92.39°, $\gamma' = 90.04°$, and $Z = 4$; the corresponding transformations[2] $x' = -{}^1/_2(x - 0.5) + z$, $y' = {}^1/_2(x - 0.5)$, $z' = y$ yield coordinates that are compatible with the symmetry of $C2/c$ essentially within the reported esd's for all atoms except the pair C(81), C(81A), which are disordered and for which convergence was not attained in the earlier refinement.[1]

We have obtained satisfactory refinement in $C2/c$, based on the original intensity data; the revised coordinates are given in the supplementary material. The change in space group requires the cation to have C_2 symmetry, but there are no substantive changes in bond lengths or angles.

Acknowledgment. This investigation was supported in part by Public Health Service Research Grant No. GM 16966 from the National Institutes of Health.

Supplementary Material Available: Table of coordinates and temperature factors for the $C2/c$ description (2 pages). Ordering information is given on any current masthead page.

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(2) The translations of 0.5 in x are needed to position the origin at a conventional center of symmetry in $C2/c$.

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Synthesis and Spectra of (*p*-Benzoquinone diimine)pentaammineosmium(II) with a Low Barrier to Rotation about the N=C Bond

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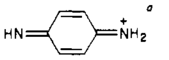
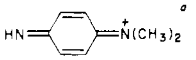
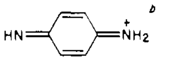
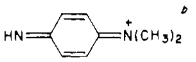
Stable imine complexes of the two d^6 metal ions Ru(II) and Os(II) have been prepared by various methods. A condensation reaction of $Os(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{3+}$ with α-diketones in conjunction with a complex redox reaction afforded $(NH_3)_2Os(diimine)_2^{2+}$ and $(NH_3)_4Ru(diimine)^{2+}$.[2] Analogous diimine chelates of Ru(II) were produced by O_2 oxidation of $Ru(en)_3^{3+}$.[3] Complex ions containing monodentate *p*-benzoquinone diimine (bqd) were prepared by oxidation of the pentaammineruthenium(II) complex with *p*-phenylenediamine.[4] Owing to the strong d–π^* interaction, all of these imine complexes show a considerable shift of the reduction potentials to more positive values compared with those of the parent hexaammines. Another distinctive feature is a very strong absorption band in the visible spectral region. This note reports the synthesis and spectroscopic properties of the novel osmium(II) complex with *p*-benzoquinone diimine.

A 136-mg (1-mmol) sample of 1-amino-4-(dimethylamino)benzene is dissolved in 20 mL of MeOH containing 0.5 mmol of HTr (Tr = triflate, $CF_3SO_3^-$). A 720-mg portion of $[(NH_3)_5OsTr]Tr_2$[5] (1 mmol) is added. The mixture when stirred under oxygen at 30 °C develops a crimson red color. For about 4 days a steady increase of the absorbance at 560 nm is observed. After 5 days addition of 10 mL of ether precipitates 500 mg of a solid, which is redissolved in MeOH. Vapor diffusion of ether produces a microcrystalline crimson red solid. Anal. Calcd. for $[(NH_3)_5Os(N,N\text{-}Me_2bqd)]Tr_3$: Os, 22.2; C, 15.4, H, 3.1; N, 11.4; S, 11.2; F, 19.9. Found: Os, 21.6; C, 15.2; H, 3.2; N, 11.2; S, 11.2; F, 19.8. The compound $[(NH_3)_5Os(Hbqd)]Tr_3$ is prepared by an analogous procedure. Anal. Calcd for $[(NH_3)_5Os(Hbqd)]Tr_3$: Os, 22.9; C, 13.0; H, 2.7; N, 11.8; S, 11.6. Found: Os, 21.8; C, 13.0; H, 2.7; N, 11.8; S, 11.5.

Table I. Visible and Near-Infrared Spectra for $(NH_3)_5Os^{2+}$ and $(NH_3)_5Ru^{2+}$ Complexes with *p*-Benzoquinone Diimines

metal	diimine	λ_{max}, nm (ϵ_{max})
Os	 [a]	526 (36 000), 1410 (900)
	 [a]	562 (39 500), 1410 (1300)
Ru	 [b]	523 (43 800), 1240 (140)
	 [b]	560 (47 000), 1220 (200)

[a] In MeOH. [b] In H_2O, D_2O.

The formation of the *p*-benzoquinone diimine complex of Os(II) is assumed to occur in a reaction sequence similar to that for the corresponding ruthenium compound.[4] The absorption spectra (Table I) measured in MeOH, H_2O, and D_2O exhibit a weak band in the near-infrared and an intense absorption in the visible part of the spectrum. The same general pattern has been observed for Ru(II) and Os(II) complexes with pyrazine and its derivatives.[6] Referring to a simple Hückel MO approach[7] (Figure 1), we assign the intense visible band to the allowed transition 5a″ → 6a″ (point group C_s) with y,z polarization; z coincides with the metal–N(imine) bond, and x is perpendicular to the plane of the diimine ligand. Since the two orbitals have comparable metal and ligand parentage, it appears unreasonable to label the strong absorption as either metal to ligand or ligand to metal charge transfer. The weak low-energy absorption is attributed to a forbidden transition (x polarization) between the nonbonding 2a′ or 1a′ orbital and 6a″.

Whereas the ^1H NMR spectra for the quinone diimine complexes with $(NH_3)_5Ru^{II}$ do not exhibit any unexpected special features,[8] the osmium complex shows a dramatic temperature dependence of the signals for the ring protons (Figure 2, Table II). This study was confined to the *N*,*N*-dimethyl compound because the two imine protons for the complex derived from 1,4-diaminobenzene have chemical shifts very similar to those for the ring protons. Otherwise, the ^1H NMR spectra for the $=NH_2$ and $=N(CH_3)_2$ complexes were virtually identical. The most obvious change is observed for the two protons H2 and H6, their signals coalescing at about 0 °C. The available experimental data do not allow assignment of the two separate low-temperature resonances to either hydrogen atom. The dynamic process that is manifested by the observed line broadening and coalescence of the H2,6 signals is attributed to a rotation of the *p*-benzoquinone diimine molecule about the coordinated N=C bond. Such a rotation would primarily affect the two H2,6 protons. The H3,5 and methyl hydrogens would be affected to a considerably lesser degree. Owing to rapid exchange of the imine proton with traces of water in the solvent, no signal corresponding to this atom was found in the spectrum.

Given the coalescence temperature T_c and the shift difference $\delta\nu$ (Hz) of the separate H2,6 signals, the free energy of activation of this restricted rotation can be calculated by using the approximation[9]

$$\Delta G^{\ddagger} = 19.13T_c[9.97 + \log (T_c/\delta\nu)] \text{ J mol}^{-1}$$

The experimental data $T_c = 273 \pm 10$ K and $\delta\nu = 155 \pm 5$ Hz correspond to $\Delta G^{\ddagger} = 52 \pm 2$ kJ mol^{-1}, the estimated error arising

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(1) Institut für Organische Chemie, Universität Bern.
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Table II. ^{1}H NMR Data for $(NH_3)_5Os^{2+}$ and $(NH_3)_5Ru^{2+}$ Complexes with *N*,*N*-Dimethyl-*p*-benzoquinone Diimine[a]

	T, °C	cis NH_3	trans NH_3	H3,5	H2,6		$=N(CH_3)_2$	
Os	25	10.26 (12.3)	9.90 (3)	6.60 (2.2)	5.26 (1.9)		3.60 (6.1)	
	0	10.33	9.96	6.56	5.2		3.6	
	−60	10.66	10.14	6.5	5.8	4.3	3.6	
Ru	25	3.54 (12.3)	6.50 (3)	7.70 (2)	8.00 (1)	8.36 (1)	1.88 (3)	1.84 (3)

[a] Chemical shifts are in ppm, with number of protons in parentheses; solvent CD_3–CO–CD_3; numbering scheme given in Figure 2.

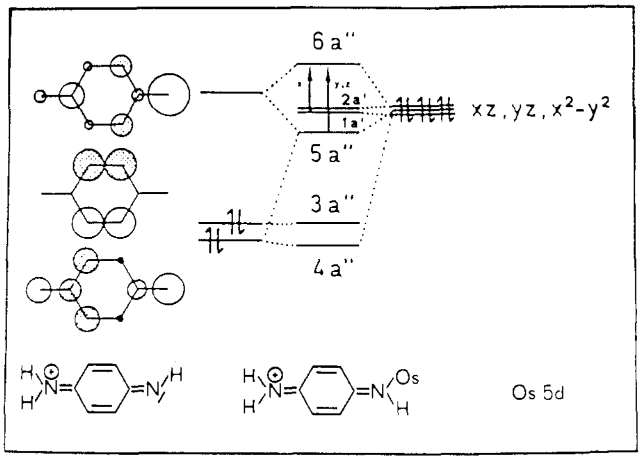
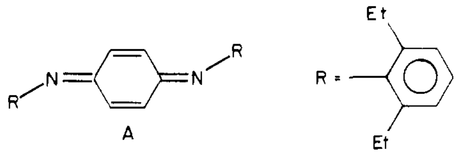
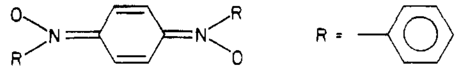


Figure 1. Hückel MO diagram for $(NH_3)_5M(Hbqd)^{3+}$ using the following parameters: $\alpha(C) = 0$; $\alpha(N) = 0.5\beta$; $\alpha(N^+) = 2\beta$; $\alpha(Ru) = 0.3\beta$; $\alpha(Os) < \alpha(Ru)$; $\beta(Ru\text{-}N) = 0.3\beta$; $\beta(C\text{-}N) = \beta$; $\beta(C\text{-}C) = \beta$ (cf. ref 7).

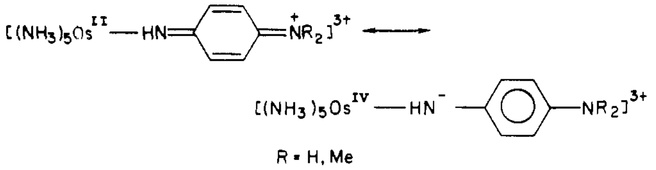
mainly from the uncertainty of T_c. This energy is much smaller than the barrier to rotation for normal C=N double bonds, which exceeds 160 kJ mol^{-1}.[10] The osmium complex may be best compared to the two quinone diimine derivatives A and B. For compound A the barrier to rotation about the C=N bond has been estimated to be approximately 80 kJ mol^{-1} (398 K); the corresponding energy for B with even more reduced double-bond character is about 50 kJ mol^{-1} (260 K).[10] We conclude that the C=N bond in the osmium-benzoquinone diimine complex is significantly weakened and that therefore rotation about this bond becomes possible. This interpretation of the temperature dependence of the ^{1}H NMR data is in complete agreement with the enhanced back-bonding capacity of Os(II) compared to that of Ru(II).[6] The actual electronic structure of the novel osmium complex may thus be described as an intermediate between the following two limiting valence structures:



A



B



This view is also supported by the chemical shift data of the ammonia protons (Table II). Their signals occur at significantly lower field for the Os than for the Ru complex, indicative of a higher formal charge on osmium.

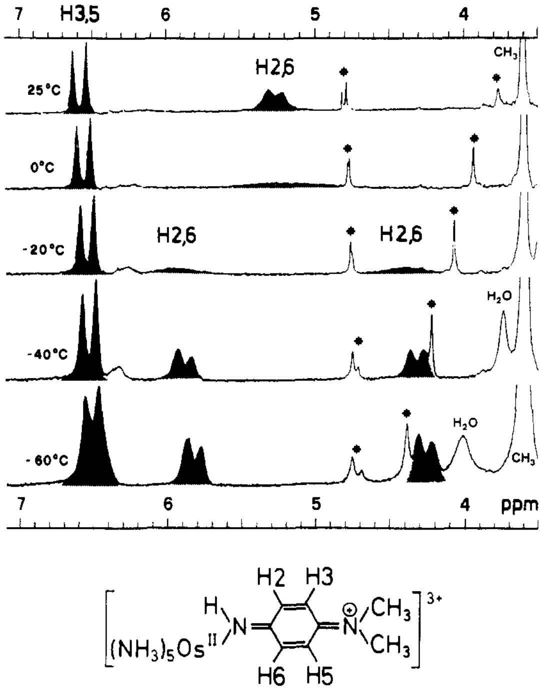


Figure 2. ^{1}H NMR spectra (Varian XL-100) at different temperatures for $(NH_3)_5Os(N,N\text{-}Me_2bqd)^{3+}$. Shaded peaks represent the ring protons; asterisks label impurity signals with integrated intensities roughly equivalent to one proton (probably a condensation product of 1-amino-4-(dimethylamino)benzene).

Acknowledgment. We thank Ciba-Geigy for the microanalyses and the Swiss National Science Foundation for financial support (Grant No. 2.209-0.81).

Registry No. $[(NH_3)_5Os(N,N\text{-}Me_2bqd)]Tr_3$, 97879-13-5; $[(NH_3)_5Os(Hbqd)]Tr_3$, 97879-15-7; $[(NH_3)_5OsTr]Tr_2$, 83781-30-0; 1-amino-4-(dimethylamino)benzene, 99-98-9; 1,4-diaminobenzene, 106-50-3.

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Copper(I) Benzenesulfinate and Copper(I) *p*-Toluenesulfinate[1]

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While copper(I)[2] and copper(II)[3] carboxylates have been prepared and characterized, the only known sulfur analogues have been the copper(II) sulfinates, e.g. copper(II) benzenesulfinate[4] and copper(II) *p*-toluenesulfinate.[5] We wish to report convenient preparations of copper(I) benzenesulfinate (**1**) and copper(I)

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