. Four R groups have been utilized: H, 4-*t*-Bu, 3,5-(*t*-Bu)$_2$ and 3,4,5,6-Cl$_4$—the corresponding RQ ligands are represented as Q, BuQ, Bu$_2$Q and Cl$_4$Q respectively. The precursor complex used for synthesis is *tc*-$[Ru(OH_2)_2(tap)_2](ClO_4)_2 \cdot H_2O$, in which the pyridine nitrogen atoms are mutually trans and the coordinated azo nitrogen atoms are cis; the water molecules are also cis.[9d]

The synthetic reactions are stated in eqs 1 and 2 where the coordinated RQ ligand is shown in appropriately localized forms

$$[Ru(OH_2)_2(tap)_2]^{2+} + H_2RQc + 2OH^- \rightarrow Ru(RQc)(tap)_2 + 4H_2O \quad (1)$$

$$Ru(RQc)(tap)_2 + Ce(IV) \rightarrow [Ru(RQs)(tap)_2]^+ + Ce(III) \quad (2)$$

as proven later. The equimolecular reaction of the diaquo complex with H_2RQc (catechols) in boiling methanol in the presence of base affords blue-violet complexes of type $Ru(RQc)(tap)_2$ in excellent yields. Only the Qc complex could be grown into X-ray quality single crystals from a dichloromethane–hexane mixture. Oxidation of $Ru(RQc)(tap)_2$ by cerium(IV) in aqueous acetonitrile furnishes violet-colored $[Ru(RQs)(tap)_2]^+$, which is isolated in near-quantitative yield as the perchlorate salt.

$Ru(RQc)(tap)_2$ complexes are diamagnetic and are nonelectrolytic in solution. On the other hand, the $[Ru(RQs)(tap)_2]ClO_4$ complexes are 1:1 electrolytic in MeCN solution (Λ = 120–140 Ω^{-1} cm^2 M^{-1} at 298 K) and behave as one-electron paramagnets (μ_{eff} at 298 K: Qs, 1.80 μ_B; BuQs, 1.78 μ_B; Bu$_2$Qs, 1.83 μ_B; Cl$_4$Qs, 1.82 μ_B). The complexes are EPR active. The spectra of microcrystalline solids consist of a relatively broad signal at g = 2.0. In frozen (77 K) dichloromethane glass the signal splits into axial components (Figure 1). Representative g values are as follows: for $[Ru(Qs)(tap)_2]^+$, $g_\perp$ = 2.004 and $g_\parallel$ = 1.979; for $[Ru(Bu_2Qs)(tap)_2]^+$, $g_\perp$ = 2.004, and $g_\parallel$ = 1.991.

The $Ru^{II}(tap)_2$ chromophore is known to absorb strongly in the visible region extending upto 600 nm or so due to the $Ru(d\pi) \rightarrow tap(azo\ \pi^*)$ MLCT excitation.[9d,10b,11a] The $Ru(RQc)(tap)_2$ and $[Ru(RQs)(tap)_2]^+$ complexes display similar absorption bands. One or two bands also occur at lower energies. Their probable origin is considered in a later section. Spectral data are collected in Table I, and representative spectra are shown in Figure 2.

Table I. Electronic Spectral Data for $Ru(RQ)(tap)_2$ in Dichloromethane at 298 K

compd	UV–vis–near-IR data λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$Ru(Qc)(tap)_2$	1150 (2620), 950^a (2570), 600 (8700), 530^a (6075), 315 (25 230)
$Ru(BuQc)(tap)_2$	1200 (2940), 960^a (2480), 600 (8000), 530^a (6155), 310 (24 615)
$Ru(Bu_2Qc)(tap)_2$	1275 (3060), 1050^a (2570), 570 (8620), 520^a (7140), 335^a (23 930), 310 (25 000)
$Ru(Cl_4Qc)(tap)_2$	1025 (1660), 815 (2590), 600 (9310), 540^a (6210), 320 (24 140)
$[Ru(Qs)(tap)_2]ClO_4$	1000^a (2720), 725 (8600), 550 (15 080), 350^a (25 800), 305 (30 200)
$[Ru(BuQs)(tap)_2]ClO_4$	1000^a (670), 715 (5410), 555 (9080), 350^a (31 020), 310 (41 220)
$[Ru(Bu_2Qs)(tap)_2]ClO_4$	1065^a (1170), 700 (10 100), 560 (16 940), 350^a (28 570), 310 (37 550)
$[Ru(Cl_4Qs)(tap)_2]ClO_4$	900 (10 150), 750^a (7810), 540 (13 125), 345 (25 780), 280 (23 125)

^{a} Shoulder.

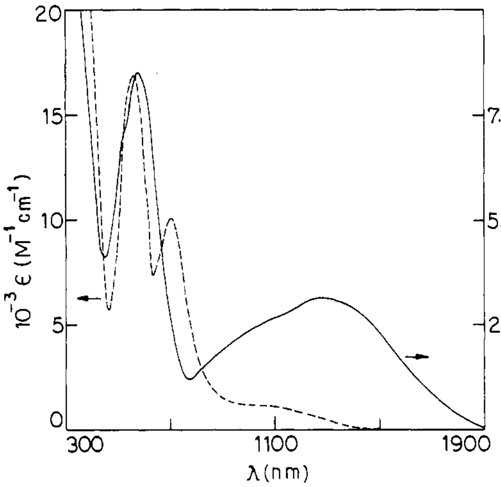

Figure 2. Electronic spectra of $Ru(Bu_2Qc)(tap)_2$ (—) and $[Ru(Bu_2Qs)(tap)_2]ClO_4$ (---) in dichloromethane.

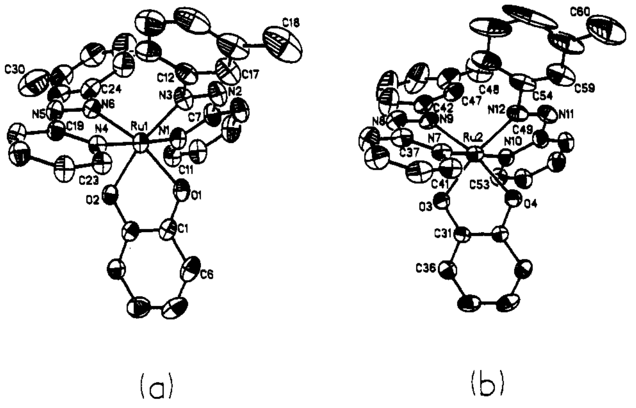

Figure 3. Perspective view and labeling scheme for the two independent $Ru(Qc)(tap)_2$ molecules.

B. Molecular and Electronic Structure. a. X-ray Structure of Ru(Qc)(tap)$_2$. The single crystals contain water and dichloromethane of crystallization in the ratio $Ru(Qc)(tap)_2$:H_2O:CH_2Cl_2 = 2:1:1. The lattice consists of two crystallographically independent $Ru(Qc)(tap)_2$ molecules, which differ conspicuously in the relative orientation of the *m*-tolyl ring; see Figure 3. These are bridged by the water molecule; see Figure 4. The O(1)··O(1W) and O(4)··O(1W) lengths are 2.829 (8) and 2.842 (8) Å, respectively, corresponding to hydrogen bonds of moderate strength. The O(1)–O(1W)–O(4) angle is 110.9 (3)°. The crystalline complex is thus $[\{Ru(Qc)(tap)_2\}_2H_2O] \cdot CH_2Cl_2$. The dichloromethane molecule is disordered in the lattice.

Selected bond distances and angles are listed in Table II. The RuN_4O_2 coordination spheres are distorted octahedral as can be seen from the angles subtended at the metal. The two pyridine

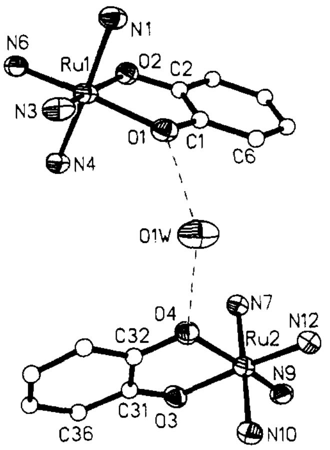

Figure 4. Perspective view showing the water bridge between the two $Ru(Qc)(tap)_2$ molecules.

Table II. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $[\{Ru(Qc)(tap)_2\}_2H_2O]\cdot CH_2Cl_2$

	Distances		
Ru(1)–O(1)	2.029 (5)	Ru(2)–O(3)	2.012 (5)
Ru(1)–O(2)	2.026 (5)	Ru(2)–O(4)	2.022 (5)
Ru(1)–N(1)	2.014 (6)	Ru(2)–N(7)	2.002 (6)
Ru(1)–N(3)	1.952 (7)	Ru(2)–N(9)	1.975 (6)
Ru(1)–N(4)	2.024 (6)	Ru(2)–N(10)	2.007 (6)
Ru(1)–N(6)	1.968 (5)	Ru(2)–N(12)	1.962 (7)
O(1)–C(1)	1.343 (9)	O(3)–C(31)	1.340 (9)
O(2)–C(2)	1.341 (8)	O(4)–C(32)	1.345 (9)
C(1)–C(2)	1.412 (9)	C(31)–C(32)	1.397 (10)
N(2)–N(3)	1.299 (9)	N(8)–N(9)	1.305 (9)
N(5)–N(6)	1.277 (8)	N(11)–N(12)	1.286 (9)
	Angles		
O(1)–Ru(1)–O(2)	82.0 (2)	O(3)–Ru(2)–O(4)	81.9 (2)
O(1)–Ru(1)–N(1)	88.4 (2)	O(3)–Ru(2)–N(7)	86.8 (2)
O(2)–Ru(1)–N(1)	93.4 (2)	O(4)–Ru(2)–N(7)	94.6 (2)
O(1)–Ru(1)–N(3)	88.3 (2)	O(3)–Ru(2)–N(9)	86.8 (2)
O(2)–Ru(1)–N(3)	166.4 (2)	O(4)–Ru(2)–N(9)	166.2 (2)
N(1)–Ru(1)–N(3)	76.8 (3)	N(7)–Ru(2)–N(9)	76.9 (2)
O(1)–Ru(1)–N(4)	94.2 (2)	O(3)–Ru(2)–N(10)	92.7 (2)
O(2)–Ru(1)–N(4)	87.0 (2)	O(4)–Ru(2)–N(10)	83.4 (2)
N(1)–Ru(1)–N(4)	177.4 (2)	N(7)–Ru(2)–N(10)	178.0 (2)
N(3)–Ru(1)–N(4)	103.2 (3)	N(9)–Ru(2)–N(10)	105.0 (2)
O(1)–Ru(1)–N(6)	166.4 (2)	O(3)–Ru(2)–N(12)	167.8 (2)
O(2)–Ru(1)–N(6)	87.2 (2)	O(4)–Ru(2)–N(12)	90.0 (2)
N(1)–Ru(1)–N(6)	100.6 (2)	N(7)–Ru(2)–N(12)	103.0 (3)
N(3)–Ru(1)–N(6)	103.6 (2)	N(9)–Ru(2)–N(12)	102.4 (3)
N(4)–Ru(1)–N(6)	76.8 (2)	N(10)–Ru(2)–N(12)	77.3 (3)

and the two azo nitrogen atoms in the coordination sphere constitute trans and cis pairs respectively in both molecules. Thus the synthetic reaction of eq 1 is stereoretentive for the $Ru(tap)_2$ fragment. The R–N(azo) distances are shorter than Ru–N(py) distances by 0.03–0.06 Å. The N–N length (average, 1.292 (9) Å) is longer than that in free azo ligands (~1.25 Å).[12] These observations are consistent with $d\pi$–$p\pi^*$ back-bonding within the Ru–azo fragment.[9d,10b,11a]

The O,O-chelating Q ligands are planar in both molecules with mean deviation of 0.02 Å in each case. The Ru(1) and Ru(2) atoms are however deflected from the respective planes by ~0.1 and ~0.3 Å, respectively. There is a corresponding fold along the O···O line within the Qc fragments, the fold angles being 2.1 and 11.5° in the cases Ru(1)Qc and Ru(2)Qc, respectively. The average Ru–O distance is 2.022 (5) Å, which is expectedly longer than the Ru^{III}–O(phenolato) distance, 1.981 (2) Å.[3]

The four C–O lengths are equal within experimental error, the range being 1.340 (9) -1.345 (9) Å. This corresponds to the model

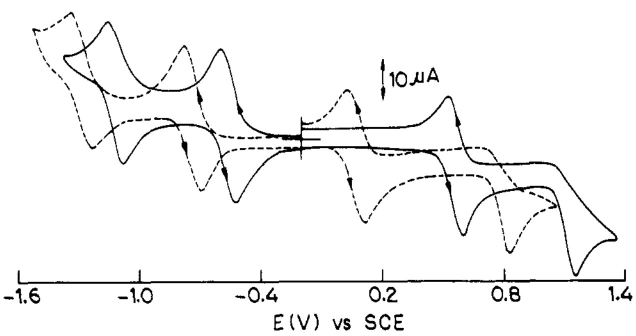

Figure 5. Cyclic voltammograms (298 K) of $Ru(Cl_4Qc)(tap)_2$ (—) and $Ru(Bu_2Qc)(tap)_2$ (---) in acetonitrile (0.1 M TEAP).

Table III. Reduction Potentials[a,b] of the Complexes at 298 K

	$E_{1/2}$, V(ΔE_p, mV)			
compd	RQn/ RQs	RQs/ RQc	$(tap)_2$/ $(tap)(tap^{\bullet-})$	$(tap)(tap^{\bullet-})$/ $(tap^{\bullet-})_2$
$Ru(Qc)(tap)_2$[c]	0.97[d]	0.20 (80)	-0.68 (80)	-1.24 (90)
$Ru(BuQc)(tap)_2$	0.86[d]	0.10 (90)	-0.72 (90)	-1.26 (80)
$Ru(Bu_2Qc)(tap)_2$	0.84[d]	0.08 (90)	-0.73 (80)	-1.29 (90)
$Ru(Cl_4Qc)(tap)_2$	1.17[d]	0.57 (70)	-0.54 (60)	-1.10 (60)

[a] Conditions: solvent, acetonitrile (unless otherwise stated); supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration, $\sim 10^{-3}$ M. [b] Determined cyclic voltammetrically at 298 K; unless otherwise stated the data correspond to $E_{1/2} = 0.5(E_{pa} + E_{pc})$ at scan rate 50 mV s^{-1}, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{pa} - E_{pc}$. [c] In dichloroethane solution values are 1.17,[d] 0.20, -0.75 and -1.23 V, respectively. [d] E_{pa} value (E_{pc} not observed).

catecholato C–O distance.[1,13] The present complex represents the only structurally characterized ruthenium–RQ species with an authentic Ru^{II}(RQc) moiety, and more generally, it represents a case where integral oxidation states can be assigned to the metal and the ligand in a straightforward manner.

b. Orbitals and Oxidation States. For ruthenium oxidation states ≥2, metal redox occurs in the $d\pi$ (t_{2g} in idealized O_h symmetry) orbital. The redox electrons of the RQ triad (**1**) reside in a $p\pi$ ($3b_1$ in C_{2v} symmetry) orbital.[6b] In distorted complexes $d\pi$–$p\pi$ mixing can occur.[14] The net symmetry of the $[Ru(RQ)(tap)_2]^z$ skeleton cannot exceed C_2 (Figure 3). In this symmetry t_{2g} becomes a + 2b and b_1 becomes b. Thus at least two of the metal $d\pi$ orbitals can mix with the RQ $p\pi$ orbital. When the $d\pi$ and $p\pi$ orbitals are both fully occupied (eight electrons) the system effectively preserves the Ru^{II}(RQc) character in spite of the mixing. Cannonical forms like Ru^I(RQs) and Ru^0(RQn) require metal $d\sigma$(e_g) participation and cannot therefore make a significant contribution. For 1:1, 1:2 and 1:3 ruthenium-RQ complexation the ruthenium(II)–catecholate situation would correspond to the charge types $[Ru(RQ)]^0$, $[Ru(RQ)_2]^{2-}$, and $[Ru(RQ)_3]^{4-}$, respectively. The $Ru(RQc)(tap)_2$ complexes represent the first type.

Oxidation state ambiguity can arise when one or more holes are introduced into the $d\pi$–$p\pi$ ensemble. The one-hole limiting formulations $[Ru^{II}(RQs)]^+$ and $[Ru^{III}(RQc)]^+$ for the 1:1 complex correspond to the hole having pure $p\pi$ and $d\pi$ characters respectively. The actual situation in a particular case depends on the extent of mixing. The very small *g* anisotropy of $[Ru(RQs)(tap)_2]^+$ (Figure 1) shows that the $[Ru^{III}(RQc)(tap)_2]^+$ form contributes only nominally and the predominant electronic form is $[Ru^{II}(RQs)(tap)_2]^+$. The formulation of our *z* = + complexes as semiquinonates is thus not exact, but it is a very good approximation.

The case is similar to that of the corresponding bpy complexes.[6a] The structure of $[Ru(Bu_2Qs)(bpy)_2]ClO_4$ is known.[5a] Unfortu-

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nately the two C–O distances are found to be very unequal (1.289 (4) and 1.327 (5) Å) and are therefore unsuitable for oxidation state characterization. We have not succeeded so far in growing good quality single crystals for a $[Ru(RQs)(tap)_2]^+$ complex.

C. Redox Behavior. a. Electron-Transfer Series. Both $Ru(RQc)(tap)_2$ and $[Ru(RQs)(tap)_2]^+$ are electroactive in solution and display the same four voltammetric responses in the potential range ±1.5 V versus SCE (298 K). A representative voltammogram is shown in Figure 5. Peak-to-peak separations lie in the range 60–90 mV. Reduction potential data are collected in Table III. The assignments of data to specific couples in Table III (only the redox site is indicated) are based on the following considerations examplified for the representative case of $Ru(Qc)(tap)_2$.

We consider the couple near 0.2 V first. Coulometric oxidation at 0.4 V consumes one-electron and quantitatively affords $[Ru(Qs)(tap)_2]^+$, which is completely reconverted to $Ru(Qc)(tap)_2$ by coulometric reduction at 0.0 V. Thus the couple near 0.2 V corresponds to the electrode reaction of eq 3. The formal potential

$$[Ru^{II}(Qs)(tap)_2]^+ + e^- \rightleftharpoons Ru^{II}(Qc)(tap)_2 \qquad (3)$$

of the couple depends on the R substituent in the expected manner, and the total span in the present group of examples is ~0.5 V (Table III). The response at ~1.0 V consists of an anodic peak only. Evidently the oxidized complex decomposes on the cyclic voltammetric time scale. Experiments carried out at 253 K did not improve the situation. The anodic process is believed to be the oxidation of $[Ru(Qs)(tap)_2]^+$ to unstable $[Ru(Qn)(tap)_2]^+$ (vide infra).

The responses near −0.7 and −1.2 V cannot involve the Q ligand since it is already fully reduced to the Qc state. These are logically assigned[9e] to azo reduction, eqs 4 and 5. The reduced species

$$Ru(Qc)(tap)_2 + e^- \rightleftharpoons Ru(Qc)(tap^{\bullet -})(tap) \qquad (4)$$

$$Ru(Qc)(tap^{\bullet -})(tap) + e^- \rightleftharpoons Ru(Qc)(tap^{\bullet -})_2 \qquad (5)$$

are not stable, forbidding their coulometric generation in bulk concentrations.

b. Effect of Coligand on Reduction Potential. The strong influence of coligand on RQ reduction potentials is revealed by comparing the Qs–Qc couples in the tap (0.2 V) and bpy (−0.57 V)[6a] complexes in dichloroethane solution. The reduction potential in the tap complex lies higher by a remarkable ~800 mV. Replacement of bpy by tap in otherwise similarly constituted ruthenium complexes is known to cause a strong upward shift (300–400 mV/replacement) of the Ru^{III}/Ru^{II} potential.[9e] The present results demonstrate that the direct or indirect (i.e. via metal) tap–RQ electronic coupling is strong and the effect of the replacement of bpy by tap on reduction is transmitted to RQ with little attenuation from the intervening metal atom. As a sequel to the raised potential $Ru(Qc)(tap)_2$ is perfectly stable in air unlike the bpy complex, which undergoes spontaneous aerobic oxidation.

The Qn/Qs and Ru^{III}/Ru^{II} reduction potentials in the bpy system lie at 0.31 and 1.40 V respectively.[6a] The corresponding potentials in the tap system are then expected to lie near 1 and 2 V, respectively. The former response is indeed observed (Table III, Figure 5) but the latter lies beyond the solvent cut-off limit.

c. Charge-Transfer Transition. Charge-transfer transition energies of ruthenium complexes can be estimated from reduction potential differences of donor and acceptor sites.[6a,7,9e,15,16] In $[Ru(RQ)(tap)_2]^z$ the $(tap)_2/(tap^{\bullet -})(tap)$ couple is separated from the RQs/RQc and RQn/RQs couples by ~1 and ~1.6 V, respectively (Table III). The moderately strong band(s) of $Ru(RQc)(tap)_2$ in the near-IR region (800–1300 nm) (Table I, Figure 2) is assigned to the interligand RQc(pπ) → tap(azo pπ*) excitation(s). Similarly the band in $[Ru(RQs)(tap)_2]^+$ near 700 nm is most likely to be due to RQs → tap excitation. The Ru^{III}/Ru^{II} reduction potential was estimated above to be ~2 V, and the RQn/RQs potential is ~1 V. The feature near 1000 nm in $[Ru(RQs)(tap)_2]^+$ is therefore consistent with the MLCT transition Ru(dπ) → RQs(pπ).

Table IV. Crystallographic Data for $[\{Ru(Qc)(tap)_2\}_2H_2O]\cdot CH_2Cl_2$

chem formula	$C_{61}H_{56}N_{12}O_5Cl_2Ru_2$	V, Å^3	2976 (1)
fw	1310.2	Z	2
space group	$P\bar{1}$	T, °C	22 ± 1
a, Å	12.465 (2)	λ, Å	0.71073
b, Å	14.983 (3)	ρ_{calcd}, g cm^{-3}	1.462
c, Å	16.775 (3)	μ, cm^{-1}	6.45
α, deg	90.21 (2)	trans coeff	0.8138–0.9507
β, deg	100.26 (1)	R^a	0.0530
γ, deg	104.86 (2)	$R_w{}^b$	0.0672

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2 / w|F_o|^2]^{1/2}$. $w^{-1} = \sigma^2(|F_o|) + 0.0008|F_o|^2$.

D. Concluding Remarks. The main results of this research will be enumerated. Complexes of type $Ru^{II}(RQc)(tap)_2$ have been synthesized and the structure of one of these (R = H)—the first structure of an authentic catecholato ruthenium complex—has been determined. The C–O distance is 1.342 (9) Å. Here the parent redox orbitals of the metal (dπ, a + 2b) and RQ (pπ, b) are fully occupied (eight electrons).

Upon oxidation by cerium(IV), a hole (seven electrons) is created in the dπ–pπ ensemble, affording a cationic complex isolated as the perchlorate. The hole is primarily pπ in character, but there is a nominal dπ character as reflected in a small g tensor anisotropy. The cationic complex is thus formulated as $[Ru(RQs)(tap)_2]^+$.

In solution the complexes display the redox series: RQn/RQs, RQs/RQc, $(tap)_2/(tap^{\bullet -})(tap)$, and $(tap^{\bullet -})(tap)/(tap^{\bullet -})_2$. The Ru^{III}/Ru^{II} couple is not observed, but its potential can be estimated. The tap ligand causes a strong positive shift of potentials. The interligand charge-transfer transition (RQ(pπ) → tap(azo pπ*) and Ru^{II}(dπ) → RQs(pπ)) energies qualitatively correlate with the relevant reduction potentials.

Experimental Section

Materials. The *tc*-$[Ru(OH_2)_2(tap)_2](ClO_4)_2\cdot H_2O$ complex was prepared according to the reported procedure.[9d] The catechols were received from Aldrich Chemical Co., Inc. Purification of solvents and preparation of tetraethylammonium perchlorate for electrochemical work was done as before.[4] All other chemicals and solvents were reagent grade and used as received.

Physical Measurements. UV–vis–near-IR spectra were recorded by using a Hitachi 330 spectrophotometer. X-Band EPR spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar flask for measurements at 77 K (liquid nitrogen). The spectra were calibrated with respect to DPPH (g = 2.0037). Electrochemical measurements were done by using PAR Model 370-4 electrochemistry system as described elsewhere.[3] All experiments were performed under pure dinitrogen atmosphere, and recorded potentials are uncorrected for junction contribution. Magnetic susceptibilities were measured on a PAR-155 vibrating-sample magnetometer fitted with a Walker magnet. Solution electrical conductivity was measured by using a Philips PR 9500 bridge. Micro-analyses (CHN) were done by using a Perkin-Elmer 240C elemental analyzer.

Preparation of Compounds. The syntheses of complexes were achieved by using general procedures. Yields varied in the range 85–95%. Details are given for one representative complex of each type.

(Catecholato)bis(2-(*m*-tolylazo)pyridine)ruthenium, $Ru(Qc)(tap)_2$. Pure nitrogen gas was passed for 15 min through a violet-colored solution of *tc*-$[Ru(OH_2)_2(tap)_2](ClO_4)_2\cdot H_2O$ (200 mg, 0.27 mmol) in 25 mL of methanol. Catechol (35 mg, 0.32 mmol) was then added, and the mixture was heated to reflux for 5 min. After addition of 5 mL of methanolic NaOH (26 mg, 0.65 mmol), heating was continued under nitrogen atmosphere for 3 h. The solution gradually became blue-violet. It was evaporated to dryness under reduced pressure, and the solid mass thus obtained was washed thoroughly with water and dried in vacuo over P_4O_{10}. The dried product was dissolved in a small volume of dichloromethane and was subjected to chromatography on a silica gel (60–120 mesh, BDH) column (20 × 1 cm). On elution with benzene a brown band separated out first and was rejected. A blue-violet band was then eluted with acetonitrile–benzene (2:3). The collected eluant was evap-

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Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients[a] ($Å^2 \times 10^3$) for $[\{Ru(Qc)(tap)_2\}_2H_2O]\cdot CH_2Cl_2$

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
Ru(1)	85 (1)	−360 (1)	2422 (1)	47 (1)	N(7)	4272 (5)	3267 (4)	1762 (4)	54 (2)
O(1)	1105 (4)	808 (4)	3035 (3)	55 (2)	N(8)	5616 (5)	4434 (4)	1308 (4)	66 (3)
O(2)	−605 (4)	568 (3)	1786 (3)	51 (2)	N(9)	6235 (5)	4247 (4)	1966 (4)	55 (2)
N(1)	−913 (5)	−455 (4)	3256 (3)	56 (2)	N(10)	6994 (5)	2894 (4)	3257 (3)	54 (2)
N(2)	428 (6)	−1138 (5)	3957 (4)	73 (3)	N(11)	6079 (6)	3387 (5)	4214 (4)	68 (3)
N(3)	738 (5)	−1072 (5)	3256 (4)	61 (3)	N(12)	5494 (5)	3585 (4)	3559 (4)	61 (3)
N(4)	1040 (4)	−318 (4)	1559 (3)	48 (2)	C(31)	5686 (5)	1502 (5)	1677 (4)	48 (3)
N(5)	−649 (5)	−1325 (4)	890 (3)	57 (2)	C(32)	5146 (5)	1183 (5)	2322 (4)	46 (3)
N(6)	−875 (5)	−1310 (4)	1603 (3)	51 (2)	C(33)	4891 (6)	240 (5)	2466 (5)	58 (3)
C(1)	809 (6)	1558 (6)	2736 (4)	53 (3)	C(34)	5173 (8)	−357 (6)	1967 (6)	81 (4)
C(2)	−111 (6)	1437 (5)	2083 (4)	50 (3)	C(35)	5659 (7)	−51 (6)	1287 (6)	79 (4)
C(3)	−459 (7)	2183 (6)	1768 (5)	63 (3)	C(36)	5932 (6)	876 (6)	1158 (5)	64 (3)
C(4)	102 (9)	3077 (6)	2099 (6)	82 (4)	C(37)	4526 (6)	3895 (6)	1192 (5)	64 (3)
C(5)	989 (8)	3211 (7)	2721 (6)	89 (5)	C(38)	3725 (7)	4004 (6)	544 (5)	80 (4)
C(6)	1349 (7)	2457 (7)	3049 (5)	74 (4)	C(39)	2643 (7)	3462 (7)	479 (6)	82 (4)
C(7)	−520 (7)	−825 (6)	3937 (4)	63 (3)	C(40)	2378 (7)	2858 (6)	1062 (6)	77 (4)
C(8)	−1095 (8)	−929 (7)	4592 (5)	83 (4)	C(41)	3193 (6)	2779 (5)	1690 (5)	64 (3)
C(9)	−2081 (8)	−651 (8)	4519 (6)	93 (5)	C(42)	7388 (6)	4808 (5)	2115 (5)	64 (3)
C(10)	−2491 (7)	−272 (7)	3814 (5)	76 (4)	C(43)	7867 (8)	5224 (8)	1509 (7)	113 (5)
C(11)	−1882 (6)	−191 (6)	3204 (5)	67 (3)	C(44)	8988 (11)	5715 (10)	1685 (9)	168 (8)
C(12)	1713 (6)	−1416 (5)	3238 (5)	63 (3)	C(45)	9600 (10)	5789 (9)	2437 (9)	144 (7)
C(13)	1738 (7)	−1922 (6)	2577 (5)	76 (4)	C(46)	9127 (8)	5411 (7)	3030 (7)	95 (5)
C(14)	2718 (10)	−2262 (7)	2567 (7)	98 (5)	C(47)	7997 (7)	4907 (5)	2878 (5)	76 (4)
C(15)	3586 (9)	−2054 (8)	3198 (9)	104 (6)	C(48)	9800 (11)	5484 (10)	3851 (8)	165 (8)
C(16)	3573 (8)	−1525 (8)	3869 (8)	91 (5)	C(49)	6927 (7)	2999 (5)	4054 (4)	61 (3)
C(17)	2621 (7)	−1228 (7)	3884 (6)	83 (4)	C(50)	7722 (8)	2770 (6)	4674 (5)	76 (4)
C(18)	4569 (8)	−1294 (9)	4563 (7)	149 (7)	C(51)	8571 (8)	2464 (6)	4485 (6)	80 (4)
C(19)	416 (6)	−786 (5)	858 (4)	53 (3)	C(52)	8649 (7)	2383 (6)	3686 (5)	75 (4)
C(20)	838 (6)	−750 (5)	148 (4)	59 (3)	C(53)	7863 (6)	2587 (5)	3093 (5)	61 (3)
C(21)	1933 (7)	−251 (6)	169 (5)	67 (4)	C(54)	4674 (7)	4071 (7)	3733 (6)	77 (4)
C(22)	2584 (6)	210 (6)	890 (4)	64 (3)	C(55)	4478 (8)	4758 (7)	3210 (7)	98 (5)
C(23)	2111 (6)	146 (5)	1558 (4)	55 (3)	C(56)	3702 (11)	5233 (9)	3377 (10)	150 (8)
C(24)	−1966 (7)	−1897 (6)	1670 (5)	67 (3)	C(57)	3220 (11)	5047 (14)	4022 (14)	208 (13)
C(25)	−2093 (8)	−2355 (7)	2382 (6)	91 (4)	C(58)	3380 (11)	4330 (10)	4496 (10)	125 (7)
C(26)	−3142 (10)	−2906 (9)	2502 (8)	127 (6)	C(59)	4131 (7)	3858 (7)	4353 (7)	96 (5)
C(27)	−3997 (10)	−2975 (8)	1877 (8)	104 (6)	C(60)	2727 (11)	4180 (10)	5111 (8)	173 (9)
C(28)	−3920 (8)	−2545 (8)	1172 (8)	94 (5)	O(1W)	3371 (5)	1188 (5)	3863 (3)	93 (3)
C(29)	−2868 (7)	−1991 (6)	1055 (6)	78 (4)	C(61)	8719 (18)	3733 (12)	39 (9)	201 (12)
C(30)	−4838 (14)	−2619 (10)	602 (9)	194 (11)	Cl(1)	8190 (6)	4422 (4)	−751 (3)	164 (4)
Ru(2)	5645 (1)	3104 (1)	2507 (1)	49 (1)	Cl(2)	7515 (4)	3201 (4)	487 (4)	146 (3)
O(3)	5930 (4)	2413 (3)	1569 (3)	54 (2)	Cl(3)	9235 (5)	2987 (3)	−315 (3)	141 (3)
O(4)	4895 (4)	1808 (3)	2784 (3)	55 (2)					

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

orated to afford a dark crystalline solid, which was stored over P_4O_{10} in vacuo.

Anal. Calcd for $Ru(Qc)(tap)_2$, $RuC_{30}H_{26}O_2N_6$: C, 59.69; H, 4.31; N, 13.93. Found: C, 60.04; H, 4.45; N, 13.65. Calcd for $Ru(BuQc)(tap)_2$, $RuC_{34}H_{34}O_2N_6$: C, 61.90; H, 5.16; N, 12.74. Found: C, 62.15; H, 5.26; N, 12.55. Calcd for $Ru(Bu_2Qc)(tap)_2$, $RuC_{38}H_{42}O_2N_6$: C, 63.77; H, 5.87; N, 11.75. Found: C, 64.04; H, 6.04; N, 11.62. Calcd for $Ru(Cl_4Qc)(tap)_2$, $RuC_{30}H_{22}O_2N_6Cl_4$: C, 48.58; H, 2.97; N, 11.33. Found: C, 48.72; H, 2.91; N, 11.26.

Single crystals were grown by slow diffusion of a dichloromethane solution of $Ru(Qc)(tap)_2$ into hexane.

Anal. Calcd for $[\{Ru(Qc)(tap)_2\}_2H_2O]CH_2Cl_2$, $Ru_2C_{61}H_{56}O_5N_{12}Cl_2$: C, 55.91; H, 4.28; N, 12.83. Found: C, 55.85; H, 4.37; N, 12.91.

(Semiquinonato)bis(2-(*m*-tolylazo)pyridine)ruthenium Perchlorate, $[Ru(Qs)(tap)_2]ClO_4$. To a solution of 100 mg (0.17 mmol) of pure $Ru(Qc)(tap)_2$ in 30 mL of acetonitrile was added 125 mg (0.20 mmol) of ceric ammonium sulfate dissolved in 20 mL of water. The mixture was stirred at room temperature for 1 h. The color of the solution turned violet. The reaction mixture was then filtered, and the filtrate was reduced to 10 mL under reduced pressure. A saturated aqueous solution of $NaClO_4$ (10 mL) was then added, and the mixture was kept in the refrigerator for 5 h. The deposited complex was collected by filtration, washed with cold water, and dried in vacuo over P_4O_{10}.

Anal. Calcd for $[Ru(Qs)(tap)_2]ClO_4$, $RuC_{30}H_{26}O_6N_6Cl$: C, 51.24; H, 3.70; N, 11.96. Found: C, 51.36; H, 3.80; N, 11.71. Calcd for $[Ru(BuQs)(tap)_2]ClO_4$, $RuC_{34}H_{34}O_6N_6Cl$: C, 53.78; H, 4.48; N, 11.07. Found: C, 53.99; H, 4.62; N, 11.11. Calcd for $[Ru(Bu_2Qs)(tap)_2]ClO_4$, $RuC_{38}H_{42}O_6N_6Cl$: C, 55.98; H, 5.16; N, 10.31. Found: C, 56.21; H, 5.25; N, 10.42. Calcd for $[Ru(Cl_4Qs)(tap)_2]ClO_4$, $RuC_{30}H_{22}O_6N_6Cl_5$: C, 42.83; H, 2.62; N, 9.99. Found: C, 43.11; H, 2.72; N, 10.15.

X-ray Structure Determination. A dark prismatic crystal of dimension 0.36 × 0.14 × 0.32 mm^3 was mounted on a glass fiber. Unit cell parameters were determined by the least-squares fit of 25 machine-centered reflections having 2θ values in the range 15–30°. Lattice dimensions and Laue group were checked by axial photography. The structure was successfully solved in the space group $P\bar{1}$. Data were collected by the ω-scan method over the 2θ range 2–50° ($+h,\pm k,\pm l$) on a Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 22 °C. Significant crystal data and data collection parameters are listed in Table IV. Two check reflections were measured after every 98 reflections during data collection to monitor crystal stability. No significant intensity reduction was observed in the 83 h of exposure to X-ray radiation. All data were corrected for Lorentz polarization effects, and an emperical absorption correction was done on the basis of azimuthal scans[17] of eight reflections. The absorption coefficient and the minimum transmission coefficient (maximum normalized to 1.0) were 6.45 cm^{-1} and 0.86, respectively. Of the 10983 reflections collected, 10450 were unique; 6202 satisfying the $I > 3\sigma(I)$ criterion were used for structure solution.

All calculations for data reduction, structure solution, and refinement were done on a MicroVAX II computer using the SHELXTL-PLUS[18] program package. The metal positions were located from a Patterson map, and the rest of the non-hydrogen atoms emerged from difference Fourier syntheses. The structure was then refined by block-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at their respective calculated positions with fixed U = 0.08 $Å^2$ in the last cycle of refinement. The solvent molecule of dichloromethane was disordered with three chlorine positions, which

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were refined with the site-occupation factor of 0.667 per position. The number of variable parameters was 748, affording a data-to-parameter ratio of 8.3. The refinement converged (maximum shift/esd of 0.093) to $R = 0.0530$, $R_w = 0.0672$, and GOF = 1.20, with the largest difference peak of 0.78 e Å^{-3} near the metal atoms. Atomic coordinates and isotropic thermal parameters are tabulated in Table V.

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Registry No. Ru(Qc)(tap)$_2$, 137495-83-1; Ru(BuQc)(tap)$_2$, 137495-84-2; Ru(Bu$_2$Qc)(tap)$_2$, 137495-85-3; Ru(Cl$_4$Qc)(tap)$_2$, 137495-86-4; [Ru(Qc)(tap)$_2$]ClO$_4$, 137495-88-6; [Ru(BuQs)(tap)$_2$]ClO$_4$, 137495-90-0; [Ru(Bu$_2$Qs)(tap)$_2$]ClO$_4$, 137495-92-2; [Ru(Cl$_4$Qs)(tap)$_2$]ClO$_4$, 137495-94-4; [{Ru(Qc)(tap)$_2$}$_2$H$_2$O]·CH$_2$Cl$_2$, 137495-95-5; *tc*-[Ru(OH$_2$)$_2$(tap)$_2$](ClO$_4$)$_2$, 84027-73-6.

Supplementary Material Available: Full listings of bond distances (Table VI), bond angles (Table VII), anisotropic thermal parameters (Table VIII), and hydrogen atom coordinates (Table IX) and a summary listing of structure determination data (Table X) (9 pages); a listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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c/o Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Via Marzolo 1, 35131 Padova, Italy,
and Dipartimento di Scienze Farmaceutiche, Via Marzolo 5, 35131 Padova, Italy

cis-Bis(phosphine)platinum(II) Complexes with Pyrimidyl Nucleobases. Synthesis, Characterization, and Crystal Structures of *cis*-(1-Methylthyminato-N^3)(N,N-dimethylformamide-O)(1,1′-bis(diphenylphosphino)ferrocene)platinum(II) Tetrafluoroborate–Dichloromethane, [(dppf)Pt(1-MeTy(-H))(DMF)]BF$_4$·CH$_2$Cl$_2$, and *cis*-(1-Methylthyminato-N^3)(1-methylcytosine-N^3)(1,1′-bis(diphenylphosphino)ferrocene)platinum(II) Tetrafluoroborate, [(dppf)Pt(1-MeTy(-H))(1-MeCy)]BF$_4$

Giuliano Bandoli,[*,†] Guendalina Trovò,[‡] Alessandro Dolmella,[†] and Bruno Longato[*,§]

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The dinuclear complex [(dppf)Pt(μ-OH)]$_2$(BF$_4$)$_2$, where dppf is 1,1′-bis(diphenylphosphino)ferrocene, reacts with 1-methylthymine (1-MeTy), in dimethylformamide, dimethyl sulfoxide, or acetonitrile, to give the mononuclear complex [(dppf)Pt(1-MeTy(-H))(S)]$^+$. The dimethylformamide adduct (S = DMF), [(dppf)Pt(1-MeTy(-H))(DMF)]BF$_4$·CH$_2$Cl$_2$ (**1**), has been characterized by single-crystal X-ray analysis. The complex crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a = 13.492$ (3) Å, $b = 14.063$ (3) Å, $c = 23.906$ (4) Å, and $Z = 4$. The structure was solved by heavy-atom methods and refined by least-squares techniques to $R = 0.078$ for 2949 unique data ($I > 3\sigma(I)$). In the cationic unit, the ligand geometry around Pt is distorted square planar, the chelating bis(phosphine) dppf, the N(3)-bonded 1-methylthyminate and the O-bonded DMF ligands defining the coordination sphere of the metal ion. The 1-MeTy(-H) ring forms an angle of 104.8° with the ligand square plane, while the DMF mean plane is at 73.0° to the same plane. Addition of 1-methylcytosine (1-MeCy) to **1** affords the corresponding adduct [(dppf)Pt(1-MeTy(-H))(1-MeCy)]$^+$ (**2**) as a mixture of two isomeric forms (**2a,b**). In solution at room temperature **2a** extensively converts in **2b** (90% in DMF) in several hours. Crystals of **2** are obtained from a chloroform solution of the two isomers and have been characterized by single-crystal X-ray analysis. They crystallize in the monoclinic system, space group $C2/c$, with $a = 17.821$ (5) Å, $b = 21.718$ (7) Å, $c = 13.814$ (3) Å, $\beta = 113.6$ (2)°, and $Z = 4$. The structure was solved by heavy-atom methods and refined by least-squares techniques to $R = 0.060$ for 2657 unique data ($I > 3\sigma(I)$). In the cationic complex [(dppf)Pt(1-MeTy(-H))(1-MeCy)]$^+$ the platinum atom is coordinated by the chelated bis(phosphine), by the deprotonated 1-MeTy, and by the neutral 1-MeCy ligands. In **2** both the nucleobases are platinated at the N(3) site with their rings being perpendicular to the PtP$_2$ plane. The structures in solution of the two isomers **2a** and **2b** are discussed on the basis of their ^{1}H and ^{31}P NMR spectra. Isomer **2b** contains the neutral cytosine ligand coordinated to the platinum through the monodeprotonated exocyclic amino group, with the proton switched to the N(3) position. The conversion of **2a** into **2b** is consistent with the migration of the platinum from the N(3) to N(4) site of 1-MeCy indicating that the thermodynamically favored adduct of this neutral ligand is its imino oxo tautomeric form. In addition, the characterization of the species [(dppf)Pt(1-MeCy(-H))]$^+$, obtained from [(dppf)Pt(μ-OH)]$_2$(BF$_4$)$_2$ and 1-MeCy in acetonitrile, is described. On the basis of ^{1}H and ^{31}P NMR spectra, the complex appears to contain the deprotonated 1-MeCy chelated to the (dppf)Pt^{2+} moiety through its N(3) and N(4) donor atoms.

Introduction

Platinum nucleobase chemistry has been extensively studied in the last two decades, in particular the complexes of Pt^{II} and Pt^{IV} stabilized by amine ligands.[1] We have been investigating in recent years the solution chemistry of bis(phosphino) complexes of platinum(II)[2] and their interactions with nucleic acid components.[3] It has been shown that the complex [(dppf)Pt(μ-OH)]$_2^{2+}$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) reacts with 3′,5′-diacetylthymidine, Ac$_2$(dT), and deoxycytidine, dC, in dimethyl sulfoxide (DMSO) or dimethylformamide (DMF), to give the two isomeric species A and B of Chart I, depending on the sequence of the addition of the biomolecules.[4] Isomer A appears

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[*] To whom correspondence should be addressed.

[†] Dipartimento di Scienze Farmaceutiche.

[‡] Dipartimento di Chimica Inorganica, Metallorganica ed Analitica.

[§] Centro di Studio sulla Stabilità e Reattività dei Composti di Coordinazione.

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