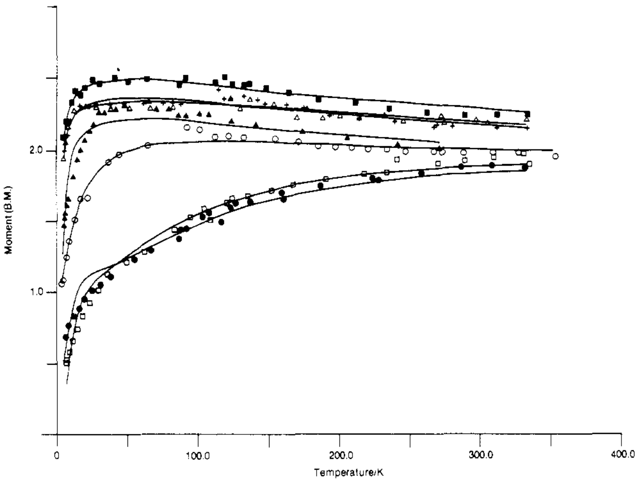

**Figure 3.** Effective magnetic moments plotted as a function of temperature for the [$Cu_4OX_6L_4$] complexes of ref 12. The smooth curves are the best fits to the Heisenberg model with parameters listed in Table I. In order of increasing theoretical moment at 200 K, the following X, L pairs are shown: Cl, Br (●); Cl, Cl (□); Br, py (○); Cl, tmu (▲); Cl, pyo (+); Cl, $Me_2SO$ (△); Br, $Me_2SO$ (■).

A striking feature of all the fits is that $J_1 + 2J_2$ is always small and negative. This corresponds to a singlet ground state with a low-lying quintet. The ferromagnetic interactions invoked with use of the Heisenberg model are larger than those of the orbitally degenerate model. As a consequence Wong's unusually high *g* values are replaced by values lying in a more normal range.

The data for $Cu_4OCl_6(3\text{-quin})_4$[7] cannot be fitted to a strict Heisenberg model. This compound is exceptional in that it has $\mu_{max} > 2.6\ \mu_B$, significantly larger than is usual for these compounds, strongly suggesting a quintet ground state with no low-lying low-spin states. This and the fact that the intercluster model fits the experimental results extremely well for $zJ'$ as small as 0.316 cm$^{-1}$ (cf. 2–8 cm$^{-1}$ typical for the model)[10] indicate that in this case intercluster exchange is probably the most important factor involved in the low-temperature magnetic behavior. All other data considered give acceptable fits to the simple Heisenberg model.

In view of the extreme sensitivity, with this model, of $\mu(T)$ to small changes in the ratio $J_2{:}J_1$, it is expected that, until an even larger range of results than is at present available is obtained, correlation between the chemical nature of the substituents on the $Cu_4O$ tetrahedron and the magnetic behavior will be extremely difficult.

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# Dehydration of Aldoximes at Ruthenium(II) Centers[1]

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Several examples of enhanced reactivity of N-bonded ligands on Ru(II) and Ru(III) centers are known.[2] In most of the previous cases the reactions involve a net change in the oxidation state of the ruthenium or the nitrogen *atom*, making it difficult to independently assess the contribution of $d\pi-\pi^*$ back-bonding to the overall driving force.

Table I. Spectral Properties of Reaction Products from $Ru(NH_3)_5H_2O^{2+}$ + HON=CHR

| R | $\nu$(C≡N),[a] cm$^{-1}$ | $\lambda_{max}(\epsilon)$,[b] nm |
|---|---|---|
| $CH_3$ | 2250 | 229 (15 400) |
| $C_6H_5$ | 2185 | 376 (8100) |
| 2-$C_4H_4N$ | 2180 | 408 (10 120)<br>505 (12 100)[c] |
| 3-$C_4H_4N$ | 2175 | 398 (8425)<br>460 (7326)[d] |
| 4-$C_4H_4N$[e] | 2175 | 522 (...); 425 (...)<br>528 (...)[d] |
| 4-$C_4H_4N$[f] | 2180 | 425 (8965)<br>535 (13 100)[d] |

[a] $ClO_4^-$ salts. [b] In aqueous solution. [c] In 2 M HCl. [d] In 1 M HCl. [e] [oxime]/[Ru] ≈ 2.0. [f] [oxime]/[Ru] ≃ 10.

We report here a case in which ligand substitution is following by rapid dehydration with no redox change.

## Experimental Section

[$Ru(NH_3)_5Cl]Cl_2$ was prepared[3] from $RuCl_3{\cdot}nH_2O$. Oximes were used as purchased or prepared by reacting the appropriate aldehyde with hydroxylamine. Aldoximes (HON=CHR) used in this study has R = $CH_3$, $C_6H_5$, and 2-, 3-, and 4-pyridyl. Reactions with pyridinecarboxaldoxime were carried out in 0.1 M $HC_2F_3O_2$, deionized water, and 0.2 M NaOH.

In a typical reaction, 100 mg (0.34 mmol) of [$Ru(NH_3)_5Cl]Cl_2$ was converted to $Ru(NH_3)_5OH_2^{3+}$(aq) by base hydrolysis or treatment with $AgCF_3COO$.[4] A twofold to tenfold molar excess of oxime was added and the final volume adjusted to 6 mL. The solution was degassed with argon for 15 min and amalgamated Zn added to initiate the reaction. The reaction proceeded for 45 min, during which time aliquots were removed to monitor reaction progress, after which the reaction mixture was filtered and treated with saturated aqueous $NaClO_4$. The products were isolated by filtration, washed successively with ethanol and ether, and air-dried. Solid-product yields were in the range of 60–70% of the theoretical values.

Products were characterized by electronic (Cary 15) and infrared (Pye-Unicam) spectral properties.

## Results

**Solution Spectra.** The reduction of $Ru(NH_3)_5OH_2^{3+}$ in the presence of oxime leads to a gradual color change, which was complete within 45 min. The solution spectra of all the reaction mixtures except the $CH_3C{=}NOH$ reaction showed strong absorptions in the visible region of the electronic spectra. With the 4-pyridinecarboxaldeoxime, the visible spectrum of the final solution was dependent on initial oxime concentration: at high oxime concentration a single peak ($H^+$ dependent) was observed, while at low oxime concentration an additional peak ($H^+$ independent) occurs. During the course of the reactions no intermediate species were detected.

**Spectral Properties of Isolated Products. Infrared.** The infrared spectral properties of the isolated solids all showed strong peaks in the 2100–2250-cm$^{-1}$ region of the spectrum. These peaks are characteristic of nitrile ligands coordinated to ruthenium(II) centers. Other peaks characteristic of ruthenium(II) ammine compounds are present at ~1280 cm$^{-1}$.[2b,5] Spectral properties of the products obtained from the reaction of pyridinecarboxaldoximes were virtually independent of solvent medium.

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**Electronic.** The electronic spectra of $\sim 10^{-4}$ M solutions of the isolated products showed peaks that corresponded with the ruthenium(II) nitrile analogues of the starting oximes.[2b,5] These spectra were also in good agreement with the solution spectra of the reaction solution before product isolation. The infrared and electronic spectral data are summarized in Table I.

## Discussion

The reaction between $(H_3N)_5RuH_2O^{2+}$ and aldoximes produces ruthenium(II) nitrile compounds, as indicated by their characteristic infrared and electronic spectral properties. These obervations can be explained by a stepwise mechanism in which $(H_3N)_5RuOH_2^{2+}$ produced by reduction of $(H_3N)_5RuOH_2^{3+}$ undergoes substitution by the oxime ligand, followed by rapid dehydration to the nitrile product (eq 1-3).

$$(H_3N)_5RuOH_2^{3+} \xrightarrow[\text{slow}]{\text{Zn/Hg}} (H_3N)_5RuOH_2^{2+} \quad (1)$$

$$(H_3N)_5RuOH_2^{2+} + HON{=}CHR \xrightarrow[\text{fast}]{k_s} [(H_3N)_5RuN(OH){=}CHR^{2+}] + H_2O \quad (2)$$

$$[(H_3N)_5RuN(OH){=}CHR^{2+}] \xrightarrow[\text{very fast}]{k_d} (H_3N)_5RuN{\equiv}Cr^{2+} + H_2O \quad (3)$$

This facile conversion contrasts greatly with the much more strenuous conditions (e.g., prolonged refluxing in glacial acetic acid) normally required for the dehydration of aldoximes and thus provides an unequivocal demonstration of the driving force provided by the Ru(II) center, via back-bonding, in going from the $sp^2$ to sp hybridization on nitrogen. An estimate of the rate of reaction 2 for R = $CH_3$ was obtained from a competition reaction in which equimolar $HON{=}CHCH_3$ and pyridine were used. A product ratio of $(H_3N)_5RuN{\equiv}CCH_3^{2+}$ to $(H_3N)_5Ru(py)^{2+}$ of 2.3 to 1 was found. Using the published rate constant[6] for the pyridine reactions leads to $k_s \simeq 0.2$ $M^{-1}$ $s^{-1}$ in good agreement with that reported for imidazole,[6] which contains a chemically similar (nonaromatic, $sp^2$) nitrogen.

With 4-pyridinecarboxaldoxime at high concentration, the only product detectable is $(H_3N)_5RuN{\equiv}Cpy^{2+}$, establishing almost exclusive attack of $(H_3N)_5RuOH_2^{2+}$ at the oxime group. This enhanced preference for oxime compared to the competition reaction described above may be due in part to a deactivation of the pyridine site in this ambidentate ligand. The appearance of a second visible peak in product formed at lower oxime concentration cannot be due to the presence of linkage isomer (which should be concentration independent); we believe it represents the bridged dimer formed when $(H_3N)_5RuOH_2^{2+}$ is generated in the presence of $(H_3N)_5Ru{\equiv}Cpy^{2+}$ at depleted oxime levels. For 2-pyridinecarboxaldoxime steric as well as electronic effects are probably involved. In the case of the 2- and 3-pyridinecarboxaldoximes, the only product observed was the cyanopyridine complex. These results parallel those found for the corresponding cyanopyridine complexes where direct substitution produces only the cyano-bound isomers.[5,7]

Similar reactivity has been found for oximes containing $\alpha$-carbonyl groups. These reactions produce a ruthenium(II) nitrile product and carboxylic acid via C–C bond scisson.[8]

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**Registry No.** $[(H_3N)_5RuN{\equiv}CCH_3](ClO_4)_2$, 41654-94-8; $[(H_3N)_5RuN{\equiv}CC_6H_5](ClO_4)_2$, 26259-25-6; $[(H_3N)_5RuN{\equiv}C\text{-}2\text{-}C_4H_4N](ClO_4)_2$, 28589-23-3; $[(H_3N)_5RuN{\equiv}C\text{-}3\text{-}C_4H_4N](ClO_4)_2$, 30897-96-2; $[(H_3N)_5RuN{\equiv}C\text{-}4\text{-}C_4H_4N](ClO_4)_2$, 85096-98-6; $[(H_3N)_5RuCl]Cl_2$, 18532-87-1; $(H_3N)_5RuOH_2^{2+}$, 21393-88-4; $HON{=}CHCH_3$, 107-29-9; $HON{=}CHC_6H_5$, 932-90-1; $HON{=}CH\text{-}2\text{-}C_4H_4N$, 873-69-8; $HON{=}CH\text{-}3\text{-}C_4H_4N$, 1193-92-6; $HON{=}CH\text{-}4\text{-}C_4H_4N$, 696-54-8.

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## Reaction Kinetics of Several Alkyl Arsenite Hydrolyses

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Arsenic compounds are known for their toxicity and are pollutants from some industrial processes.[2,3] On the other hand, certain arsenic compounds enhance the growth of poultry and swine, and there is evidence to suggest that it is an essential element in rat physiology.[4] In order to more fully understand the role of arsenic compounds in physiological systems, we have been investigating the kinetic behavior of simple systems containing As–O bonds with the arsenic in the 5+[5-8] and 3+[9,10] states. The hydrolysis of trialkyl arsenites (reactions 1-3)

$$H_2O + As(OR)_3 \xrightarrow{k_1} HOAs(OR)_2 + ROH \quad (1)$$

$$H_2O + HOAs(OR)_2 \xrightarrow{k_2} (HO)_2AsOR + ROH \quad (2)$$

$$H_2O + (HO)_2AsOR \xrightarrow{k_3} H_3AsO_3 + ROH \quad (3)$$

has been shown to occur with exclusive As–O bond fission.[11] We report here the kinetics of the first step (reaction 1) for $As(OR)_3$ (R = Me, Et, *i*-Pr), as well as the cage arsenite (4-methyl-2,6,7-trioxa-1-arsabicyclo[2.2.2]octane), and for R = Et we report an indication of the rates of reaction 2 and/or 3.

## Experimental Section

**Materials.** The trialkyl arsenites were prepared by a variety of methods[12,13] although the methods of Brill and Campbell[14] were found to be the most convenient. The compounds were characterized by NMR, IR, and boiling point data. The cage arsenite, previously prepared by Verkade and Reynolds,[15] was obtained by the transesterification reaction of trimethyl arsenite with 2-(hydroxymethyl)-2-methyl-1,3-propanediol. Stoichiometric amounts of the

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